

6th AUSTRIAN POLYMER MEETING
XXIst INTERNATIONAL H.F. MARK - SYMPOSIUM

15th - 17th September 2003
Vienna | Austria

jointly organized by the

Division of Macromolecular Chemistry
Institute of Applied Synthetic Chemistry
Vienna University of Technology

and

Austrian Chemical Society, Macromolecular Chemistry Group
Austrian Physical Society, Polymer Physics Group

and

Austrian Plastics Institute
Österreichisches Forschungsinstitut für Chemie & Technik (OFI)

Table of Contents

<i>Imprint</i>	ii
<i>Table of Contents</i>	iii
<i>Welcome from the Organizing Committee</i>	v
General Information	G-1
<i>Venue Maps</i>	G-4
<i>Social Program</i>	G-6
<i>Time Table</i>	G-9
Scientific Program	S-10
<i>Detailed Schedule</i>	S-12
- Monday, Sept. 15 th	S-12
- Tuesday, Sept. 16 th	S-16
- Wednesday, Sept. 15 th	S-20
Abstracts	S-24
<i>Plenary Lectures (PL)</i>	S-25
<i>Keynote Lectures (KL)</i>	S-37
<i>H. F. Mark Lectures (HM)</i>	S-49
<i>Oral Presentations (OP)</i>	S-59
<i>Poster Presentations (PO)</i>	S-105
Author Index	I-176
Memo Sheets	M-191

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Welcome from the Organizing Committee

On behalf of the Austrian Chemical Society we would like to welcome you to the 6th Austrian Polymer Meeting.

Since the first „Polymertage“ in 1995 which was rather a kind of family celebration of our small but nice „Austrian Macromolecular Family“ this meeting has been developed to a real international conference. Thus it is a great pleasure for the organizing committee to extend our welcome to the more than 200 participants coming not only from Austria but from other european countries, the USA, Russia, Japan, India, Turkey and Australia.

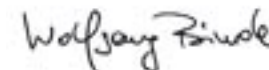
We hope that this meeting will be a significant event for all participants. The auspices are promising: the topics of our conference cover the most important fields of polymer science, such as polymer synthesis and modification, polymer characterization and processing, polymers in medical technology and polymer physics. Since many chemists from industry participate at this conference it will be another opportunity to approximate the sometimes different points of view in academic and industrial research.

Thus we hope that here in Vienna you will both conceive novel ideas for your own research and make new and long-lasting personal contacts. The unique atmosphere of Vienna which has so often catalyzed progress in human relations will hopefully inspire us all during the conference and for long thereafter.

So enjoy fully the stay in our wonderful city and once again a warm welcome to you all.



Heinrich Gruber



Wolfgang Binder

SCIENTIFIC COMMITTEE

Michael R. Buchmeiser

(Institute of Analytical Chemistry & Radiochemistry, Innsbruck)

Gerhard Eder

(Institute for Chemistry, Linz)

Heinrich Gruber

(Institute of Applied Synthetic Chemistry, Vienna)

Christa Hametner

(OFI - Institute for Medical Devices, Vienna)

Klaus Lederer

(Institute for Chemistry of Polymeric Materials, Leoben)

Sabine Seidler

(Institute for Materials Science and Testing, Vienna)

Franz Stelzer

(Institute for Chemistry and Technology of Organic Materials, Graz)

ORGANIZING COMMITTEE

Wolfgang Binder, Heinrich Gruber

(Institute of Applied Synthetic Chemistry, Vienna)

ORGANIZING SECRETARIATES

AUSTRIAN POLYMER MEETING

Dr. Wolfgang Binder
Institute of Applied Synthetic Chemistry
Division of Macromolecular Chemistry

Getreidemarkt 9/163/MC
A-1060 Vienna / Austria

E-MAIL polymerdays@ias.tuwien.ac.at

INTERNATIONAL H.F. MARK- SYMPOSIUM

Dr. Dietmar Loidl
Austrian Plastics Institute
Österreichisches Forschungsinstitut für
Chemie & Technik (OFI)

Arsenal, Obj. 213
A-1030 Vienna / Austria

E-MAIL office@ofi.co.at
PHONE 0043-1-7981601-480

General Information

The conference deals with the chemical, physical and biomedical aspects of polymer science. For the first time the Austrian Polymer Meeting and the H. F. Mark Symposium are held together in one conference venue organized by:

- Division of Macromolecular Chemistry, Institute of Applied Synthetic Chemistry (Vienna University of Technology)
- Austrian Plastics Institute (OFI)
- Austrian Chemical Society, Macromolecular Chemistry Group
- Austrian Physical Society, Polymer Physics Group

Conference Language : English

The meeting will start on Monday, 15th of September 2003 at 8:00 a.m. and will end on Wednesday, 17th of September 2003 at 6:00p.m.

Scientific Scope

The following Topics will be highlighted:

6th Austrian Polymer meeting:

- Polymer Synthesis and Modification
- Polymer Physics
- Polymer Characterization and Processing

XXIst International H.F. Mark - Symposium:

- Polymers in Medical Technology

Registration Center and Information Desk

The registration center and information desk (cf. *Venue map 2*, page G-5) will be located at the red area on the first floor of the FREIHAUS, Vienna University of Technology (cf. *Venue map 1*, page G-4) within the following business hours:

Sept. 15th 2003: 8:00 – 17:00

Sept. 16th 2003: 8:00 – 12:00

Sept. 17th 2003: 8:00 – 12:00

Registration fees

Full time (from Monday to Wednesday)*:

Austrian Polymer Meeting / International H.F. Mark-Symposium

- 150 Euro - regular participant
- 130 Euro - members of GOECH and OFI
- 50 Euro - students **

Part time (only Wednesday)*:

International H.F. Mark-Symposium

- 100 Euro - regular participant
- 80 Euro - members of GOECH and OFI
- 30 Euro - students **

*) after August 10th, 2003: plus 25%

**) Proof required by fax to Austropa Interconvention 043-58800-520, otherwise the full fee will be charged

Cancellation before August 30th, 2003 - a processing fee of 30 Euro will be charged
Cancellation after September 1st, 2003 - full fee will be charged

Registered participants are entitled to attend all the scientific sessions, the exhibits and to receive a copy of the Conference Program and the Book of Abstracts. In addition coffee and refreshment drinks as well as **lunches** are included in the registration fee.

The **conference dinner** will be held on Monday, September 15th and is included in the conference fee.

Registration Office and Travel Agency

AUSTROPA INTERCONVENTION

Helga Eismair

Austrian Travel Agency Corp.

Friedrichstrasse 7

A - 1010 Vienna / Austria

PHONE 0043-1-588 00-517

FAX 0043-1-588 00 520

Conference Venue

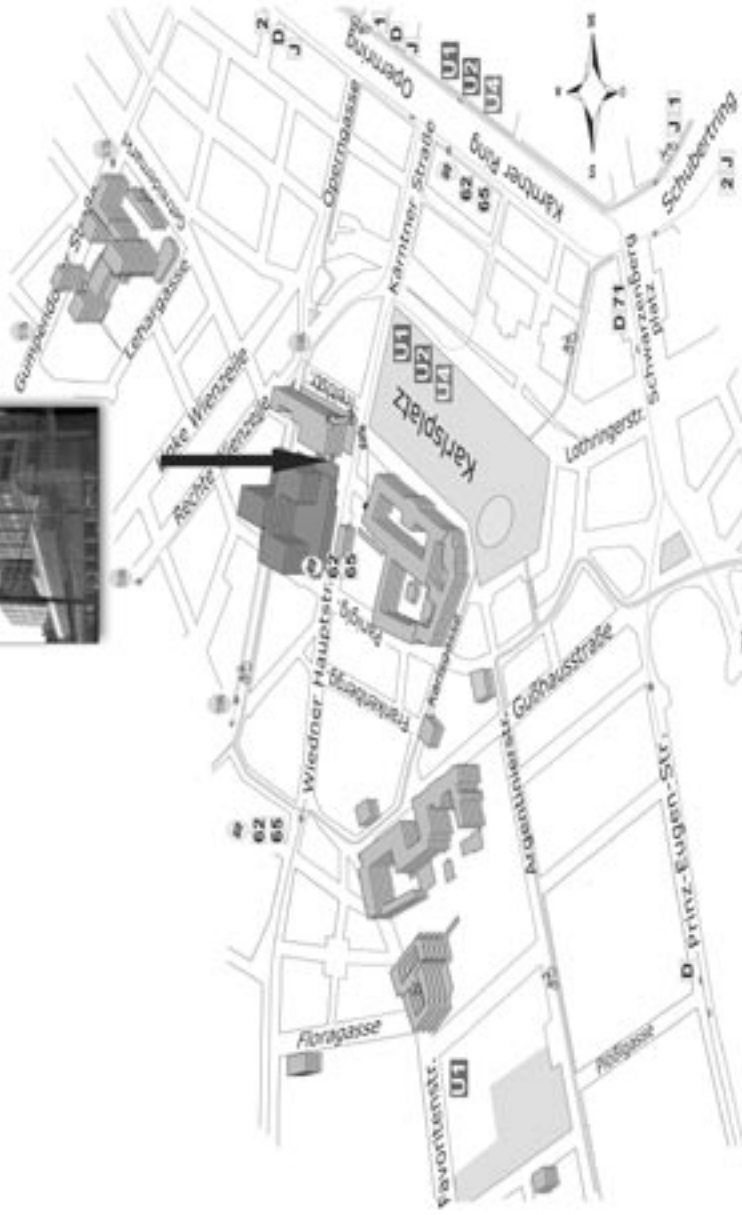
Vienna University of Technology / Freihaus - 2nd floor (cf. *Venue map 1*, page G-4 and *Venue map 2*, page G-5)

A-1040 Wien, Wiedner Hauptstr. 8-10

The conference venue can be reached by public transport using the lines 62, 65, U1, U2 or U4, exiting at station "Karlsplatz"



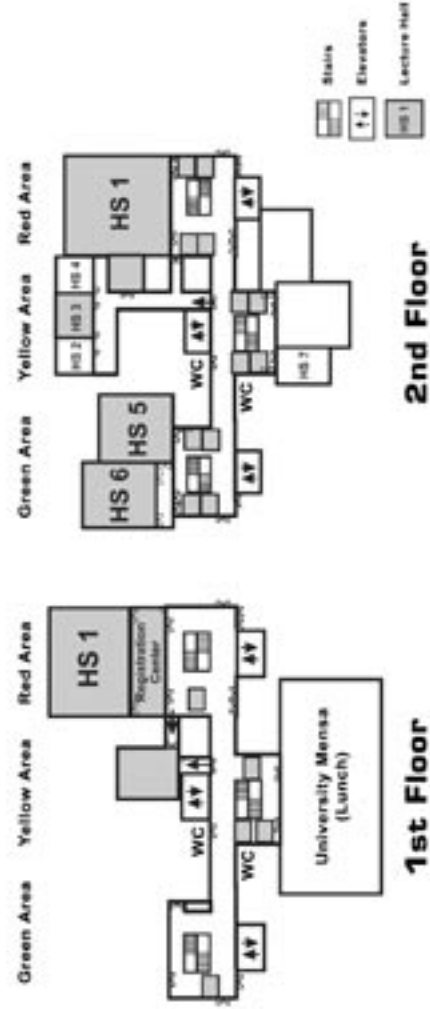
**Vienna University of Technology
FREIHAUS**
Wiedner Hauptstraße 6-10
1040 Vienna



Venue Map 1



**Vienna University of Technology
FREIHAUS**



Venue Map 2

Social Program

The city of Vienna offers a wide variety of touristic, cultural and recreational activities in September. There is a large number of museums, historic sites and events to be visited together with the pleasant surroundings including hills and vineyards. The well known Viennese cooking represents itself in numerous restaurants offering tasty food for everyone.

The conference venue, the Vienna University of Technology is located directly in the center of Vienna with most of the historic parts of Vienna located in walking distance. Additionally an excellent public transportation system offers easy travelling throughout the city by subway (U-Bahn), tram (Strassenbahn) and buses.

Travelling to Vienna

Vienna can be reached by

- plane via Vienna International Airport. To reach the city you can use taxis (ride takes approximately 20 minutes), buses (ride takes approximately 20 minutes, departure in front of the arrival area of VIE, interval 20 minutes) or train ('Schnellbahn', ride takes approximately 35 minutes, interval 30 minutes, City Terminal is station 'Landstraße').
- train. Arrival is at Wien-Südbahnhof or Wien-Westbahnhof. From Wien Südbahnhof take line D (until Schwarzenbergplatz) after which Karlsplatz can be reached in a short walk (10 minutes)
- car via the A1 (from the west) or the A2 (from the south). Follow the signs directly to the center of Vienna (Zentrum) and proceed to Karlsplatz. Within and around the center of Vienna there is a short term parking zone (payment zone) requiring to park the car in a garage.

Currency

Since the beginning of 2002 the EURO is the official currency in Austria.
1 Euro = 100 Cents. The symbol of the Euro is €.

Coins: 1, 2, 5, 10, 20, 50 Cents; 1, 2 Euros

Banknotes: 5, 10, 20, 50, 100, 200, 500 Euros

Money can be changed at the airport, at banks, exchange bureaus and larger hotels. For a cash advance, credit cards can be used at cash dispensers (Bankomat) which are available all over the city.

Business hours of banks:

Monday – Wednesday, Friday 08:00 – 12:30 and 13:30 – 15:00

Thursday 08:00 – 12:30 and 13:30 – 17:30

Shopping

Typical shopping hours are Monday to Friday 09:00 – 18:00 and Saturday 10:00 – 13:00 (17:00). Apart from some tobacconists and small supermarkets at petrol stations and at the main railway stations, shops are closed on Sundays. Luxury shops with an elegant clientele can be found in the pedestrian zone of the Graben and of Kärntnerstraße (underground U1, U3 / station Stephansplatz). Street entertainers and outdoor cafe's contribute to the special atmosphere of this area. A well known shopping area is Mariahilferstraße (underground U3 / station Neubaugasse).

Conference Dinner

Monday, September 15th 2003, 20⁰⁰ (included in the conference fee).

The conference dinner will be held at **Wegensteins Gösser Bräu**, Elisabethstrasse 3 (Number 11 on Vienna Area Map 1, page G-8)

Meals

Lunches are provided at the Mensa (yellow area, 1st floor), included in the price on Monday, Tuesday and Wednesday.

A variety of restaurants can be found within 5 minutes walking distance. Menu prices usually include service and taxes. In restaurants, a tip of approximately 10 % is expected. For more details on the locations of the restaurants listed below, please refer to the *Vienna Area Map 1* (page G-8).

1) Café Restaurant Kunsthalle Karlsplatz
Treitlstraße 2
Business hours 10:00-2:00, international cuisine, room for 70 people

2) Bierlagune
Karlsplatz 1
Business hours 11:00-2:00, Viennese food, barbecue, room for 20 people

3) Il Principe
Friedrichstraße 8
Business hours 11:00-2:00, Italian food, snacks, room for 50 people

4) Camelot
Bösendorferstraße 2
Business hours 19:00-2:00, home made food, Thai food, room for 30 people

5) Eat it
Karlsplatz 2
Business hours 18:00-24:00, Asian, Indian, and Thai food, room for 30 people and for 20 people in the 'Schanigarten'

6) Sektbar Schampus
Friedrichstraße 2
Business hours 16:00-2:00, international cuisine, room for 70 people and for 20 in the 'Schanigarten'

7) Café-Restaurant Resselpark
Wiedner Hauptstraße 1
Business hours 8:00-22:00, home made food, room for 50 people

8) Flic Flac
Resselgasse 5
Business hours 8:00-24:00, Italian food, Viennese food, room for 70 people

9) Alcazar
Bösendorferstraße 2
Business hours 19:00-2:00, home made food, Viennese food, room for 50 people

10) Café Les Fleurs
Bösendorferstraße 5
Business hours 10:00-24:00, home made food, Viennese food, snacks, room for 40 people

11) Wegenstein's Gösser Bräu Elisabethstraße 3
Business hours 11:30-23:30, home made food, vegetarian food, room for 100 people

12) Kostas
Friedrichstraße 6
Business hours 11:00-24:00, Greek food, home made food, room for 40 people

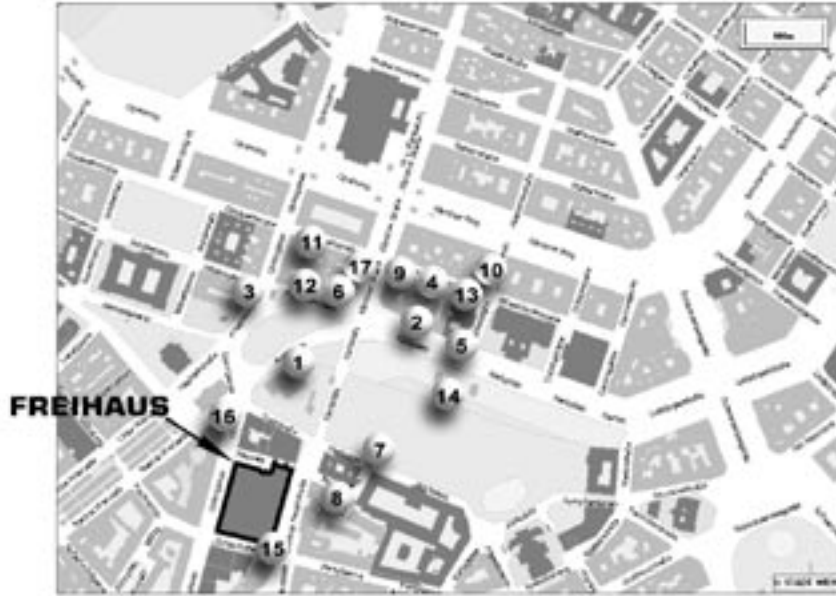
13) Siam
 Bösendorferstraße 2-4
 Business hours 11:30-23:30,
 Thai food, room for 70 people

16) Sportcafé
 Opengasse 8
 Business hours 7:00-20:00,
 international cuisine, room for
 60 people

**14) Café Karl-Otto im Wagner-
 Pavillon**
 Club U Karlsplatz Künstlerhauspassage
 Business hours 9:00-2:00, Viennese
 food, room for 70 people

17) New Asia
 Friedrichsstraße 2
 Business hours 11:30-22:30, Japanese
 and Chinese food, room for 30 people

15) Café Schrödinger (TU Vienna)
 Wiedner Hauptstraße 8-10
 Business hours 9:00-19:00, home
 made food, snacks, room for 100
 people



Vienna Area Map 1

Time	Monday September 15 th	Tuesday September 16 th	Wednesday September 17 th
08:00			
08:30	REGISTRATION & WELCOME	Plenary Lectures PL-5, PL-6, PL-7 (HS 1)	Plenary Lecture PL-10 (HS 1)
09:00	Plenary Lectures PL-1, PL-2 (HS 1)		H. F. Mark Medal Lecture HM-1 (HS 1)
09:30		BREAK	HM-2 (HS1)
10:00			BREAK
10:30			
11:00			
11:30	PC-1 KL-1 / OP 1-3 (HS 6)	PC-3 KL-6 OP 18-20 (HS 6)	PC-5 KL-11 / OP 35-38 (HS 6)
12:00	PS-1 KL-2 / OP 4-6 (HS 5)	PS-4 KL-7 OP 21-23 (HS 5)	PM-1 OP 39-43 (HS 5)
12:30	PS-2 OP 7-11 (HS 3)	PP-1 OP 24-28 (HS 3)	
13:00	LUNCH	LUNCH	LUNCH
13:30			
14:00	Plenary Lectures PL-3, PL-4 (HS 1)	Plenary Lectures PL-8, PL-9 (HS 1)	HM-3 (HS 6)
14:30			HM-4 (HS 6)
15:00			HM-5 (HS 6)
15:30			BREAK
16:00	BREAK	BREAK	HM-6 (HS 6)
16:30	POSTER SESSION PO 1-71	PC-4 KL-8 OP 29-31 (HS 6)	OP 44 (HS 6)
17:00			HM-7 (HS 6)
17:30	PC-2 KL-3 / OP 12-14 (HS 6)	PS-5 KL 9-10 OP 32-34 (HS 5)	HM-8 (HS 6)
18:00			CLOSING CEREMONY
18:30	PS-3 KL 4-5 / OP 15-17 (HS 5)		
19:00		H. F. MARK MEDAL (by invitation only)	
19:30			
20:00	CONFERENCE DINNER		
20:30	Open End		
21:00			

PC: Polymer Characterisation and Processing
 PS: Polymer Synthesis
 PP: Polymer Physics
 PO: Posters in Medical Technology
 PM: Poster Presentation
 HM: H. F. Mark Lectures

Lectures
 HM: H. F. Mark Lecture (30 min)
 PL: Plenary Lecture (50 min)
 KL: KeyNote Lecture (30 min)
 OP: Oral Presentation (20 min)

Lecture Halls
 HS-1: Lecture Hall 1, red area, 1st, 2nd floor
 HS-3: Lecture Hall 3, yellow area, 2nd floor
 HS-5: Lecture Hall 5, green area, 2nd floor
 HS-6: Lecture Hall 6, green area, 2nd floor

Scientific Programm

6TH AUSTRIAN POLYMER MEETING

Plenary Lectures:

- Gerhard BUSSE** (University Stuttgart)
Modern Nondestructive Testing-Methods for Polymeric Materials
- James CRIVELLO** (Rensselaer Polytechnic Institute)
Photoinitiated Cationic Polymerization: New Developments and Applications
- Kurt DIETLIKER** (Ciba Speciality Chemicals Inc.)
Recent Developments in Photoinitiators
- Bela IVAN** (Eötvös Lorand University)
Polyisobutylene-Based Nanostructured Intelligent Amphiphilic Conetworks
- Robert JEROME** (Universite de Liege)
Recent Strategies for Tuning the Properties of Poly(ϵ -caprolactone) and Poly(lactides)
- Klaus MÜLLEN** (Max-Planck Institut für Polymerforschung)
Graphite Molecules
- Oskar NUYKEN** (TU-München)
Synthesis and Applications of 2-Oxazoline Based Amphiphilic Blockcopolymers
- Thomas SCHALKHAMMER** (TU-Delft)
Polymer Technology for Nanodevices and Biochips
- Sabine SEIDLER** (TU-Wien)
Morphology-Property-Correlations by Means of Microhardness Measurements
- Helmut SIXTA** (Lenzing AG)
Recent Trends in Manufacturing and Application of Cellulose Based Materials
- Keynote Lectures:**
- Peter BÄUERLE** (University Ulm)
Self-organizing conjugated Oligomers and Polymers
- Wolfgang H. BINDER** (Vienna University of Technology)
Self Assembly of Hydrogen Bonded Supramolecular Polymers
- Michael R. BUCHMEISER** (University of Innsbruck)
Stereoselective Cyclopolymerization of Dienes: Smart Materials for Electronics and Sensors
- Manfred DUNKY** (Dynea Austria)
Adhesives Based on Formaldehyde Condensation Resins

- Stephan FÖRSTER** (University of Hamburg)
From Self-Organizing Polymers to Nanohybrid and Biomaterials
- Josze KARGER-KOCSIS** (Kaiserslautern University of Technology)
Toughness Improvement of Thermosets via IPN-Formation
- Wolfgang KERN** (TU-Graz)
Functional Polymer Surfaces Generated by Photochemical Techniques
- Manfred RÄTZSCH** (Agrolinz Melamin)
The Reaction Mechanism of the Transesterification and Crosslinking of Melamine Resins
- Helmut RITTER** (University of Düsseldorf)
Green Polymer Chemistry by use of Cyclodextrin
- Robert SAF** (TU-Graz)
Characterization of Functional Oligomers, Polymers and Composites
- Franz STELZER** (TU-Graz)
Synthesis of New Functional Polymers Using the Olefin Metathesis Reaction

XXIST INTERNATIONAL H.F. MARK - SYMPOSIUM

- Hartwig HÖCKER** (DWI - RWTH Aachen e.V.)
Verbesserung der Biokompatibilität von Biomaterialien durch Oberflächenmodifizierung
- Klaus LEDERER** (Montanuniversität Leoben)
UHMPE für Gelenk-Endoprothesen
- Norbert MOSZNER** (Ivoclar AG)
New Monomers for Dental Applications
- Erhard MÜLLER** (ITV Denkendorf)
Nonwovens as Scaffolds for the Tissue Engineering
- Heinz PUDLEINER** (Bayer AG)
Engineering Plastics for the Medical Device Industry
- Karl-Heinz RENZ** (Heraeus Kulzer GmbH & Co KG)
Versyo[®].com – eine lighthärtende Alternative zu herkömmlichen Prothesenbasiswerkstoffen
- Johannes WOLFSCHWENGER** (Borealis GmbH)
Sterilisation Effects on Polypropylene: Technology and Polymer Type Effects
- Felix UNGER** (Europ. Akademie der Wissenschaften und Künste)
Bedeutung der Kunststoff-Forschung für den medizinischen Fortschritt

Monday, September 15th - MorningMonday, September 15th - Morning

08.30 - 09.30 REGISTRATION AND WELCOME (HS1)

PLENARY LECTURES (HS-1)

PL-1 09.30
Chair: H. Gruber
K. Müllen
Max Planck-Institute for Polymer Research, Mainz,
Germany
GRAPHITE MOLECULES

PL-2 10.30
Chair: H. Gruber
T. Schalkhammer
Delft University of Technology, Delft, The Netherlands
POLYMER TECHNOLOGY FOR NANODEVICES AND BIOCHIPS

SESSION PC1 (HS-6)
Chair: G. Busse

KL-1 11.30
J. Karger-Kocsis
University of Technology of Kaiserslautern,
Kaiserslautern, Germany
TOUGHNESS IMPROVEMENT OF THERMOSETS VIA
INTERPENETRATING NETWORK (IPN) FORMATION

OP-1 12.00
G. Locati
Ceast S.p.A., Torino, Italy
RHEOLOGY AT WORK IN COMPOUNDING INDUSTRY

OP-2 12.20
M. Stephan
Institute of Polymer Research Dresden, Dresden, Germany
MICROPHOTOMETRIC DETECTION OF PARTICLES/
INHOMOGENEITIES IN FLOWING POLYMER MELTS

OP-3 12.40
Z. Ahmadi
Amirkabir University of Technology, Tehran, Iran
STABILIZATION OF TWO PHASE POLYMER BLEND
MORPHOLOGY BY USING ELECTRON BEAM RADIATION
PROCESS

SESSION PS1 (HS-5)
Chair: T. Schalkhammer

KL-2 11.30
P. Bäuerle
University of Ulm, Ulm, Germany
SELF-ORGANIZING CONJUGATED OLIGOMERS AND POLYMERS

OP-4 12.00
S. Oberoi
Dresden University of Technology, Dresden, Germany
BIFUNCTIONAL ADHESION PROMOTER FOR GRAFTING
POLYPYRROLE FILMS ON METAL/METAL OXIDE SURFACES

OP-5 12.20
W. Jaeger
Fraunhofer-Institut für Applied Polymer Research,
Golm, Germany
REGULAR POLYMERS WITH CATIONIC AND ANIONIC CHARGES

OP-6 12.40
G. Kickelbick
Vienna University of Technology, Vienna, Austria
CONTROL OF MORPHOLOGY AND COMPOSITION OF
INORGANIC-ORGANIC HYBRID MATERIALS VIA ATOM
TRANSFER RADICAL POLYMERIZATION

SESSION PS2 (HS-3)
Chair: U. Schubert

OP-7 11.20
R. Mülhaupt
Freiburger Materialforschungszentrum (FMF) and
Albert-Ludwigs-University, Freiburg, Germany
CATALYTIC POLYMER MODIFICATION AND TANDEM
CATALYSIS IN AQUEOUS EMULSIONS

OP-8 11.40
R. Nuisin
Chulalongkorn University, Bangkok, Thailand
SYNTHESIS AND PROPERTY BEHAVIOR OF DOP PLASTICIZED
STYRENE-ACRYLATE PARTICLES BY SPG EMULSIFICATION
AND SUBSEQUENT SUSPENSION COPOLYMERIZATION

OP-9 12.00
A. Hirao
Tokyo Institute of Technology, Tokyo, Japan
SYNTHESIS OF HIGHLY DENSED COMBLIKE BRANCHED
POLYMERS WITH WELL-DEFINED STRUCTURES BY COUPLING
REACTION OF LIVING ANIONIC POLYMERS WITH EPOXY-
FUNCTIONALIZED POLYSTYRENES

OP-10 12.20
G. Deák
University of Debrecen, Debrecen, Hungary
STEREOREGULARITY OF CATIONIC POLYMERIZATION:
CATIONIC POLYMERIZATION OF N-BUTYL VINYL ETHER BY
ALANES

OP-11 12.40
W. Kangwansupamonkon
University of Sydney, NSW 2006, Australia
KINETICS OF SURFACE GRAFTING REACTIONS ON
POLYISOPRENE LATICES BY REACTION CALORIMETRY

Sessions
PC: Polymer Characterisation and Processing
PS: Polymer Synthesis
PP: Polymer Physics
PM: Polymers in Medical Technology
HM: H. F. Mark Lectures

Lectures
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HS-6: Lecture Hall 6, green area, 2nd floor

13.00 - 14.00 LUNCH

Monday, September 15th - Afternoon

PLENARY LECTURES (HS-1)

PL-3 **14.00**
Chair: W. H. Binder

B. Iván
 Hungarian Academy of Sciences, Budapest, Hungary
 POLYISOBUTYLENE-BASED NANOSTRUCTURED INTELLIGENT
 AMPHIPHILIC CO-NETWORKS

PL-4 **15.00**
Chair: F. Stelzer

R. Jerome
 University of Liège, Sart-Tilman, Liège, Belgium
 RECENT STRATEGIES FOR TUNING THE PROPERTIES OF
 POLY(ϵ -CAPROLACTONE) AND POLYLACTIDES

16.00 - 16.30 BREAK

16.30 - 17.30 POSTER SESSION

PO-1 - PO-71

SESSION PC2 (HS-6)

Chair: J. V. Crivello

KL-3 **17.30**
M. Dunky
 Dynea Austria GmbH., Krems, Austria
 ADHESIVES BASED ON FORMALDEHYDE CONDENSATION
 RESINS

OP-12 **18.00**
J. Stampfl
 Vienna University of Technology, Vienna, Austria
 WATER SOLUBLE, PHOTOCURABLE RESINS FOR RAPID
 PROTOTYPING APPLICATIONS

OP-13 **18.20**
S. Lüftl
 Vienna University of Technology, Vienna, Austria
 INFLUENCE OF COLORATION ON PHOTO-AND
 PHOTOOXIDATIVE DEGRADATION OF POLYOXYMETHYLENE
 (POM)

OP-14 **18.40**
V.-M. Archodoulaki
 Vienna University of Technology, Vienna, Austria
 DETERMINATION OF OXIDATION INDUCTION TIME
 AND OXIDATION INDUCTION TEMPERATURE (OIT) FOR
 POLYOXYMETHYLENE

SESSION PS3 (HS-5)

Chair: O. Nuyken

KL-4 **17.20**
F. Stelzer
 Graz University of Technology, Graz, Austria
 SYNTHESIS OF NEW FUNCTIONAL POLYMERS USING THE
 OLEFIN METATHESIS REACTION

KL-5 **17.50**
M. R. Buchmeiser
 University of Innsbruck, Innsbruck, Austria
 STEREOSELECTIVE CYCLOPOLYMERIZATION OF DIYNES:
 SMART MATERIALS FOR ELECTRONICS AND SENSORS

OP-15 **18.20**
S. Riegler
 Graz University of Technology, Graz, Austria
 HIGHLY DEFINED BLOCKCOPOLYMERS PREPARED BY ROMP
 USING 3RD GENERATION GRUBBS' INITIATOR

OP-16 **18.40**
S. Itsuno
 Toyohashi University of Technology, Toyohashi, Japan
 PREPARATION OF POLYMER-SUPPORTED OPTICALLY ACTIVE
 1,2-DIAMINE AND ITS APPLICATION TO ASYMMETRIC
 HYDROGENATION CATALYST

OP-17 **19.00**
S. Demel
 Graz University of Technology, Graz, Austria
 ACYCLIC DIENE INSERTION METATHESIS
 POLYCONDENSATION (ADIMET)

Sessions
 PC: Polymer Characterisation and Processing
 PS: Polymer Synthesis
 PP: Polymer Physics
 PM: Polymers in Medical Technology
 HM: H. F. Mark Lectures

Lectures
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 HS-6: Lecture Hall 6, green area, 2nd floor

20.00 CONFERENCE DINNER

Monday, September 15th - Afternoon

Tuesday, September 16th - Morning

PLENARY LECTURES (HS-1)

PL-5 **08.00**

Chair: N Moszner

J. V. Crivello

Rensselaer Polytechnic Institute, New York, USA

PHOTOINITIATED CATIONIC POLYMERIZATION: NEW DEVELOPMENTS AND APPLICATIONS

PL-6 **08.50**

Chair: N. Moszner

K. Dietliker

Ciba Specialty Chemicals Inc., Basel, Switzerland

RECENT DEVELOPMENTS IN PHOTOINITIATORS

PL-7 **09.40**

Chair: M. R. Buchmeiser

O. Nuyken

University of Technology Munich, Germany

SYNTHESIS AND APPLICATION OF 2-OXAZOLINES BASED AMPHIPHILIC BLOCKCOPOLYMERS

10.30 - 11.00 BREAKTuesday, September 16th - Morning

SESSION PP1 (HS-3)

Chair: G. Zifferer

OP-24 **10.50****T. Koch**

Vienna University of Technology, Vienna, Austria

MICROHARDNESS OF QUENCHED POLYPROPYLENE

OP-25 **11.10****B.-A. Zahnt**

Polymer Competence Center Leoben GmbH, Leoben, Austria

FATIGUE OF GLASS-FIBER REINFORCED POLYPROPYLENE (PP-GF)

OP-26 **11.30****A. Kornherr**

University of Vienna, Vienna, Austria

MOLECULAR DYNAMICS SIMULATIONS OF THE FIRST STEPS OF THE FORMATION OF POLYSILOXANE LAYERS AT A ZINC OXIDE SURFACE

OP-27 **11.50****M. Kroutieva**

Kazan State University, Kazan, Russia

NUMERICAL STUDIES OF N-RENORMALIZED ROUSE THEORIES OF POLYMER DYNAMICS

OP-28 **12.10****A. Sikorski**

University of Warsaw, Warsaw, Poland

PROPERTIES OF CONFINED STAR-BRANCHED POLYMER CHAINS

SESSION PC3 (HS-6)

Chair: G. Kickelbick

KL-6 **11.00****R. Saf**

Graz University of Technology, Graz, Austria

CHARACTERIZATION OF FUNCTIONAL OLIGOMERS, POLYMERS AND COMPOSITES

OP-18 **11.30****S. Kéki**

University of Debrecen, Debrecen, Hungary

MALDI-TOF MS CHARACTERIZATION OF TELECHELIC POLYISOBUTYLENES

OP-19 **11.50****M. Kniendl**

Graz University of Technology, Graz, Austria

KINETICS OF RING OPENING METATHESIS POLYMERISATIONS IN THIN FILMS VIA FTIR.

OP-20 **12.10****G. Pinter**

University of Leoben, Leoben, Austria

CHARACTERIZATION OF LOCAL AGING PROCESSES IN PE-HD BY FTIR SPECTROSCOPY

SESSION PS4 (HS-5)

Chair: S. Förster

KL-7 **11.00****W. H. Binder**

Vienna University of Technology, Vienna, Austria

SELF ASSEMBLY OF HYDROGEN BONDED SUPRAMOLECULAR POLYMERS

OP-21 **11.30****J. Borda**

University of Debrecen, Debrecen, Hungary

RECYCLING OF POLYAMIDES: BIOLOGICALLY DEGRADABLE BLOCK-COPOLYMERS

OP-22 **11.50****V. Shadurka**

Vienna University of Technology, Vienna, Austria

FORMATION OF AN INTERPENETRATING NETWORK BY CROSSLINKING OF UF-RESINS WITH BLOCKED ISOCYANATES

OP-23 **12.10****K. Sugiyama**

Tokyo Institute of Technology, Tokyo, Japan

SYNTHESIS AND SURFACE CHARACTERIZATION OF WELL-DEFINED CHAIN-END-FUNCTIONALIZED POLYSTYRENES WITH 2, 4, 8, 16, AND 32 PERFLUOROCTYL GROUPS

Sessions

PC: Polymer Characterisation and Processing

PS: Polymer Synthesis

PP: Polymer Physics

PM: Polymers in Medical Technology

HM: H. F. Mark Lectures

Lectures

HM: H. F. Mark Lecture (30 min)

PL: Plenary Lecture (50 min)

KL: KeyNote Lecture (30 min)

OP: Oral Presentation (20 min)

PO: Poster Presentation

Lecture HallsHS-1: Lecture Hall 1, red area, 1st - 2nd floorHS-3: Lecture Hall 3, yellow area, 2nd floorHS-5: Lecture Hall 5, green area, 2nd floorHS-6: Lecture Hall 6, green area, 2nd floor**12.30 - 13.30 LUNCH**

Tuesday, September 16th - Afternoon

PLENARY LECTURES (HS-1)

PL-8 13.30
Chair: S. Seidler

G. Busse

University Stuttgart, Stuttgart, Germany

MODERN NONDESTRUCTIVE TESTING METHODS FOR POLYMERIC MATERIALS

PL-9 14.30
Chair: J. Karger-Kocsis

S. Seidler

Vienna University of Technology, Vienna, Austria

MORPHOLOGY-PROPERTY-CORRELATIONS BY MEANS OF MICROHARDNESS MEASUREMENTS

15.30 - 16.00 **BREAK**

SESSION PC4 (HS-6)

Chair: R.Saf

KL-8 16.00

S. Förster

University of Hamburg, Hamburg, Germany

FROM SELF-ORGANIZING POLYMERS TO NANOHYBRID AND BIOMATERIALS

OP-29 16.30

G. Reinhold

PSS Polymer Standards Service GmbH, Mainz, Germany

BIOPOLYMERS: A CHALLENGE FOR GPC CHARACTERIZATION

OP-30 16.50

I. Schnöll-Bitai

University of Vienna, Vienna, Austria

AN EXPERIMENTALLY FAST AND STRAIGHTFORWARD METHOD FOR THE DIRECT DETERMINATION OF AXIAL DISPERSION σ_{ax} AS OCCURRING IN SIZE EXCLUSION CHROMATOGRAPHY

OP-31 17.10

G. Heinzmann

Viscotek GmbH, Weingarten, Germany

HYALURONIC ACID AND OTHER BIOPOLYSACCHARIDES: CHARACTERIZATION BY GPC/SEC USING LOW ANGLE LIGHT SCATTERING AND VISCOSITY DETECTION

SESSION PS5 (HS-5)

Chair: K. Dietliker

KL-9 16.00

W. Kern

Graz University of Technology, Graz, Austria

FUNCTIONAL POLYMER SURFACES GENERATED BY PHOTOCHEMICAL TECHNIQUES

KL-10 16.30

H. Ritter

University of Düsseldorf, Düsseldorf, Germany

GREEN POLYMER CHEMISTRY BY USE OF CYCLODEXTRINES

OP-32 17.00

R. Liska

Vienna University of Technology, Vienna, Austria

NEW CHROMOPHORES FOR PHOTOINITIATORS

OP-33 17.20

T. Kakuchi

Hokkaido University, Sapporo, Japan

SYNTHESIS OF HYPERBRANCHED POLYSACCHARIDE BY RING-OPENING POLYMERIZATION OF 1,6-ANHYDROHEXOPYRANOSE USING THERMALLY INDUCED CATIONIC INITIATOR

OP-34 17.50

R. Jordan

Munich University of Technology, Garching, Germany

POLYMER BRUSHES BY SURFACE-INITIATED POLYMERIZATION STRUCTURING ON THE MICRO- AND NANOMETER SCALE

Sessions

PC: Polymer Characterisation and Processing

PS: Polymer Synthesis

PP: Polymer Physics

PM: Polymers in Medical Technology

HM: H. F. Mark Lectures

Lectures

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PL: Plenary Lecture (50 min)

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HS-5: Lecture Hall 5, green area, 2nd floor

HS-6: Lecture Hall 6, green area, 2nd floor

19.00 **H. F. MARK MEDAL**

Tuesday, September 16th - Afternoon

Wednesday, September 17th - Morning

PLENARY LECTURES (HS-1)

PL-10 08.30

Chair: M. Rätzsch

H. Sixta

R&D Lenzing AG, Lenzing, Austria

RECENT TRENDS IN MANUFACTURING AND APPLICATION OF CELLULOSE BASED MATERIALS

HM-1 09.30

Chair: Manfred Tacker

H. Höcker

Deutsches Wollforschungsinstitut an der RWTH Aachen e.V., Aachen, Germany

VERBESSERUNG DER BIOKOMPATIBILITÄT VON BIOMATERIALIEN DURCH OBERFLÄCHENMODIFIZIERUNG

HM-2 10.30

Chair: Manfred Tacker

F. Unger

Europäische Akademie der Wissenschaften und Künste, Salzburg, Austria

BEDEUTUNG DER KUNSTSTOFFFORSCHUNG FÜR DEN MEDIZINISCHEN FORTSCHRITT

11.00 - 11.20 **BREAK**

SESSION PC5 (HS-6)

Chair: M. Dunky

KL-11 11.20**M. Rätzsch**

Agrolinz Melamin GmbH, Linz, Austria

THE REACTION MECHANISM OF THE TRANSESTERIFICATION AND CROSSLINKING OF MELAMINE RESINS

OP-35 11.50**G. Weichsberger**

Vienna University of Technology, Vienna, Austria

SILYLATION OF WOOD

OP-36 12.10**G. Steiner**

IB Steiner, Spielberg, Austria

THERMAL STABILITY OF LGF POLYPROPYLEN

OP-37 12.30**T. Sabu**

Mahatma Gandhi University, Kerala, India

CELLULOSE FIBRE REINFORCED COMPOSITES: NEW CHALLENGES AND OPPORTUNITIES

OP-38 12.50**E.-J. Spindler**

Vinnolit GmbH & Co. KG, Burghausen, Germany

THE ROLE OF PLASTICS IN A SUSTAINABLE DEVELOPMENT

SESSION PM1 (HS-5)

Chair: Dietmar Loidl

OP-39 11.30**A. Eder**

Gabriel Chemie GmbH, Gumpoldskirchen, Austria

CARBON-NANOFIBER-COMPOSITES FOR MEDICAL APPLICATIONS

OP-40 11.50**X. Mo**

Aachen University of Applied Sciences, Aachen, Germany

ELECTROSPINNING P(LLA-CL) NANOFIBER: A BIOMIMETIC EXTRACELLULAR MATRIX FOR CARDIOVASCULAR TISSUE ENGINEERING

OP-41 12.10**B.-S. Hsiao**

State University of New York, Stony Brook, USA

BIOPOLYMER NANOFIBER SCAFFOLDS FOR BIOMEDICAL APPLICATIONS

OP-42 12.30**Ch. Fritz**

University of Leoben, Leoben, Austria

POLYMER PROPERTIES AS A FUNCTION OF REPEATED INSTRUMENT PROCESSING

OP-43 12.50**W.G. Pohl**

Austrian Chemical Society, Vienna, Austria

WERNER KUHN - A PIONEER OF POLYMER RESEARCH

Sessions

PC: Polymer Characterisation and Processing

PS: Polymer Synthesis

PP: Polymer Physics

PM: Polymers in Medical Technology

HM: H. F. Mark Lectures

Lectures

HM: H. F. Mark Lecture (30 min)

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Wednesday, September 17th - Afternoon

H. F. MARK LECTURES (HS-6)

Chair: Otakar Seycek

HM-3 14.15

N. Moszner
Ivoclar Vivadent AG, Schaan, Liechtenstein
NEW MONOMERS FOR DENTAL APPLICATIONS

HM-4 14.45

K-H. Renz
Heraeus Kulzer GmbH & Co KG, Wehrheim, Germany
VERSYO®.COM - EINE LICHTHÄRTENDE ALTERNATIVE ZU
HERKÖMMLICHEN PROTHESENBASISWERKSTOFFEN

HM-5 15.15

E. Müller
ITV Denkendorf Produktservice GmbH, Denkendorf,
Germany
NONWOVENS AS SCAFFOLDS FOR THE TISSUE ENGINEERING

15.45 - 16.10 BREAK

Chair: Christa Hametner

HM-6 16.10

H. Pudleiner
Bayer AG, Krefeld, Germany
ENGINEERING PLASTICS FOR THE MEDICAL DEVICE INDUSTRY

OP-44 16.40

Ch. Gornik
Battenfeld Kunststoffmaschinen GmbH, Kottlingbrunn,
Austria

DIE ABFORMUNG FUNKTIONELLER MIKROSTRUKTUREN FÜR DIE
MEDIZINTECHNIK IM SPRITZGIEßVERFAHREN

HM-7 17.00

K. Lederer
Montanuniversität Leoben, Leoben, Austria
ALPHA-TOCOPHEROL - A POTENTIAL STABILIZER FOR STANDARD
AND CROSSLINKED ULTRA-HIGH MOLECULAR WEIGHT
POLYETHYLENE (UHMW-PE) USED FOR JOINT ENDOPROSTHESE

HM-8 17.30

J. Wolfschwenger
Borealis GmbH, Linz, Austria
STERILIZATION EFFECTS ON POLYPROPYLENE: TECHNOLOGY AND
POLYMER TYPE EFFECT

Sessions

PC: Polymer Characterisation and Processing
PS: Polymer Synthesis
PP: Polymer Physics
PM: Polymers in Medical Technology
HM: H. F. Mark Lectures

Lectures

HM: H. F. Mark Lecture (30 min)
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HS-6: Lecture Hall 6, green area, 2nd floor

18.00 CLOSING CEREMONY

Graphit Molecules

Mark D. Watson and Klaus Müllen*

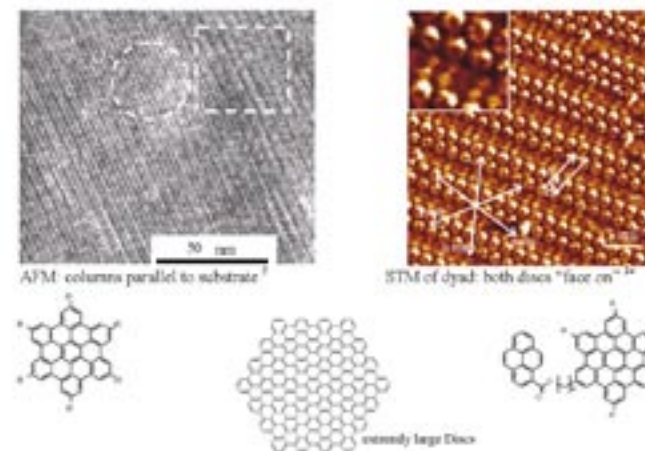
Max-Planck-Institute for Polymer Research, Mainz, Germany

This presentation is based on three central points:

Polymer synthesis is able to produce all sorts of coil structures and topologies derived from them such as stars and brushes, but disc-like polymers with two-dimensional molecular forms are unknown;

Graphite, a single sheet of which can be viewed as a 2D-macromolecule, is an attractive material for solid-state physics, especially in view of its allotropes such as fullerene and nanotubes, but is hardly a definable objective for polymer synthesis; Polycyclic aromatic hydrocarbons (PAHs) have played a central role in the development of organic chemistry, but possess no polymer analogs.

We demonstrate practical routes to make extremely large PAHs, which act as structurally defined processable graphite molecules.[1] Connected with the synthesis is the attainment of complex supramolecular architectures by processing from solution or from the melt. In this way a hierarchy of structures is developed, which leads from single molecules [2] and their visualization towards, for example, epitaxially ordered multilayers[3] fibres[4] and films[5] containing perfect columnar arrangements of discotic molecules. This organisation produces remarkable physical properties, which are responsible for very high charge carrier mobilities[6] in photoconduction and efficient energy conversion in solar cells.[7] Other possible applications include efficient lithium storage or selective thermolytic conversion of PAHs into novel carbon nano- and microtubes.



PLENARY LECTURES

References

- [1] (a) Simpson, C.D.; Brand, J.D.; Berresheim, A.J.; Przybilla, L.; Räder, H.J.; Müllen, K. *Chem. Eur. J.* **2002**, *8*, 1424-29. (b) Watson, M.D. Fechtenkötter, A.; Müllen *Chem. Rev.* **2001**, *101*, 1267-1300.
- [2] (a) Samori, P.; Fechtenkötter, A.; Jäckel, F.; Bohme, T.; Müllen, K.; Rabe, J.P. *J. Amer. Chem. Soc.* **2001**, *123*, 11462-67. (b) Samori, P.; Severin, N.; Simpson, C.D.; Müllen, K.; Rabe, J.P. *J. Amer. Chem. Soc.* **2002**, *124*, 9454-57. (c) Tchegotareva, N.; Yin, X.; Watson, M.D.; Samori, P.; Rabe, J.P.; Müllen, K. *J. Amer. Chem. Soc.* accepted November 2002.
- [3] Schmitz-Hübsch, T.; Sellam, F.; Staub, R.; Torker, M.; Fritz, T.; Kübel, C.; Müllen, K.; Leo, K. *Surf. Sci.* **2000**, *445*, 358.
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- [5] Tracz, A.; Jeszka, J.K.; Watson, M.D.; Pisula, W.; Müllen, K.; Pakula, T. *J. Amer. Chem. Soc.* accepted November 2002
- [6] van de Craats, A.M.; Warman, J.M.; Fechtenkötter, A.; Brand, J.D.; Harbison, M.A.; Müllen, K. *Adv. Mat.* **1999**, *11*, 1469-72.
- [7] Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R.H.; MacKenzie, J.D. *Science* **2001**, *293*, 1119-21.

PL-2

Polymer technology for nanodevices and biochips

H. Rauter², V. Matyushin¹, Y. Alguet², Th. Schalkhammer^{1,2,*}1) AnalyticalBioTechnology, TU-Delft, Julianalaan 67, 2628 BC Delft, The Netherlands,
2) Institut für Biochemie und molekulare Zellbiologie, Dr. Bohrgasse 9, 1030 Wien, Austria
E-mail: Schalkhammer@bionanotec.org

Within the last decade the use of nano-structured polymers for biochips, biosensors and novel nano-optical devices gained world-wide attention due to a number of key-developments. The use of nano-layers as elements and building blocks for nano-devices opened novel and cost efficient routes in photonic, electronic as well as analytical devices. Defined nano-assemblies enable to construct three-dimensional nanostructures with ultra-high packing density. Decisive for these types of devices and sensors is the ultra-precise nanometric assembly.

Thus, manufacturing of bio-nano-devices requires the development of a completely new set of techniques to arrange, manipulate and couple nano-building blocks. New techniques are first developed to build key elements of novel nano-devices.

In nano optical devices coupling of the local field surrounding a nano-resonator allows resonance with other elements interacting with this field. High throughput transducers using metal cluster resonance technology are based on surface-enhancement of metal cluster light absorption. These devices are used for detection of biorecognitive binding as well as structural changes of nucleic acids, proteins or polymer nano-layers. The optical property for the analytical application of metal cluster coated nano-films is the so-called anomalous absorption. An absorbing film of clusters is positioned at 10-400 nm to an electromagnetic wave reflecting layer. At a well defined distance of the cluster to the mirror the reflected electromagnetic field has the same phase at the position of the absorbing cluster as the incident fields. This feedback mechanism strongly enhances the effective cluster absorption coefficient. These systems are characterized by a narrow reflection minimum whose spectral position shifts sensitively with the polymer layer, because a given cluster-mirror distance and wavelength defines the optimum phase. In biosensor technology new principles can overcome the problems of established transducers at a membrane interface. Polymer-membrane supported devices allow to control the ion flux through a membrane channel or integral membrane protein similar to a human nerve cell.



The critical part of the sensor concept is a novel membrane technology building picoliter-sized artificial cell-compartments. The choice of a photo crosslinked or electro-polymerized gel polymer as the membrane support and the covalent coupling of the lipids at the gel surface results in an increased mechanical stability and in an inhibition of the floating of the top lipid layer. To create the artificial cell a photo-resist membrane frame is required being compatible with aqueous bio environment.

For application in biochips, nanosensors and smart coatings photo-crosslinked, photo-etchable and nano-structured polyvinyl-pyrrolidones, photo-crosslinked acrylic polymers, protein-nanogels, DNA-assemblies as well as modified polypyrroles or polyphenols coated via electro-polymerization are important bio-nano-tools.



PL-3

Polyisobutylene-Based Nanostructured Intelligent Amphiphilic Conetworks

Béla Iván

Department of Polymer Chemistry and Material Science, Institute of Material and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, Pusztaszeri u. 59-67, P. O. Box 17, Hungary and Department of Chemical Technology and Environmental Chemistry, Eötvös Loránd Science University, Budapest, Hungary,
E-mail: bi@chemres.hu

Polyisobutylene (PIB) is a fully saturated, thermally, oxidatively, chemically stable elastic polymer with low glass transition temperature. Therefore this polymer is a useful building block in numerous bi- and multicomponent polymer systems[1]. PIBs with well-defined structure, molecular weight (MW) and narrow molecular weight distribution (MWD) can be obtained only by quasilingiving carbocationic polymerization (QLCCP). We have recently discovered a new catalytic system for this polymerization which yields PIBs with desired structure, MW and unprecedented ultra narrow MWD, narrower than Poisson distribution claimed as the limiting possible MWD for synthetic polymers obtained by quasilingiving addition polymerizations[2] in the absence of permanent chain breaking reactions (termination and chain transfer). Utilization of well-defined telechelic PIB macromonomers obtained via QLCCP, a new class of crosslinked polymers, amphiphilic conetworks (APCN)[3,4] composed of covalently bonded otherwise immiscible hydrophilic and hydrophobic polymer chains have been synthesized. The amphiphilic nature of these new crosslinked polymers is indicated by their swelling ability in both hydrophilic and hydrophobic solvents. Special synthetic techniques have been developed by us for the preparation of these new unique materials[4]. Due to the covalent bonds between the components, large scale phase separation of the immiscible polymers is prevented by the chemical bonding in the conetworks. As a result, phase separation leads to nanodomains as it has been proved with systematic TEM, AFM, SAXS, SANS and solid state NMR measurements, recently. The nanodomains can be utilized as nanotemplates for producing, for instance, nanocrystals in APCNs yielding new organic-inorganic nanohybrids[3]. The unique nanophase separated morphology may also lead to temperature responsive gels with high mechanical stability, such as in the case of poly(N,N-dimethylaminoethyl methacrylate)-*l*-polyisobutylene APCNs as discovered by us recently. In another approach, poly(methacrylic acid)-*l*-polyisobutylene APCNs were prepared by a special two-step process. These new polyelectrolyte APCNs possess smart (intelligent) reversible pH-responsive properties in aqueous media[4].

This presentation summarizes the recent advances in the synthesis, structure, properties and potential applications of these new emerging materials.

References

- [1] (a) J. P. Kennedy, B. Iván, *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*, Hanser Publishers, Munich, New York, 1992. (b) B. Iván, *Makromol. Chem., Macromol. Symp.* **1993**, *75*, 181-186. (c) B. Iván, P. W. Groh, T. Fónagy, K. Tóth, *Polym. Mater. Sci. Eng.* **2001**, *84*, 841-842.
- [2] B. Iván, *Macromol. Chem. Phys.* **2000**, *201*, 2621-2628.
- [3] J. Scherble, R. Thomann, B. Iván, R. Mülhaupt, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1429-1436.
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PL-4

Recent strategies for tuning the properties of poly(ϵ -caprolactone) and polylactides**R. Jerome**

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6a, 4000 Liège, Belgium,
E-mail: rjerome@ulg.ac.be

Poly(ϵ -caprolactone) (PCL) and polylactides (PLA) are thermoplastics with quite unusual properties of polymer miscibility (PCL), biocompatibility and (bio)degradability. They are thus environmentally friendly polymers and they have potential in biomedical applications. The ring-opening polymerization of ϵ -caprolactone (seven numbered cyclic ester) and lactide (cyclic diester of lactic acid) is known for «livingness» when initiated by Al and Sn alkoxides under appropriate experimental conditions. The macromolecular engineering of PCL and PLA has therefore been successfully achieved. Quite recently, several strategies have been proposed for making headway in this field that remains of a vivid interest.

- New initiators have been searched for with the purpose to increase the activity while preserving the polymerization control. A special attention has also been paid to restrict (or completely avoid) contamination by metallic residues known for adversary effect in biomedical applications.
- The use of organic solvents in polymer synthesis is a rapidly increasing environmental concern. Therefore, bulk polymerization (e.g. by reactive extrusion) and polymerization in supercritical fluids are currently investigated.
- Physico-mechanical properties of PCL and PLA are actively upgraded by filling these aliphatic polyesters by nanofillers. Foaming is another valuable modification, e.g., for the production of porous supports for cell culture and tissue engineering.
- Chemical modification for imparting reactivity and functionality is the fourth strategy which is contemplated. In this respect, functionalized derivatives of ϵ -caprolactone have been synthesized which increases dramatically the range of materials that can be made available.

Contribution of CERM to these strategies will be discussed.

PL-5

Photoinitiated Cationic Polymerization: New Developments and Applications**James V. Crivello***

Department of Chemistry, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York, USA
E-mail: crivej@rpi.edu

This lecture will focus primarily on progress made within the last two years in our laboratory in the field of photoinitiated cationic polymerization. Three major areas will be discussed: the synthesis of new, highly efficient photoinitiators, development of novel long wavelength UV and visible light absorbing photosensitizers for various onium salt photoinitiators and the use of photoinitiated cationic polymerizations in a number of applications.

Dialkylphenacylsulfonium salts are excellent photoinitiators for cationic polymerization that are readily prepared in high yields by simple, straightforward reactions.[1] These photoinitiators initiate cationic polymerization by a generating strong acid on UV irradiation by a reversible mechanism in which an ylide is formed as an intermediate. The structures of these photoinitiators can be varied widely to optimize their photosensitivity and to provide solubility in both polar and nonpolar monomers. Dialkylphenacylsulfonium salts can be photosensitized to increase their efficiency and to enhance their spectral response. Several different means of photosensitizing onium salt induced cationic polymerization have been explored. The most broadly applicable method involves the use of electron-transfer photosensitizers. Recently, we have observed that a wide variety of carbazole compounds are excellent and highly general photosensitizers for onium salts.[2] Especially, interesting was the observation that polymers and copolymers of N-vinylcarbazole were excellent photosensitizers. An additional class of highly active photosensitizers is phenothiazine compounds.[3] Using appropriate substitution, the wavelength of absorption and response of these systems can be easily tailored. Considerable recent progress has been made in the adoption of photoinitiated cationic polymerization in a variety of new commercial applications. High technology uses such as high resolution photolithography, holographic recording and stereolithography are examples of applications that take advantage of the unique characteristics of photoinitiated cationic polymerizations.

References

- [1] J.V. Crivello, S. Kong *Macromolecules*, 2000, 33(3), 825.
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PL-6

Recent Developments in Photoinitiators

Kurt Dietliker

*Ciba Specialty Chemicals Inc., Coating Effects Segment; Photoactive Chromophores Research, CH-4002 Basel, Switzerland.
E-mail: kurt.dietliker@cibasc.com*

Photoinitiators are key components in all photopolymerizable formulations, which allow the efficient transformation of the energy of light into chemical energy in the form of initiating species. A variety of photoinitiators for different applications are today commercially available and find widespread use. However, new developments in radiation curing are emerging that require further improvements in photoinitiator chemistry.

While a high curing efficiency is crucial, other properties become equally important in novel applications. Acylphosphine oxides are a class of photoinitiators that had a high impact on the development of radiation curing over the last years. Developed for the curing of pigmented coatings, these initiators allow for the first time the efficient curing of clear lacquers that contain a full light stabilizer package for outdoor use. An improved understanding of the photoinitiation process supports ongoing improvements towards even more efficient compounds of this type. The study of this process has become possible due to a new experimental technique, based on time-resolved ESR spectroscopy, which allows to monitor the formation and decay of the initiating radicals.[1]

Photoinitiators for resist applications have to provide outstanding lithographic properties besides high photospeed. In addition, compound designed for use in color filter resists have to meet severe requirements regarding the light transmission in the cured film in order to guarantee the purity of the color in the display. Novel substituted oxime ester derivative can meet these requirements best.[2]

New exploratory developments in photoinitiator research are aimed at compounds that produce a strong base upon irradiation, which can efficiently catalyze the crosslinking of suitable resins. While the feasibility of this process using a newly developed photolabile amine has been proven,[3] the resin chemistry has to be developed in parallel. The novel photocurable system is expected to find broad technical acceptance and to open new opportunities for radiation curing.

Modern photoinitiators are thus more than initiators for the polymerization process: they are an integral part of sophisticated formulations providing excellent properties during the manufacturing process and the service time of the cured article.

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PL-7

Synthesis and Application of 2-Oxazolines based amphiphilic Blockcopolymers

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Metal-catalyzed reactions have attracted enormous interest in academia and industry as one of the most versatile synthetic methodologies, that give access to a wide variety of organic compounds, such as pharmaceuticals, fine chemicals as well as polymers. From an industrial point of view, two important goals have to be realized in the near future: i) the use of water as the preferred solvent due to economical, physiological and safety related process engineering reasons and ii) easy separation of the metal catalyst from the product, allowing catalyst recycling and preparation of metal-free products. Several approaches have been presented in the past to transfer transition-metal catalyzed reactions into aqueous media, either by liquid-liquid two phase systems or by the use of soluble polymer supports, such as poly(ethylene glycol) or poly(N-alkylacrylamides). However, efficient transformation of hydrophobic substrates in neat water with the option of catalyst recycling remains still a challenging task.

In this contribution we will report on the synthesis of amphiphilic block copolymers, consisting of a hydrophilic block and a hydrophobic block bearing transition-metal complexes. These polymers were prepared by ring-opening cationic polymerization of 2-Alkyl-2-oxazoline monomers.[1] The use of amphiphilic block copolymers was guided by several considerations. i) Micelles formed in aqueous solution provide a hydrophobic reservoir for substrate solubilization and concentration, ii) the number of catalytic sites and their steric flexibility on the polymeric support can be easily varied by the block copolymer structure and composition, and iii) separation of the polymeric macroligand from the product is facilitated. The versatility of this approach is demonstrated by several successful applications, including the ATRP of various acrylate monomers[2], the hydroformylation of 1-octene[1,3], the Heck reaction and the enantioselective hydrogenation of amino acid precursors[4].

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PL-8

Modern Nondestructive Testing Methods for Polymeric MaterialsG. Busse*Institute for Polymer Testing and Polymer Science -Nondestructive Testing- (IKP-ZFP),
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Non-metallic materials are of technological interest because of their low production costs (easy access to raw materials) and resistance against corrosion or because of their specific strength that may be much better than for metal. This makes them attractive for light weight structures for sports, aerospace- and automotive applications. As manufacturers have a strong responsibility for their product, quality control is an important task including processing, maintenance and service inspection. The main goal of nondestructive testing (NDT) is to replace low quality products early enough in order to avoid failure and to avoid time-consuming and expensive unnecessary replacement of intact components. The considerable experience in NDT of metals is based on ultrasonics, x-rays, and eddy-currents. However, these established methods are less applicable to non-metals due to lower atomic weight, higher acoustic attenuation and much lower electrical conductivity. On the other hand, these properties can favour other methods that fit to the specific inspection needs of non-metals, e.g. curing, fibre orientation, impact detection, and delamination. In any case, every NDT-method exposes the component to be inspected to some kind of external excitation (electromagnetic, elastic, or thermal waves) and characterises the component and potential defects in it by the observed response to this input. Therefore every result shows the component and its defects under the specific aspect of the physical interaction involved. Consequently one needs more than just one method to characterise the broad variety of non-metals and their defects. Of particular interest are those methods which do not require physical contact with the inspected object and which are applicable not only in the laboratory but also under industrial conditions.

The paper highlights modern NDT-methods, e.g. ultrasound activated speckle and lockin speckle interferometry displacement imaging, elastic wave thermography, microwaves, non-linear scanning-vibrometry, air-coupled ultrasound in linear and non-linear methods. It will be discussed which information these methods provide, also their specific advantages and limitations. The materials on which these methods are demonstrated are glass fibre (GFRP) or carbon fibre reinforced polymer materials (CFRP) and ceramics. The examples relate to general problems in aerospace- and automotive applications of these polymeric materials. It is a challenge to further develop these techniques, in order to make the new non-metal materials safer and hence more applicable to new fields.

PL-9

Morphology-Property-Correlations by Means of Microhardness MeasurementsS. Seidler*Vienna University of Technology, Institute of Materials Science and Testing, Favoritenstr. 9-11, A-1040 Vienna
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The search for quantitative structure – property correlations for the control and prediction of the mechanical behaviour of polymers has occupied a central role in the development of polymer science and engineering. Mechanical performance factors such as creep resistance, fatigue life, toughness and the stability of properties with time, stress and temperature have become subjects of major activities. Within this context microhardness is a property which is sensitive to structural changes. Nowadays, the microhardness and especially the instrumented microhardness technique, being an elegant, nearly non-destructive, sensitive, and relatively simple method, enjoys wide application. In addition to some methodological contributions to the technique, the microhardness method has to be successfully used to gain a deeper understanding of the microhardness – structure correlation of polymers. A very attractive feature of this technique is that it can be used for the micromechanical characterization of some components, phases or morphological entities that are otherwise not accessible for direct determination of their hardness and modulus.[1] These possibilities are very useful for the quantification of phase properties.[2,3], the determination of phase and bulk properties on one specimen, surface and cross section properties and orientations on materials, but also on components and structures.

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PL-10**Recent Trends in Manufacturing and Application of Cellulose based Materials****Herbert Sixta***, Heinrich Firgo*R&D Lenzing AG, A-4860 Lenzing, Austria**E-mail: h.sixta@lenzing.com, h.firgo@lenzing.com*

Cellulose, the most abundant natural $\beta(1\rightarrow4)$ -polysaccharide, is one of the oldest raw material with outstanding properties and a variety of useful applications. With an estimated annual output of approximately 10^{11} - 10^{12} tons, the availability of this biopolymer is at least four to five orders of magnitude higher as compared to the annual production of synthetic polymers. Being fully biocompatible, renewable and compostable, the demand for cellulosic products, will continue to grow. In more recent times, research on both native structures and structure formation in cellulosic materials have benefited from the rapid advances in theoretical and experimental polymer physics, especially in the field of crystal structure and supramolecular architecture[1].

The widespread use of cellulose products, however, is significantly affected by both the costly manufacturing and purification processes and its difficulty of chemical processing in general because cellulose is not meltable and not soluble in usual solvents due to its hydrogen bonded, partially crystalline structure. Thus it is mandatory to improve the economic basis of cellulose production by new pulping and bleaching technologies including enhanced by-product utilization.

The present work reviews the latest developments in the field of dissolving pulp production, the major source for all cellulose based products. During pulping and bleaching oxidized groups are introduced, which significantly influence the properties of cellulosic materials. A novel method to accurately determine the carbonyl content in these substrates by fluorescence will be introduced[2]. The method provides also carbonyl profiles relative to the molecular weight, which allow a much more precise evaluation of oxidative changes. The production of regenerated cellulosic fibers is based largely on the more than 100year old viscose technology. The new Lyocell process being established within the last decade as an environmentally friendly alternative offers besides reinforced fiber properties a variety of new cellulosic products, such as functionalized fibers, films and sponges [3,4]. Furthermore, new application fields, like liquid crystalline polymers, biomaterial as an artificial blood vessel[5], surface functionalized fibers and films and molecular recognition will be presented.

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KL-1

Toughness Improvement of Thermosets via Interpenetrating Network (IPN) Formation**J. Karger-Kocsis***Institut für Verbundwerkstoffe GmbH, Technische Universität Kaiserslautern, POBox 3049,
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Albeit thermoset resins offer many beneficial properties, they lack of toughness. For the toughness improvement of thermosets various methods are introduced and practiced. The target is always to achieve a sudden and efficient relieve of the triaxial stress state accommodated at the crack tip of the loaded specimen or structure. Note that shear deformation is the major energy absorbing mechanism in thermosets. It is intuitive that resins combinations resulting in interpenetrating network (IPN) structure should show improved shear deformability and thus possess high toughness. Unfortunately, the rules of how to produce such systems are not fully explored yet irrespective to the vivid interest for IPN-type materials.

Bisphenol-A based vinylester (VE) resins when crosslinked via copolymerization with styrene exhibit outstanding mechanical and thermal properties. Based on their beneficial properties/cost performance VEs compete with epoxy resins (EP) in several fields. A drawback of VEs is their low toughness. This work was aimed at toughening of VE by producing a hybrid resin system of IPN structure. Thus, VE (crosslinked by styrene) was combined with various EP resins (crosslinked by amine compounds via polyaddition) according to a proprietary technology and the fracture mechanical response of the related systems determined. The fracture energy (G_c) of the IPN structured systems reached a level of 6-8 kJ/m² which is an outstanding value even for thermoplastics [1-2]. The fracture mechanical characteristics strongly depended on the build-up of the EP component. Especially, the presence of cyclohexylene linkages either in the EP resin or in the hardener were found beneficial. The formation of the IPN structure were verified by atomic force microscopy (AFM) using physically etched specimens [3]. Successful attempts were made to use this new hybrid resin in various fiber-reinforced composites produced by resin transfer molding.

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KEYNOTE LECTURES

KL-2

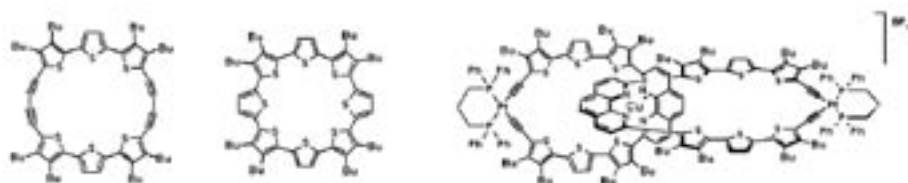
Self-organizing Conjugated Oligomers and Polymers

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Conjugated oligo- and polyheterocycles represent an important class of compounds in the field of organic materials and have successfully been used as active components in organic electronic devices, such as field effect transistors (FET) and logic circuits, light emitting diodes (LED) and full-colour displays or solar cells. In this respect, we recently could add novel structures and topologies to this field: the first fully α -conjugated macrocyclic oligothiophenes have been prepared, which combine the excellent properties of the corresponding linearly conjugated oligomers and host/guest chemistry as a completely novel perspective.

On this basis, the synthesis of interlocked conjugated macrocycles namely catenanes has been started. Intriguing self-assembling properties of the linear conjugated oligo- and polythiophenes, as well as of the macrocycles on substrates were investigated by scanning tunneling microscopy (STM) and directly allowed the determination of molecular parameters. Unprecedented superstructures of host/guest molecules on surfaces allow the formation of molecular architectures into the third dimension.



KL-3

Adhesives based on Formaldehyde Condensation Resins

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In the wood based panels industry a great variety of adhesives currently is in use. Condensation resins based on formaldehyde represent the biggest volumes within these wood adhesives. They are formed by the reaction of formaldehyde with various chemicals like urea, melamine, phenol or resorcinol or with combinations of these substances. During the duroplastic hardening and gelling they convert to three dimensionally crosslinked and therefore insoluble and nonmeltable networks. The hardening conditions can be acidic (aminoplastic resins), highly alkaline (phenolic resins) or neutral to light alkaline (resorcinol resins).

The various aminoplastic glue resins are the most important types of adhesives in the wood based panels industry. According to the used raw materials various types of resins are possible like UF (urea-formaldehyde-resin), MF (melamine-formaldehyde-resin), MUF (melamine-urea-formaldehyde-cocondensation resin), mUF (melamine fortified UF-resins), MF+UF (mixture of a MF- and an UF-resin) and MUPF or PMUF (melamine-urea-phenol-formaldehyde-cocondensation resin).

The most important parameters for the aminoplastic resins are (i) the type of monomers, (ii) the molar ratio of the various monomers in the resin like F/U or F/(NH₂)₂, (iii) the cooking procedure, e.g. pH- and temperature program, types and amounts of alkaline and acidic catalysts, sequence of addition of the different raw materials and duration of the different steps of the cooking procedure, and (iv) the molar mass distribution (degree of condensation). Forced by the necessity to limit the subsequent formaldehyde emission the molar ratio F/U had been decreased distinctly within the last 2-3 decades. The main differences between UF-resins with high and with low content of formaldehyde, resp., are the crosslinking/hardening reactivity of the resin due to the different content of free formaldehyde and the hence achievable degree of crosslinking in the cured network. In UF-resins the aminomethylene link is susceptible to hydrolysis and it therefore is not stable at higher relative humidity, especially at elevated temperatures. Therefore UF-resins mainly are used for interior boards (for use in dry conditions, e.g. in furniture manufacturing), a higher hydrolysis resistance can be achieved by incorporating melamine and in case phenol into the resin (melamine fortified UF-resins, MUF, MUPF, PMUF). The different resistance of these resins against hydrolysis is based on molecular level.

Phenolic resins show a high resistance of the C-C-bonding between the aromatic nucleus and the methylolgroup or the methylene bridge and therefore are used for boards for use under humid conditions. Another advantage of the phenolic resins is the very low subsequent formaldehyde emission also due to the strong C-C-bonding. The properties of the resins are determined mainly by the molar ratio F/P, the type and amount of the catalyst (in most cases caustic) and the reaction conditions. Disadvantages of the phenolic resins are the necessary distinct longer press times compared to UF-resins, the dark colour of the glue line and of the board surface as well as a higher moisture content of the boards stored at higher relative humidity of the surrounding air due to the hygroscopic behaviour of the caustic in the board.

KL-4

Synthesis of new functional polymers using the olefin metathesis reactionFranz Stelzer*Institut für chemische Technologie organischer Stoffe der Technischen Universität Graz,
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The olefin metathesis reaction has gained increasing interest for the synthesis of specialty polymers during the last decade. As the initiators /catalysts became more and more compatible with various functionalities the field of applicability of this interesting reaction has broadened remarkably.

This presentation highlights methods for the synthesis and characterisation of liquid crystalline polymers (LCPs) - side chain LCPs (SCLCPs) and main chain LCPs (MCLCPs) as well. SCLCPs are mainly synthesised via the ring opening metathesis polymerisation (ROMP) of norbornene derivatives and other cycloolefins. The livingness of the most recent initiator systems basing on Ru-carbenes allows the synthesis of well defined block copolymers, but also of truly statistically distributed copolymers. A number of examples will be given for side chain LCPs with various mesogenes, spacer lengths and composition. The main goals are improvement and tuning of optical properties or a combination of optical and electronic properties for applications in optical or optoelectronic devices. Alternating MCLCPs were synthesised via the recently developed "Alternating Metathesis Condensation" (AMCON). This polymerisation method allows the synthesis of strictly alternating polymers with soft/columnar diads or columnar/banana shaped mesogene diads as well. Especially the latter type is very new.

All polymers were characterised with respect to their molecular weight (SEC), optical (IR, NMR, UV-VIS, refractive index), thermal (DSC/TGA/DMTA), various physical properties (light emission, elasticity) and morphology (XRD, TEM/REM, polarised optical microscopy).

KL-5

Stereoselective Cyclopolymerization of Diynes: Smart Materials for Electronics and SensorsJens Krause, Dongren Wang, Udo Anders, Oskar Nuyken*, Michael R. Buchmeiser**Institut für Analytische Chemie und Radiochemie, Leopold-Franzens-Universität Innsbruck, Innrain 52a, A-6020 Innsbruck
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A series of heptadiynes and hexadiynes was cyclopolymerized by new Schrock initiators to produce polyenes exclusively based on one single repetitive unit, i.e. 1,2-cyclopent-2-enylvinylenes and 3,4-cyclobut-1-enylvinylenes, respectively. Polymers containing virtually 100 % 1,2-cyclopent-2-enylvinylene units were obtained by various routes, e.g. by low-temperature-initiated cyclopolymerization. A chiral polyene was prepared from 4-(ethoxycarbonyl)-4-(1S, 2R, 5S)-(+)-menthyl-1,6-heptadiyne (ECMHD) to determine the configuration of the double bonds and the tacticity of the polyene backbone. Poly-ECMHD consisted of 100 % 5-membered rings and possessed an alternating cis-trans isotactic structure. Molecular weights and polydispersity indices of the polymers were determined in CHCl₃ by GPC vs PS. Complementary, light scattering data were collected at $\lambda = 690$ nm and MALDI-TOF MS was applied in order to calculate absolute molecular weights. The cyclopolymerization of DEDPM proceeded in a living manner fulfilling the criteria for a class V living system.[1, 2] Alternatively, poly-DEDPM exclusively based on 1,2-(cyclopent-1-enylene)vinylene units was prepared using MoCl₅-*n*-Bu₄Sn-EtOH-quinuclidine (1:1:5:1) and MoCl₅-*n*-Bu₄Sn-EtOH-quinuclidine (1:1:2:1). The initiator efficiency of MoCl₅-*n*-Bu₄Sn-EtOH-quinuclidine (1:1:2:1) was as high as 91%, the highest value ever reported for such systems. Multistage polymerizations of DEDPM indicated for both initiator systems that the catalytic species were active for at least 6 hours in the presence of monomer yet did not fulfill the criteria of a truly living polymerization.[3] Measurement of λ_{max} of poly(DEDPM)₅₀ solutions in CHCl₃ between 25 and 55 °C revealed a reversible thermoresponsive behavior with changes in λ_{max} of 8 nm. Unlike other polyenes, poly-DEDPM is stable under air over months in the solid state as well as in solution using non-acidic solvents.[4] The synthetic concepts as well as applications in electronics and sensors will be presented.

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KL-6

Characterization of Functional Oligomers, Polymers and Composites

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The interest in functional organic oligomers, polymers and composites with special physical or chemical properties has continuously increased during the last decades. Very often the observable properties of these materials can be directly correlated to the chemical structure. Thus, a detailed characterization at the molecular level is essential for the understanding of various phenomena, and subsequently for continuous improvements and/or new developments. But often a combination of the results obtained by different analytical techniques is necessary to find an unambiguous answer for a specific problem.

A comparably young technique, that has become 'state-of-the-art' in the area of polymer characterization within a rather short time, is matrix-assisted laser desorption/ionisation (MALDI) time-of-flight (TOF) mass spectrometry (MS). The method is one of the 'softest' ionization techniques available and can produce intact molecular ions of species with masses up to several hundred kDa. Thus, various aspects important in polymer chemistry / material science can be studied in detail. But the technique has several limitations that have to be kept in mind too. Several selected examples for the characterization of functional macromolecular materials by MALDI-TOF MS will be presented (e.g. biologically active oligomers, electroactive materials). The examples will be used to discuss fundamentals of the technique as well as some of the most important limitations (e.g. by comparison of the results obtained by MALDI-TOF MS with those obtained by other analytical techniques).

The financial support by the Austrian Science Fund (SFB Electroactive Materials, Project P13962) is gratefully acknowledged.

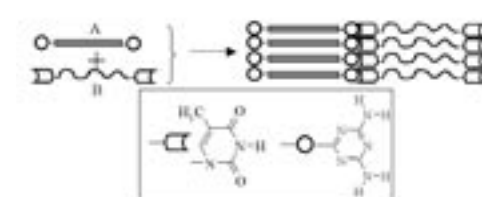
KL-7

Self Assembly of Hydrogen Bonded Supramolecular Polymers

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The ordering of polymers using directed noncovalent bonds has received increased attention due to the possibility of adjusting the nanoscale ordering of polymers.[1] Thus ionic bonds, metal coordinative bonds as well as hydrogen bonds have been used to tune the materials properties of short polymer chains by self assembly processes. Thermoplastic elastomeric behavior as well as nanostructured materials can be obtained by tailoring the interplay between polymer/polymer phase separation and molecular attraction.

The present talk discusses polymers derived from polyetherketones (PEK) [2] and polyisobutylenes (PIB) [3] with complementing hydrogen bonds in the sense of a lock-key-system to obtain attractive forces between the two different types of telechelic polymers. Directed hydrogen bonding is achieved via 2,4-diamino-1,3,5-triazine moieties as well as the complementing (5-methyl-1,3-pyrimidine-2,4-dione) - reminiscent of the molecular interactions in DNA - fixed at the end of the respective polymer chains.



The synthesis of the respective telechelic polymers as well as the structure and stability of the resulting aggregates are discussed in terms of NMR-, SAXS-, and TEM-investigations. Our investigations show ordering in solution and the solid state yielding nanostructured "pseudo"-block copolymers,[4] which are fixed together by hydrogen-bonding patterns. The hitherto immiscible PEK- and PIB-telechelics yield fully miscible materials in the solid state due to the attractive forces exerted by the hydrogen bonds.

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KL-8

From Self-Organizing Polymers to Nanohybrid and Biomaterials

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Block copolymers form a large number of superstructures with characteristic dimensions in the range of a few nanometers up to several micrometers by self-organization. The interplay of supramolecular physics and chemistry opens up new approaches to the production of inorganic, organic, and biological structures and their integration into functional units [1]. Block copolymers have been used for the production of inorganic nanoparticles (metals, semiconductors, magnets) and mesoporous materials as well as take-up/release systems for chemo- and gene therapy. Possible applications in the fields of materials science and molecular biology are being investigated.

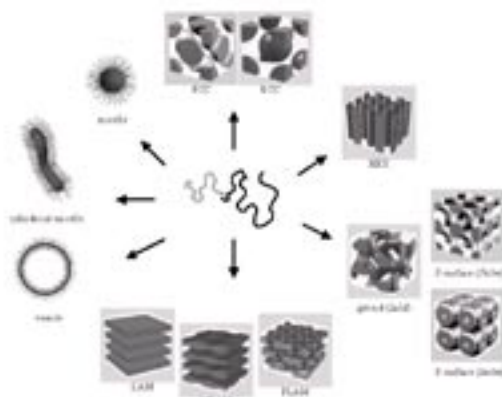


Fig. 1: Overview of structures formed by block copolymers via self-assembly.

We show how topology and dimension of block copolymer structures can be tailored to obtain spherical micelles, cylindrical micelles, vesicles and their respective lyotropic phases. Cylindrical micelles can be oriented in shear flow. Their lyotropic phases can be used as templates for the production of ordered mesoporous silicates via sol/gel-chemistry. pH-sensitive vesicles are used for the controlled release of drugs and genes. These examples demonstrate the versatility of self-organizing polymers in organizing matter from nano- to micrometers.

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KL-9

Functional polymer surfaces generated by photochemical techniques

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The modification of polymer surfaces has attracted a lot of interest during the past years. While etching, plasma and corona techniques are well established, UV induced processes are far less common. The presentation will describe various processes for the functionalization of polymer surfaces by UV irradiation in the presence of photoreactive gaseous compounds, among them BrCN, SO₂, N₂H₄, thiols and other compounds. These processes lead to the attachment of functional groups onto the surface of polymers. Various techniques (ATR-FTIR, XPS, EDX, MALDI-TOF, zeta potential and others) have been utilized to obtain information on the composition of the polymer surfaces. From experiments with low-molecular weight model compounds additional information on the photoproducts is accessible.

Functional polymer surfaces were also obtained by UV-irradiation of polymers containing photosensitive thiocyanate (SCN) groups. As UV irradiation generates isothiocyanates (NCS) units, these surfaces can be further modified with amines to give derivatives of thiourea. Moreover, index and relief patterns are obtained on the surface using interference patterning with $\lambda = 266$ nm. The presentation also describes applications of functionalized polymers. Examples are dyeing with cationic dyes, binding of antimicrobial compounds, the covalent immobilization of biomolecules (e.g. amino-terminated DNA oligomers) and the variation of the optical properties. Index and relief gratings have been successfully applied to set up optically pumped DFB lasers. Photochemical techniques have been adapted to modify the absorptive and emissive properties of thin films of conjugated polymers (PPV type). Reactive photopatterning is now examined to obtain multi-color emission from polymer-based light emitting devices.

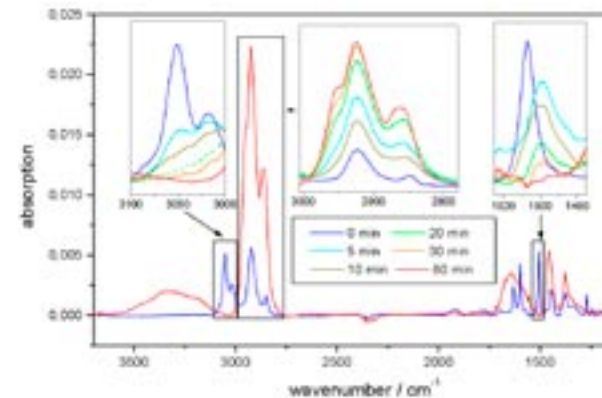


Fig 1: FTIR spectra of poly(2-vinylnaphthalene) after UV irradiation in the presence of hydrazine: transformation of aromatic units

Financial support by FWF Vienna (Project P 13962-CHE) and SFB Elektroaktive Stoffe (TU Graz) is gratefully acknowledged. Thanks also to Polymer Competence Center Leoben (Project S13).

KL-10

Green polymer chemistry by use of cyclodextrines

Helmut Ritter

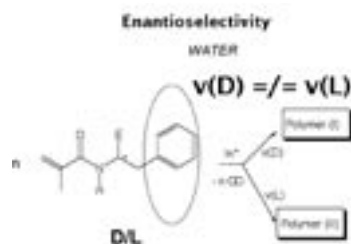
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Very recently, we have investigated a new method to polymerize different kinds of suitable hydrophobic liquid and even solid monomers in water by use of CDs



Figure 1 X-ray analysis of isobornyl-acrylate CD-complex.

These hydrophobic monomers are included as guests into the cavity of the hydrophilic ring shaped molecules resulting in water-soluble molecular dispersed complexes. We found that many complexed monomers may be readily polymerized in water yielding water insoluble polymers while the CD ring slips off during the growing steps.



Scheme 1 Enantioselective controlled polymerization of a racemic monomer included in a beta CD ring

Polymerization experiments of CD complexed acrylates at very low temperatures evidenced that the tacticity of e.g. PMMA is influenced from the CD host. Furthermore, the polymerization of racemic N-methacryloyl phenylalanine is slightly stereoselective due to the influence of CD (Scheme 1). The copolymerization of CD-complexed monomers was carried out in a broad range to investigate the special behavior of the new systems. It can be concluded that CDs offer a new way to polymerize suitable hydrophobic monomers in water. In contrast to classical emulsion polymerization the complexes may contain monomer molecules that may form high melting crystals. Also fluorinated acryl-monomers can be readily polymerized by this method. The reactivity and copolymerization parameters are controlled by complex stability and dynamic effects.

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KL-11

The Reaction Mechanism of the Transesterification and Crosslinking of Melamine Resins

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The mechanism and the kinetic of the transesterification and the crosslinking reactions of melamine resins with longchained ether- and esterdiols is of interest in the coating- and the compounding-industry. In the presentation the methanol etherificated melamine resins of the type hexamethylol melamine (HM3) and the type trimethylol melamine (TM3) will be compared. The transesterification of HM3 needs strong protonic acids (H⁺) as catalysts. At high diol concentrations the transesterification reaction prevail and the self-crosslinking can be neglected.

Strong protonic acids (H⁺) are not suitable as catalysts to the transesterification reaction of the high reactive TM3. On the other hand weak acids (H⁺ + A) have been described as useful catalysts. At temperatures >150°C the reaction proceeds thermal activated without catalysts. With TM3 the transesterification and the self-crosslinking reactions are running always side-by-side because the hydrogen atom from the amide group is reactive for the crosslinking reaction. The target of our investigations was to find out reactions conditions with reduced crosslinking reactions in favour of the transesterification reaction. Therefore we measure the reaction rates of the parallel reactions in dependence of the temperature, concentration and resistance time. The reaction rates and the activation parameter in the temperature range of 150°C to 250°C don't demonstrate significant differences between the crosslinking and the transesterification reactions.

From the literature [1,2] at temperatures below 150°C the transesterification reaction of TM3 with oligoesterdiols is preferred in comparison to the self-crosslinking. Our experimental results are demonstrating the dependence of the rates of the parallel reactions form the structure of the resin and a differentiate behaviour of different diols. From the mechanism and the reactions conditions of the HM3 and TM3 we make conclusions in direction of the applications.

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HM-1

Verbesserung der Biokompatibilität von Biomaterialien durch OberflächenmodifizierungHartwig Höcker*Deutsches Wollforschungsinstitut an der RWTH Aachen e.V. (Aachen / D)**E-mail: hoecker@dwf.rwth-aachen.de*

Während die Technik Anwendungen für ihre Errungenschaften in der Medizin sucht, fordert die zunehmende Lebenserwartung der Menschen wachsenden Einsatz von Technik bei der Behandlung körperlicher Leiden. In den allermeisten Fällen ist dies mit einem unmittelbaren Eingriff in das Biosystem verbunden, so dass die verwendeten Materialien zumindest für den mittel- bis langfristigen Einsatz biokompatibel sein müssen. Daher hat die Biokompatibilität der Werkstoffe oder Biomaterialien zentrale Bedeutung.

Biokompatibilität bezieht sich jedoch neben den mechanischen Eigenschaften insbesondere auf die Oberflächen- oder Grenzflächeneigenschaften und ggf. auf Biofunktionalität der Oberfläche. Aus diesem Grund ist die Anpassung der Oberfläche an das Biosystem bzw. die Modifizierung der Oberfläche zur Erzielung einer verbesserten Biokompatibilität von großer Wichtigkeit. Durch Hydrophilierung von Oberflächen bzw. die Hydrogelgestaltung der Oberfläche kann die Wechselwirkung mit dem Biosystem, insbesondere die unspezifische Proteinadsorption, minimiert werden. Durch die kovalente Anbindung von Proteinen der Extrazellulärmatrix (Fibronectin, Laminin, Collagen-IV) wird die Zelladhäsion und -proliferation gefördert. Falls notwendig (wie im Fall des Hirudins) ist die Spacer-Technik oder die Schutzgruppentechnik erforderlich, um eine gezielte kovalente Anbindung eines Proteins an eine Oberfläche zu realisieren, ohne dass das aktive Zentrum des Proteins blockiert wird.

Auch Metalle sind einer chemischen Modifizierung zugänglich, besonders wenn mit Hilfe der Chemical Vapour Deposition (CVD) Polymerisation von funktionalisierten Paracyclophanen eine dünne höchst resistente Polymerschicht erzeugt wird, deren funktionelle Gruppen für weitere Reaktionen zur Verfügung stehen. Solche Reaktionen eignen sich für die Oberflächenmodifizierung von Koronarstents nach einer transluminalen koronaren Angioplastie oder für Embolisationsspiralen zur Behandlung von Aneurismen. Die Oberflächenmodifizierung von Materialien kann nur ein erster Schritt sein; schlussendlich wird jedes Material als Fremdmaterial erkannt werden. Daher ist die Entwicklung bioabbaubarer Gerüststrukturen, die die Ansiedlung und Differenzierung von Zellen und damit die Bildung natürlichen Gewebes erlauben, während im gleichen Zuge das künstliche Material abgebaut wird (tissue engineering), ein erklärtes Ziel der Zukunft.

H. F. MARK LECTURES

HM-2

Bedeutung der Kunststoffforschung für den medizinischen Fortschritt

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Kunststoffe sind für den medizinischen Fortschritt unabdingbar und werden in vielen Varianten gebraucht. Am meisten eignen sich Polymere, wie PVC, Polyurethan, Polysaccharide, PTFE, Metalle, die man unterschiedlich verwendet. Viele Kunststoffe werden dauerhaft implantiert, wie chirurgisches Nahtmaterial. Implantate, wie Herzklappen, Gefäßprothesen, Gelenkersatz, Silikonpräparate, PVC- und Polyurethan-Teile. Der Entwicklung dieser Kunststoffe geht immer eine intensive interdisziplinäre Entwicklung voran, sodass gesichert Kunststoff in den Körper eingesetzt werden kann.

Darüber hinaus gibt es Kunststoffe, die temporär eingebracht werden, wie Blasenkatheter, Drainagenschläuchen, Infusionsschläuchen, Infusionsbeutel. Auch sie müssen dementsprechend Charakteristika aufweisen, um nicht toxisch im Körper zu wirken. Ein Wesentliches hat sich aber gezeigt, dass ein Kunststoff, der einmal implantiert war, nicht mehr verwendet werden kann. In der Infrarotspektroskopie zeigt sich bereits nach 60 Minuten Implantation eine Anreicherung von Eiweißkörpern, die trotz Spülen nicht mehr weggebracht werden können und damit pyrogen wird. Ziel des Vortrages ist es, die vielen Möglichkeiten von Langzeitverwendungen, Kurzzeitanwendungen aufzuzeigen, die in der Medizin einen wesentlichen Beitrag zum Fortschritt gebracht haben.

HM-3

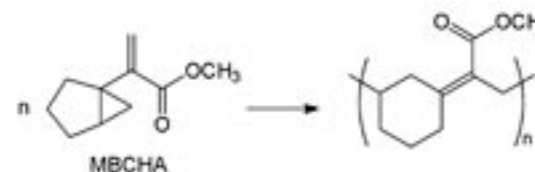
New Monomers for Dental Applications

Norbert Moszner

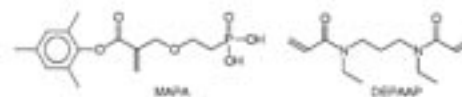
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Dental filling materials are an interesting field of application for new monomers, because on the one hand they enable the improvement of important properties, such as reduction of polymerization shrinkage in the case of restorative composites or enhancement of the stability and adhesive properties of dentin adhesives. On the other hand, the high price of new monomers is in general no killer criterium for their use in dental filling materials.

Cyclic monomers, such as spiro orthocarbonates, vinylcyclopropanes or cyclic ketene acetals, which undergo radical ring-opening polymerization show a low polymerization shrinkage and are therefore of interest for dental fillings.[1] We reported about the synthesis and polymerization of a new vinylcyclopropyl acrylate (MBCHA), which is more reactive than MMA, shows a lower volume shrinkage than MMA, and may form polymers with a number-average molecular weight higher than 100000 g/mol.[2]



The currently used self-etching dentin adhesives are based on mixtures of crosslinking monomers, strongly acidic adhesive monomers, and water as solvent. If the monomers used are not hydrolytically stable their hydrolysis may result in changes of the chemical composition of the adhesive and deterioration of its performance. In view of these disadvantages, we synthesized new hydrolytically stable monomers, for example, the phosphonic acid MAPA or the crosslinking monomer DEPAAP.[3,4]



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HM-4

Versyo®. com - eine lichterhärtende Alternative zu herkömmlichen ProthesenwerkstoffenKarl-Heinz Renz

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Seit ca. 60 Jahren werden in der Zahnprothesenherstellung fast ausschließlich Kunststoffe auf Basis von Polymethylmethacrylat (PMMA) verwendet. Diese werden beim Anwender durch Mischen von PMMA-Perlpolymerisat mit Methylmethacrylat (MMA) zu einem Teig verarbeitet, und anschließend durch Heiß- oder Selbstpolymerisation ausgehärtet. Im klinischen Alltag hat sich der Kunststoff PMMA als Prothesenmaterial bewährt, jedoch bleiben einige prinzipbedingte Nachteile bestehen. Zum Einen ist dies die Belastung des Verarbeiters durch MMA. Zum Anderen das Vorhandensein von Peroxiden, was in Einzelfällen zu Allergien und damit Prothesenunverträglichkeiten beim Patienten führen kann. Zudem führen wechselnde Anmischverhältnisse zu unterschiedlichen Materialeigenschaften.

Eine Alternative zu den erwähnten Kunststoffen ist Versyo®. com. Der Kunststoff ist frei von MMA und Peroxiden. Als Monomerkomponenten sind mehrfachfunktionelle, größtenteils hochmolekulare Acrylate und Methacrylate mit sehr niedrigem toxischen Potential enthalten. Die Polymerisation erfolgt durch Anregung einer Kombination verschiedener Photoinitiatoren. Eine geringe Menge an Füllstoffen steuert die rheologischen Eigenschaften.

Vorteile dieses Werkstoffes für den Verarbeiter sind eine schnelle Verfestigung durch kurze Polymerisationszeit, sowie konstante Viskositäts- und Materialeigenschaften durch Wegfall des Anmischprozesses.

Eine niedrige Wasserlöslichkeit, gute mechanische Eigenschaften und glatte Oberflächen sind die Eigenschaften, die für den Gebrauch der hergestellten Zahnprothesen von Interesse sind. Alle diese Punkte werden von Versyo®. com erfüllt. Der Vortrag stellt das Produkt Versyo®. com, dessen Verarbeitung im Zahntechniklabor, sowie dessen werkstoffkundlichen Eigenschaften vor.

HM-5

Nonwovens as scaffolds for the Tissue Engineering

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Introduction: The aim of tissue engineering is to use the potential of biological regeneration of cells to rebuild body-own structures. There are already some products of tissue engineering available on the market which are helpful to regenerate skin, cartilage or bone and a lot of possible applications are under development. Synthetic, resorbable biomaterials based on glycolide, lactide, ε-caprolacton, trimethylene carbonate and dioxanon are often used in medical applications. Examples are sutures, clips, foils, meshes or ligaments. Synthetic scaffolds are also used since the early 80's for the 3-dimensional cultivation of cells. Generally, the materials and the design chosen seem to be selected rather by availability of techniques and structures than by suitability. Favorite structures - because easily to produce - are foams and sponges manufactured by the particle leaching technique but they are often not the optimized structures for tissue engineering technologies:

At the clean room laboratories of the ITV different textile and namely nonwoven technologies have been developed in order to produce scaffolds for the tissue engineering. By spunbonding highly porous (>95%) nonwovens with regular fibers are produced without any spin finishes. With carded and needled nonwovens it was possible to even increase the porosity (98%). By the process conditions the carding of washed, i.e. finish free fibers could be managed. Both techniques are applicable to almost all polymers but crystalline polymers are favored. A unique melt blow equipment allows the production of microfiber nonwovens or the processing of amorphous polymers. Using a 3D robot system three dimensional shapes can be produced easily. Their porosity is limited (93%), but a wide range of pore sizes are possible. Solution spraying technique is used mainly for tubular microporous structures.

Materials: Today resorbable materials are commercially available in a limited number from PGA to P-L-LA. In order to cover the complete range of degradation kinetics but also to adapt the polymers to the need of the processing techniques, the polymerisation of any (co)-polymers of glycolic and lactide acid and other monomers were established at ITV. For temporary extracorporeal applications there is no need for degradable polymers. Here polyurethanes are used mainly.

Conclusions: Each cell type has its specific requirement on the scaffold. Furthermore material selection depends mainly on the cell cultivation and the therapeutical concept used. With the above sketched processing methods for nonwovens a wide variety of structures can be produced of a number of different materials.

HM-6

Engineering Plastics for the Medical Device Industry

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The worldwide market for medical products is growing rapidly, especially in high-end applications that require high performance capabilities like heat stability, processability, sterilisability and strength. World demand for plastics rose from about six million tons in 1959 to about 160 million tons in 1999. The Business Communication Company reports that about 850,000 tons were used worldwide for medical devices. The standard resins like polyvinylchloride (PVC) or polyethylene (PE) represent more than 80% of this demand. The remaining 187 thousand tons are divided between the so-called engineering resins like polycarbonate (PC). Medical device engineers in the midst 40 of this century happened to recognize that plastics are unexpectedly biocompatible and offer many of these properties and more. Since these beginnings polymer chemists, processing engineers, physicians have learnt a lot about the interaction of foreign body surfaces with human fluids, blood, and cells and how materials and the different processing steps till the final device affect this interaction. Basic research efforts have been focused on a better understanding of biocompatibility and are the key to the success of plastic resins in medical devices. Nowadays, the use of plastics in medical device industry are often driven by the following health care trends: constant drive towards cost containment, increase in self treatment, e.g. powder inhalers, increase in the evolution of mini-clinics (merge of physicians' offices).

The presentation will focus on the following subjects:

- Overview medical plastics market
- Applications and requirements
- Biocompatibility
- New property requirements (heat stability, sterilisation technology)
- Plastics in high-end medical applications

HM-7

Alpha-Tocopherol - A Potential Stabilizer for Standard and Crosslinked Ultra-High Molecular Weight Polyethylene (UHMW-PE) used for Joint Endoprostheses

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The lifetime of articulating surfaces in joint endoprostheses made of UHMW-PE, especially of hip-cups, is usually limited to 10 to 15 years due to material failure as a result of oxidation of the UHMW-PE in-vivo. To inhibit this oxidation, the suitability of the natural antioxidant α -tocopherol (vitamin E) as a stabilizer for UHMW-PE was investigated. Specimens with varying mass content of α -tocopherol were processed in accordance with standard processing methods of hip cups and chemically aged subsequently. The degree of oxidation was observed by means of FTIR-spectroscopy and DSC analysis. The FTIR-measurements showed that α -tocopherol can prolong the lifetime of UHMW-PE in an oxidative environment by a factor of more than 2.5. The added α -tocopherol undergoes chemical transformations during manufacturing and sterilization by γ -irradiation of hip cups which may differ from human metabolism. Therefore, the question of the biocompatibility of the respective transformation products was investigated.

Recently, crosslinked UHMW-PE has established itself as a new promising material for endoprostheses. The wear resistance of UHMW-PE can be enhanced further by crosslinking the material with high energy electron beam irradiation. Crosslinked UHMW-PE is said to have a higher oxidation resistance, nevertheless, the chemical structure of crosslinked UHMW-PE is still very similar to standard UHMW-PE, thus adding vitamin E could further increase the resistance to oxidative degradation. Due to the irradiation it is impossible to apply the standard procedure of adding the α -tocopherol to the PE-powder before processing since it would inhibit the crosslinking process and be degraded at the same time. Therefore, the vitamin E must be added to the irradiated preforms. Two methods are presented to introduce the vitamin E in the crosslinked PE-bulk:

In the first method a saturated surface layer of vitamin E is produced by simple diffusion of pure α -tocopherol at 100 °C to 200 °C. Subsequently, the preforms can be stored in nitrogen at 160 °C to 200 °C for several hours leading to a more homogeneous tocopherol-distribution. By varying the diffusion temperature, time as well as the annealing temperature and time, the distribution of vitamin E in the preforms can be set in a broad range. In the second method, the vitamin E is dissolved in supercritical CO₂ which supports the diffusion of the vitamin into the PE. As in method 1, nearly any distribution can be achieved by varying the time, temperature and pressure during diffusion as well as the tocopherol-concentration in the CO₂.

HM-8

Sterilisation Effects on Polypropylene: Technology and Polymer Type Effects

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Polypropylene, one of the most widely used plastics for packaging applications, is increasingly applied also in the medical area and for pharmaceutical packaging, where the material is mostly sterilized. To gain an overview of sterilization effects various polypropylene grades different in structure and additivation were investigated in two forms – cast film and injection molded – and with five different sterilization techniques in a screening study performed at OFI Vienna. Special attention was payed to radiation-induced degradation and thermally stimulated post-crystallization, which continue for a long time after the actual sterilization event. Here, additional results from internal investigations at Borealis are presented. Special copolymers are the most interesting solution to embrittlement problems occurring with standard grades, but also special stabilization systems also can give some advantage, especially for reducing the discoloration problems.

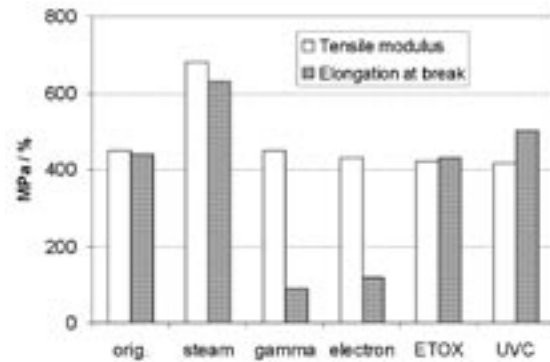


Fig. 1: Effect of different sterilization techniques on tensile properties of a PP random copolymer (RC-P1)

OP-1

Rheology at work in compounding industry**Giancarlo Locati*, Andrea Valle***Ceast S.p.A., via Airauda 12, 10044 Torino, Italy**E-mail: g.locati@inwind.it; a.valle@ceast.com*

Rheology, far from being only a purely scientific theory, offers powerful means to help compounders. This comes especially true with the tools made available from recent developments in testing equipment. Accordingly, the presentation will shortly review the novelties of recent equipment with the aim to highlight those functions from which compounders may benefit. Then, some selected examples of applications will be shown. They range from improved quality control of incoming and outgoing products, to recycling management, masterbatches characterization, evaluation of dispersion effects on filled materials and assessment of compatibility in polymer blends.

ORAL PRESENTATIONS

OP-2

**Microphotometric Detection of Particles / Inhomogeneities
in Flowing Polymer Melts**

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Realtime process control of temperature and pressure in flowing high viscous liquids and melts during polymer production/processing are well developed. IR- spectroscopic methods (MIR, NIR, Raman) are successfully used for analyzing chemical reactions inside industrial reactors/extruders [1]. By labeling of polymers with suitable radioactive nuclides the melt residence time and residence time distributions at different positions along an extruder can be measured in realtime [2]. Ultrasonic sensors adapted to extruders are available for realtime detecting of fluctuation in particle content fluctuation and residence times in flowing polymer blend melts [3]. A novel technique for inline color monitoring of polymers melts during extrusion is reported recently [4].

In contrast methods for an industrial realtime controlling of particles (blends, filler, additives, agglomerates, gels, fisheyes, gas bubbles etc.) in flowing high viscous liquids and melts today are still quite poor developed. Our unique particle sensors from PMP- type (Process-Micro-Photometer) are based on microphotometric analyzing principle and is working in different measuring modes (transmission and/or backscattering) [5,6]. The PMP 's are adaptable at different positions of polymer reactors and plastics extruders to control particles and/or inhomogeneities as well. Hence a high effective new equipment for realtime process control and quality assurance in industrial polymer processing is now available. Examples will be presented concerning particle sizing in polymer blend melts, detection of gels or gas bubbles and for evaluation pellets melting behaviour in twin screw extrusion processing.

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OP-3

**Stabilization of Two Phase Polymer Blend Morphology by Using
Electron Beam Radiation Process**

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Properties and behavior of multiphase polymer blends strongly depends on the phase structure and morphology, also interfacial adhesion between phases is among parameters which play a significant role in determining the mechanical performance of blend.[1] One of the ways to obtain multiphase polymer blends with ordered structure and properties is freezing the concentration fluctuations developing at different stage of the spinodal decomposition process in polymer blend by crosslinking between polymer chains and interfacial adhesion improvement by crosslinking of chains present on interphase, therefore the diffusion of polymer chains can be slowed down, and as a result polymer blends with varying ordered structures and stabilized morphology can be obtained. Polystyrene (PS) and Poly vinyl methyl ether (PVME) are a rather unique pair of polymers in that they are chemically dissimilar and also dissimilar in their response to irradiation. The PS/PVME blend exhibits a lower critical solution temperature (LCST) [2] , i.e., phase separation upon heating. This combination of dissimilarity and compatibility provides the necessary prerequisites for a unique and informative radiation study. In this work, we consider the effect of electron beam irradiation on the behavior, properties and morphology of two phase polymer blend induced by temperature elevation from the one phase region into the spinodal region. The blends were produced using solution casting method in miscible and Brabender mixer, in two phase region. Two phase blend was produced with phase separation process that occurring during heating of miscible blend at temperature upper than LCST and interdiffusion process.[3,4,5] Miscible and two phase polymer blends samples were imposed to electron beam using Rhodotron TT200 accelerator , irradiation doses of 10,25,50,100,150 and 200 KGy were applied. Optical microscopy is used for morphology and phase separation kinetics study.[6,7] FTIR analysis of the composition of the insoluble gels was performed to determine the composition of the crosslinked gels and probability of graft copolymer between two phase in interphase. Gel contents of the irradiated blends were determined by extracting in THF with a Soxhelt extractor for at least 24 hr. A Charlesby-Pinner plot is a used for determining radiochemical yields (G values) for crosslinking systems that form gels in the dose range. Mechanical properties of phase separated blends versus radiation dose were studied. Aging test is used for morphology stabilization test. Results shows experimental values higher than theoretical values that calculated from parallel elements model, due radiation copolymerization on the interphase of two phase blends.

Electron beam irradiation is a technique to controlling and stabilization of morphology induced by temperature elevation from the one phase region into the spinodal region. FTIR results shown grafting is present on the interphase of blends also electron beam induced mechanical properties improvement and interphase reinforcement. Thus, the electron beam radiation is a technique to design multiphase polymer blends with controllable ordered structure.

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OP-4

Bifunctional adhesion promoter for grafting polypyrrole films on metal/metal oxide surfaces [1,2,3]

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A new class of pyrrole derivatives, 3-phenyl-(pyrrol-1-yl alkyl) phosphonic acids with long chains of 10 and 12 carbon atoms, were synthesised to graft polypyrrole layers on the metal/metal oxide surfaces. These compounds are bifunctional containing two reactive moieties, pyrrole as the polymerisable group and phosphonic acid as the anchoring group. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis indicate high temperature stability. Preparation of strongly adhering film on metal surface is a two step procedure: 1. Adsorption of adhesion promoter and 2. Surface-induced polymerisation with an appropriate monomer. We will present some analytical results from the modified surface. Contact angle measurement and X-ray photoelectron spectroscopy (XPS) confirmed adsorption with phosphonic acid group attached to the surface. Surface plasmon resonance (SPR) spectroscopy indicated that adsorption start in few seconds and is completed in few hours. Adsorption is followed by surface-induced polymerisation with further monomer. We obtained dense and homogeneous polypyrrole films which were characterised for their morphology by scanning electron microscopy (SEM) and thickness by atomic force microscopy (AFM). The derivatives result in strongly bonded composite of metal with polymer. Electrochemical impedance spectroscopy (EIS) was used to determine the conductivity of these grafted polymer layer indicating it to be a p-type semiconductor. Further these compounds were investigated for corrosion protection of metals.

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OP-5

Regular Polymers with Cationic and Anionic Charges

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Ionically charged macromolecules containing both cationic quarternary nitrogen and anionic carboxylic functionalities are polymers of growing interest because of their relationship to proteins and living matter as well as to upcoming industrial applications. Polymers useful as models in this area require precise polymerization techniques leading to well defined structures. Two types of corresponding polymers were investigated: polycarboxybetaines containing the functionalities in the same monomer unit and polyampholytes containing these alternating in neighbouring units.

Polycarboxybetaine homo- and blockcopolymers with adjusted molecular architecture were synthesized via controlled free radical polymerization of suitable monomers (4-vinylpyridine (4-VP) or p-chloromethylstyrene (p-CMS)) followed by quantitative functionalization of the reactive precursors. A wide variety of the chemical structure including the distance between the charged groups, the shielding between nitrogen and carboxylic groups, the variation of hydrophobic parts and the hybridization of the nitrogen was established [1]. A narrow molecular weight distribution of the polycarboxybetaines supports the investigations of the behaviour in aqueous solution by titration methods, ultracentrifugation, SEC, capillary electrophoresis, viscometry and FTIR. Depending on pH and ionic strength of the solution the homopolymers show two different types of interaction. The intramolecular Coulombic interaction between anionic carboxylic groups and cationic quarternized nitrogen in general increases with increasing pH, but decreases with increasing length of spacers between the ionic parts as well as with increasing shielding of the nitrogen and hydrophobization of the molecule. Contrarily, the intermolecular aggregation via H-bridges and hydrophobic interactions increases at lower pH-values. A model considering these findings will be discussed. Extending the polymer analogous derivatization to block copolymers poly(p-CMS)- β -styrene or poly(4-VP)- β -styrene results in a new type of amphiphilic block copolymers containing carboxybetaine blocks besides a polystyrene block with variable block length and block length ratio. Solution properties of the novel polymers were determined by ultracentrifugation.

Polyampholytes with strong alternating positively and negatively charged units in the backbone were obtained by cyclocopolymerization of diallylammonium compounds and derivatives of maleamic acid. A wide variety of structures is available resulting in polymers with different solution properties, including novel polymeric surfactants. The complexation of the polyampholytes with perfluorododecanoic acid is a self-assembled process and generates nanoparticles with sizes in the range of 3-5 nm, which were characterized by ultracentrifugation, dynamic light scattering and isothermal titration calorimetry [2] Additionally, the complexation of nonalternating polyampholytes leads to particles with diameters of about 30 nm.

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OP-6

Control of Morphology and Composition of Inorganic-Organic Hybrid Materials via Atom Transfer Radical Polymerization

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The incorporation of inorganic moieties into organic polymers can change the properties of the final hybrid materials dramatically, such as mechanical, thermal, optical, electronic, etc.. In recent years particularly the incorporation of inorganic entities on the molecular- and nano-scale into polymers resulting in so-called nanocomposites became increasingly important.[1] The major challenges in the preparation of these materials are the tailoring of the interaction between the inorganic and organic species, as well as the control over their morphology and composition. Two preparation methods revolutionized the formation of organized homogeneous hybrid materials: (i) controlled polymerization techniques, such as atom transfer radical polymerization (ATRP) and (ii) the sol-gel process for the formation of the inorganic species.

In this contribution, we show how the combination of ATRP and the sol-gel process can be used to form polymer/metal oxide hybrid materials. The organic polymer was connected to the inorganic moiety via covalent or coordinative bonds using either ATRP initiators or functionalized monomers to form grafted polymers or interpenetrating networks. Silane coupling agents with ATRP initiating functional groups were used to modify different metal oxide nanoparticles and silica surfaces.[2] Functionalized bidentate ligands such as carboxylic acids and 1,3-diketones showed their ability to react with metal alkoxide, which are the precursors for the sol-gel process, to form either crystalline surface-modified metal oxo clusters[3] or amorphous nanoparticles. All obtained systems were used as multifunctional initiators in copper-mediated ATRP. The resulting hybrid materials were analyzed via TEM, X-ray and light scattering, EXAFS, AFM, NMR, TGA and DSC. The polymers were cleaved from the surfaces and were analyzed by conventional techniques, such as NMR and SEC. Kinetic studies showed that all polymerizations occurred in a controlled way.

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OP-7

Catalytic polymer modification and tandem catalysis in aqueous emulsions

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Ring-opening metathesis polymerization (ROMP) of bicyclic monomers affords a wide range of highly unsaturated polymers ranging from rubbers to highly rigid engineering plastics. In order to improve stability against oxidation and to expand polymer property as well as application ranges, we are exploring catalytic post polymerization conversion of ROMP-based polymers. This catalytic polymer modification is performed either in solution or aqueous emulsions. In addition to the well-known catalytic hydrogenation of ROMP polymers, catalytic syn-hydroxylation on OsO₄ was applied successfully for the first time to convert double bonds in the backbone quantitatively into the corresponding diols. This route was employed to prepare novel families of carbohydrate analogous polymers.[1] Syn-dihydroxylation of polyoctenamers afforded novel ethylene/vinylalcohol copolymers comprising strictly alternating segments of the head-to-head linked vinylalcohol dimer and ethylene oligomers. The segment length of the ethylene oligomers can be varied by selecting the appropriate ring size of the cycloolefins. In comparison to polyvinylalcohol the thermal stability of such novel poly(oligoethylene-alt-head-to-head divinylalcohol) copolymers is remarkably high. In order to eliminate the need for organic solvents and problems associated with high viscosity of polymer solutions, polymerization and subsequent polymer modification were performed in aqueous catalyst miniemulsions which produced stable polyolefin latex. In tandem catalysis both ROMP and polymer hydrogenation were performed on the same Grubbs-type catalyst system dispersed in miniemulsions. The tandem ROMP/hydrogenation emulsion reactions based upon cyclooctadiene feedstocks gave emulsions of linear 1,4-butadiene/ethylene copolymers linear polyethylenes. The degree of hydrogenation, as reflected by the presence of 1,4-butadiene units, was controlled by the hydrogenation temperature. Basic structure/property correlations, the influence of process conditions, latex and film formation will be reported.

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OP-8

Synthesis and Property Behavior of DOP Plasticized Styrene-Acrylate Particles by SPG Emulsification and Subsequent Suspension Copolymerization [1,2]Roongkan Nuisin¹, Shinzo Omi², Suda Kiatkamjornwong^{3*}

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Two-phase model styrene-acrylate copolymers were synthesized with a soft phase consisting of methyl acrylate. Besides, the styrenic copolymers, copolymers containing of a hard phase of methyl methacrylate and methyl acrylate were also synthesized. Comonomer droplets with a narrow size distribution and fairly uniformity were prepared using an SPG (Shirasu Porous Glass) membrane having pore size of 0.90 μm . After the single-step SPG emulsion, the emulsion droplets were composed mainly of monomers, hydrophobic additives, and an oil-soluble initiator, suspended in the aqueous phase containing a stabilizer and inhibitor. These were then transferred to a reactor, and subsequent suspension polymerization was carried out. Uniform copolymer particles with a mean diameter ranging from 3 to 7 μm , depending on the recipe, with a narrow particle size distribution and a coefficient of variation of about 10% were achieved. Based on the glass transition temperatures, as measured by differential scanning calorimetry, the resulting copolymer particles containing a soft phase of acrylate are better compatibilized with a hard phase of methyl methacrylate than with styrene with dioctyl phthalate (DOP) addition. Glass transition temperatures of poly(MMA-co-MA) particles were strongly affected by the composition drift in the copolymer caused by their high difference in reactivity ratio. Incorporation of DOP in the copolymer particles does not significantly affect the glass transition temperature of MMA or MA containing copolymer particles, but it does affect the St containing copolymer and particle morphology of the copolymers.

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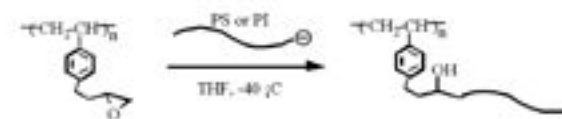
OP-9

Synthesis of Highly Densed Comblike Branched Polymers with Well-Defined Structures by Coupling Reaction of Living Anionic Polymers with Epoxy-Functionalized Polystyrenes

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We have recently demonstrated that poly(3-bromomethylstyrene) prepared via living anionic polymerization efficiently undergoes coupling reaction with living anionic polymers of styrene, isoprene, 2-vinylpyridine, and tert-butyl methacrylate in THF at $-40\text{ }^{\circ}\text{C}$. With use of poly(3-bromomethylstyrene) whose degree of polymerization was less than 150, the coupling reaction with either of living anionic polymers quantitatively proceeded to afford highly densed comblike branched polymers and graft copolymers having one branch in each repeating unit [1,2]. In this presentation, we report on the synthesis of comblike branched polymers by the coupling reaction of epoxy-functionalized polystyrenes with living anionic polymers as shown below: The epoxy-functionalized polystyrenes used as main chain polymers were prepared by the living anionic polymerization of 4-(3-butenyl)styrene followed by oxidation with 3-chloroperbenzoic acid.



Therefore, both main and branched chains were well controlled in molecular weight and molecular weight distribution in the resulting branched polymers obtained by the coupling reaction. The reaction proceeded with high to quantitative coupling efficiencies (70 ~ 100 %) in THF at $-40\text{ }^{\circ}\text{C}$. The effect of molecular weights of main and branched polymer chains on the coupling efficiency was studied in detail. Furthermore, a new functionalized polystyrene having two epoxy rings in each monomer unit was prepared and used as a main chain in the coupling reaction of polystyryllithium for the synthesis of highly densed comblike branched polymers having two branches in each repeating unit.

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OP-10

Stereoregularity of Cationic Polymerization: Cationic Polymerization of n-Butyl Vinyl Ether by Alanes

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The carbocationic polymerization of n-butyl vinyl ether (BVE) in the presence of the new $\text{LiAlH}_4/\text{AlCl}_3$ initiating system is reported. The kinetics of the polymerizations were investigated in diethylether (Et_2O), and in a mixture of diethyl ether and dichloromethane (1:1 v/v) at various temperatures. Based on the kinetic data obtained the apparent rate constants and the temperature dependence of the rate constants were determined. According to $^1\text{H-NMR}$ and MALDI-TOF MS investigations formation of poly(nbutyl vinyl ether) with three different interconvertible endgroups, i.e., heteroacetal, homoacetal and aldehyde were observed. Based on detailed kinetic and structural investigations a direct initiation mechanism for the polymerization is suggested.

The polymerization proved to be stereoregular. Polymerization reactions were performed in various solvent mixtures at different temperatures ranging from 25 °C to -60 °C. The polymers were studied by ^{13}C NMR and the isotactic content were determined from the ^{13}C NMR spectra according to the integral ratios of the signals of the chain methylene carbons. The highest isotactic polymer content were achieved at -40 °C in hexane/diethyl-ether(1:1 v/v). According to our investigations, the isotactic content changed inversely with the temperature until -40 °C but below this temperature lower isotactic content was obtained. The dependence of the solvent polarity on the reaction rate, conversion and on the isotactic content was also studied.

OP-11

Kinetics of Surface Grafting Reactions on Polyisoprene Latices by Reaction CalorimetryWiyong Kangwansupamonkon^{a,b}, Christopher M. Fellows^a, Robert G. Gilbert^a, Suda Kiatkamjornwong^{c*}*aKey Centre for Polymer Colloids, University of Sydney, NSW 2006, Australia.**bDepartment of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.**cDepartment of Imaging and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.**E-mail: ksuda@chula.ac.th*

A hairy-layer of hydrophilic chains chemically grafted to the surface of a hydrophobic polymer colloid has been created by the second-stage polymerization of dimethylaminoethyl methacrylate (DMAEMA) onto synthetic polyisoprene latex. To control the locus of radical formation, the process was initiated by a redox coupling comprising one water-soluble component, tetraethylene pentamine (TEPA), and a water-insoluble one, cumene hydroperoxide (CHP) [1]. The modified latices displayed a dramatic increase in colloidal stability at low pH, which is attributed to the grafted hydrophilic polymer acting as an electrosteric stabilizer. The mechanism by which such a novel morphology can be generated is postulated to be via a radical process at the particle surface followed by the subsequent grafting to the hydrophobic backbone and polymerization of hydrophilic monomer in the aqueous phase. The kinetic of such a modification of polyisoprene latices has been examined using RC1 microcalorimeter [2].

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OP-12

Water Soluble, Photocurable Resins for Rapid Prototyping Applications

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Rapid Prototyping (RP) is a suitable manufacturing method for fabricating structures with high geometric complexity and heavily undercut features. A special class of such structures which cannot easily be fabricated with traditional manufacturing methods are cellular materials [1]. Rapid Prototyping allows the fabrication of cellular materials on a similar size scale like in natural material-structures (e.g. trabecular bone). By using appropriate moulding techniques, these structures can be fabricated out of a wide variety of materials (polymers, ceramics, composites). In this work, several RP techniques are investigated regarding their suitability for the fabrication of cellular solids. The main focus is on using direct light projection (stereolithography) in combination with gelcasting [2] as moulding technique. Besides using commercial light-sensitive resins, a class of newly developed water soluble resins has been evaluated regarding its usability as sacrificial mould material. These water soluble resins are compatible with a wide range of moulding techniques and therefore offer new routes for the fabrication of complex shapes out of more advanced materials than it is possible with currently used manufacturing techniques.

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OP-13

Influence of Coloration on Photo- and Photooxidative Degradation of Polyoxymethylene (POM)

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Polymers having been exposed to direct sunlight or intensive artificial light during weeks or month show ageing signs extending from discoloration over an increased surface roughness to diminution of mechanical properties. Chemically the damages can be characterized as diminution in molecular weight, as crosslinking, as formation of volatile and nonvolatile oxidation products similar to those found by an oxidative induced ageing[1]. For polyoxymethylene (POM) former investigations on the influence of photodegradation have shown the formation of water and carbon monoxide for specific irradiation wavelengths[2]. Gardette et al.[3] proposed a mechanism involving primary hydroperoxides leading to the formation of carbonates, formates and hydroxylated compounds.

The aim of the present study is to elaborate the influence of different colorants on the photodegradation behaviour of POM. Masterbatches on the basis of POM or PE were added in an amount of 3 % by weight to commercially available POM materials to obtain the desired colouration. The tested specimens were injection molded loudspeaker grids. Material properties were investigated before and after UV-exposition for uncoloured and coloured specimens. The UV-exposition was performed in an ATLAS Suntest XL+ for the equivalent UV-dose of one year occurring in Middleeurope indoor for material that had no specific additives against UV-degradation and for the equivalent of two years for the same material containing UV-stabilizer. Test results showed that only the presence of colourants could restrain the UV-degradation of POM in comparison to uncoloured material without UV-stabilizer but not so effective as in coloured material containing UV-stabilizer.

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OP-14

Determination of Oxidation Induction Time and Oxidation Induction Temperature (OIT) for Polyoxymethylene

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The DSC-OIT is a thermal analysis method combining conventional Differential Scanning Calorimetry (DSC) with oxygen as purge gas instead of nitrogen. There are two methods, which are commonly used for the characterization of the thermal stability of polymers:

The Oxidative Induction Time is an analytical method used to assess thermal stability of polymeric materials under high temperature conditions above melting point. The thermal stability degree for a given temperature can be assessed measuring the time necessary to start degradation in an oxidative atmosphere. The OIT depends on the antioxidant concentration, its effectiveness, and the temperature beyond the peak maximum, antioxidant is completely consumed and the polymer has lost its thermal stability [1]. This method is widely used to assess thermal stability of polyolefins and was developed as a rapid screening test for the relative effectiveness of stabilizer packages for olefinic cable jackets.

The Oxidative Induction Temperature is used to determine the temperature at which a polymeric material starts thermal degradation in an oxidative atmosphere. The sample is heated up with a defined heating rate until oxidation of the material occurs.

In the present study the thermal stability of commercially available heat stabilized poly(oxymethylene) (POM) is characterized with the OIT method and these results were compared with investigations on the degradation behaviour of POM which are performed with TGA. For the quantification of the degradation behaviour of poly(oxymethylene) as an engineering material for the automobile industry two different ways are examined:

Ageing in a drying furnace (oven-storage), as the most common conditioning procedure at a temperature of 140 °C, and artificial weathering through UV-Irradiation (xenon tests), as a short test for predicting the service lifetime. The results demonstrate that the OIT is confirmed to be an appropriate method to characterize the antioxidant consumption for POM and furthermore in combination with the thermo-gravimetric analysis for understanding the degradation behaviour of POM.

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OP-15

Highly Defined Blockcopolymers Prepared by ROMP Using 3rd Generation Grubbs' Initiator

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Ring opening metathesis polymerisation (ROMP) is a powerful tool to prepare well defined and highly functionalized polymers.[1] 3rd generation Grubbs' initiator (H₂IMes)(3-bromo-pyridine)₂(Cl)₂Ru=CHPh (1)^[2] accomplishes the synthesis of blockcopolymers via living ring opening metathesis polymerisation of norbornene derivatives. Complete initiation and an outstanding functional group tolerance are provided, which is proven by a combined MALDI-GPC-NMR study on an ABC triblock copolymer.[3]

The presented example of an ABC triblock copolymer would neither be accessible by using (PCy₃)₂(Cl)₂Ru=CHPh, the 1st generation Grubbs' initiator (not compatible with cyano-groups) nor by (H₂IMes)(PCy₃)(Cl)₂Ru=CHPh (produces polymers with rather high polydispersities and does not provide complete initiation).[4]

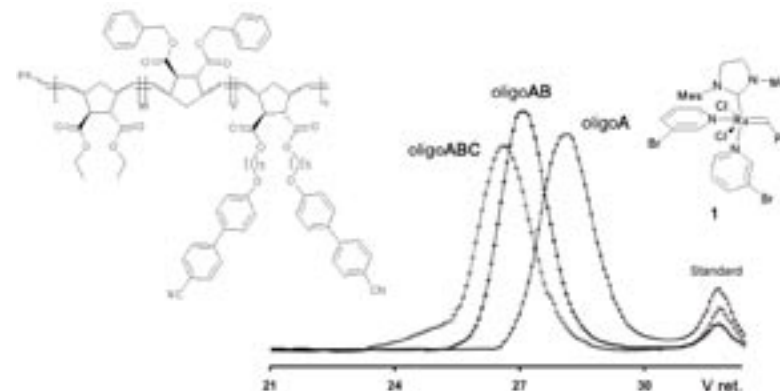


Fig. 1: Structure of ABC triblock copolymer, the initiator and GPC spectra of oligoA, oligoAB and oligoABC

In this work we also show the applicability of these findings on the synthesis of well defined liquid crystal block copolymers.

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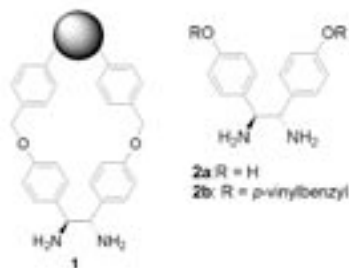
OP-16

Preparation of polymer-supported optically active 1,2-diamine and its application to asymmetric hydrogenation catalyst

Shinichi Itsuno*, Atsushi Tsuji, Miyuki Takahashi

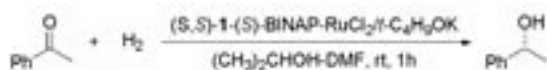
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Enantiopure 1,2-diamines have recently been known as an efficient chiral auxiliary in various kinds of chiral catalysts and reagents.[1] However, to our knowledge, there has been no report of chiral diamine containing polymer.



We have designed and prepared such polymer (1) by means of chemical modification of functionalized polystyrene. We have prepared enantiopure 1,2-diamine having phenolic OH groups (2a), which was used for its attachment into the functionalized polystyrene.[2] Vinylbenzyl groups were also introduced to the chiral diamine to give new monomer (2b). This chiral diamine monomer was polymerized with styrene to give the chiral polymer having the same structure as that obtained through the chemical modification method.

As a test asymmetric reaction enantioselective hydrogenation of ketones using Noyori catalyst system was performed with above polymer 1. When 1 was treated with $\text{RuCl}_2\text{-BINAP}$ in the presence of a base, polymer-supported catalyst was formed. The polymeric catalyst performed well in asymmetric hydrogenation of acetophenone to afford the corresponding secondary alcohol in quantitative conversion with good enantioselectivity.



In the case of low molecular weight catalyst, 2-propanol is a solvent that usually shows excellent performance in this reaction.[1] However in this solvent the network of the polymeric catalyst shrank and lost its catalytic activity. Since the polymer swells well in DMF, mixed solvent of 2-propanol and DMF was a choice of the solvent system for the reaction with polymeric catalyst.

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OP-17

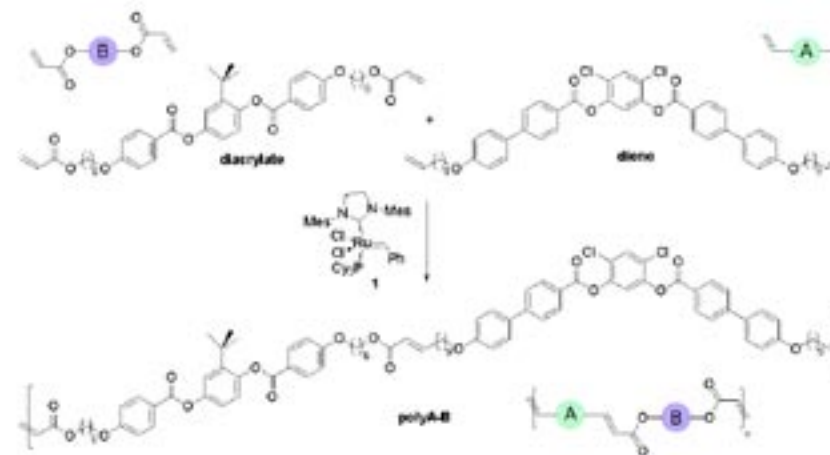
**Acyclic Diene Insertion Metathesis Polycondensation (ADIMET):
A Versatile Tool for the Preparation of Perfectly Alternating
A_nB_n Copolymers**

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During the last years, metathesis polymerisation has become an effective tool for the preparation of a wide variety of macromolecule architectures. Recently a breakthrough in the preparation of highly defined homo- and block-copolymers has been made.[1] Herein we present the development of acyclic diene insertion metathesis condensation polymerisation (ADIMET) for the preparation of strictly alternating A_nB_n-copolymers starting from dienes and diacrylates. This method enlarges the possibilities of the Ring Opening Insertion Metathesis Polymerisation (ROIMP),[2] where the source of cyclic monomers necessary for ROMP is limited.

Treatment of a 1:1 mixture of monomers A (diene) and B (diacrylate) with catalyst 1 $\text{RuCl}_2(\text{H}_2\text{IMes})(\text{PCy}_3)(=\text{CHPh})$ yielded the corresponding alternating polymers polyA-B in high yields.



This method is very versatile and enables the preparation of a broad variety of alternating copolymers, including main chain liquid crystalline polymers.

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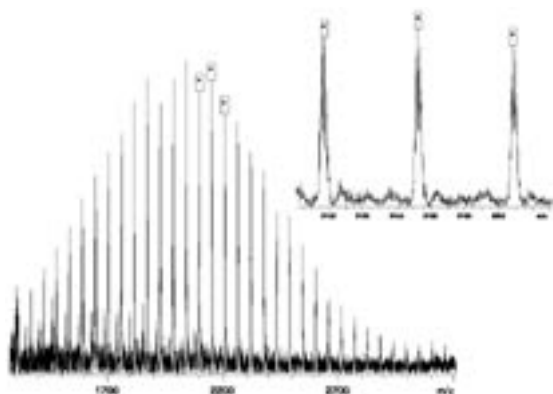
OP-18

MALDI-TOF MS Characterization of Telechelic Polyisobutylenes

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In this presentation MALDI-TOF MS characterization of different functionalized telechelic polyisobutylenes will be reported. A novel synthesis of dihydroxy telechelic polyisobutylene starting from α,ω -di(isobutenyl)polyisobutylene will also be presented. According to this method, the epoxidation of α,ω -di(isobutenyl)polyisobutylene was achieved at room temperature using dimethyldioxirane (DMD), which proved to be a very effective reagent for the epoxidation without formation of side products. A very good agreement was found for the conversion determined by ¹H-NMR and MALDI MS. The kinetics of the reaction of α,ω -di(isobutenyl)polyisobutylene with DMD will also be discussed. The epoxy termini were converted quantitatively to aldehyde endgroups in the presence of zinc bromide catalyst. The aldehyde groups were then reduced with LiAlH₄ into primary hydroxyl functions to obtain α,ω -di(2-methyl-3-hydroxypropyl)polyisobutylene with high efficiency. The MALDI-TOF MS spectrum of the dihydroxy telechelic polyisobutylene is shown below.



OP-19

Kinetics of Ring Opening Metathesis Polymerisations in Thin Films via FTIR

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Our aim is to develop tailor-made low shrinkage composites for various applications (e.g. dental materials) by exploiting Ring Opening Metathesis Polymerisation (ROMP). The rational development of compounds is up to now hampered by lack of information on the kinetics of the polymerisation reaction in bulk. We therefore designed a FTIR based method for monitoring the polymerisation progress even in the presence of high filler amounts.

Using a Large Angle Reflection Cell (LARC), kinetics of various monomer-initiator systems can be determined by pursuing intensity changes of characteristic IR-bands. The LARC can be operated in a broad temperature range and also under inert atmosphere.

Various Ruthenium based ROMP initiators were tested in model reactions using different monomers. Reaction rates were found to be exceedingly higher than in solution. Moreover the temperatures necessary for initiation could be easily determined by applying defined temperature programs. The results of the studies were systematically cross-checked using different analysis methods like GPC, optical microscopy and NMR. With regard to composite materials also supported initiator systems and polymerisations in presence of inorganic filler materials were investigated. Measurements with filler contents up to 70 % were possible and delivered accurate results

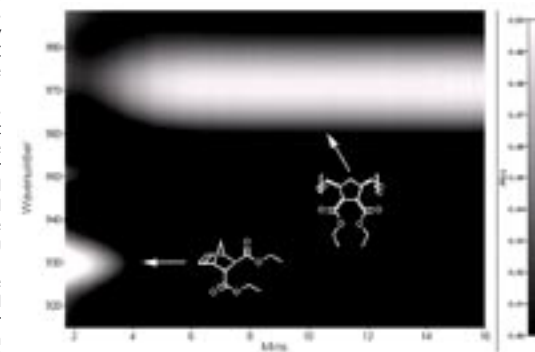


Fig 1: Topographic plot of monomer and polymer IR-bands.

OP-20

Characterization of Local Aging Processes in PE-HD by FTIR Spectroscopy

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It is generally accepted that the rate of chemical reactions in solid polymers may change significantly under the influence of external or internal stresses. The accelerating effects of mechanical stresses on oxidative aging processes were first observed with rubber and designated as mechanical-chemical aging. Then also for other polymers (primarily for polyethylene (PE) and polypropylene (PP)) effects of stresses on chemical aging were reported[1]. In this work it should be proven that the high stresses at quasi-brittle cracks growing through polymers are responsible for very localized aging processes in the immediate surrounding of the cracks. Therefore creep crack growth experiments under static loads were done with polyethylene high density (PE-HD) and the degree of oxidation at the cracks was estimated by FTIR spectroscopy. According to DIN 53383 the degree of oxidation of polyethylene can be observed by the detection of the CO-number with the help of FTIR-spectroscopy. The CO-number is the ratio of the peak of oxidation products at approx. 1720 cm⁻¹ to an inherent PE-peak at 2920 cm⁻¹ and represents a direct measure for oxidative damage. In order to investigate the local oxidation along the crack surface a FTIR-microscope with a resolution of 20 x 20 μm² was used. As shown in Fig. 1 higher CO numbers could be measured near the crack surfaces. However, this phenomenon could only be found in the low crack growth rate regime, where there is sufficiently time for oxidation processes. Moreover, local aging decreases very quickly in some distance away from the crack path. A direct influence of different stabilizer systems on the degree of these local aging processes could not be found.

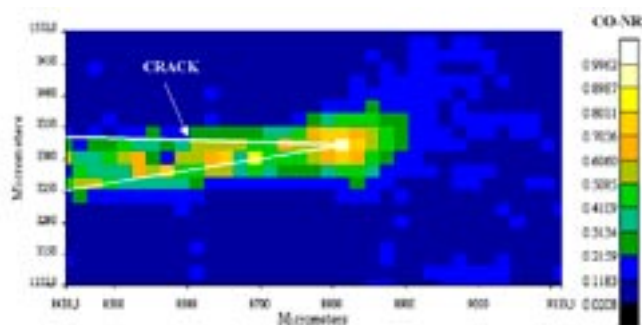


Fig. 1: Distribution of CO numbers in the immediate surrounding of a crack in PE-HD.

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OP-21

Recycling of Polyamides: Biologically degradable block-copolymers

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Nowadays the amount of plastic wastes is continuously increasing and biologically degradable polymers are expected to introduce.

In our work we connected these expectations to obtain biologically degradable block-copolymers from partially degraded Polyamide wastes as starting materials. Polyamide 6 and 66 were degraded (to boil in 80% acetic acid for 4 hours) to obtain suitable oligomers with 1000-1500 g/mol molecular weight. Then these oligomers were reacted with polylactic acid (PLA, molecular weight 1000g/mol) and polyethylene glycols (PEG, molecular weight 400-6000 g/mol). Sometimes we used toluene diisocyanate (TDI) as a coupling agent. In this case we regulated the reaction conditions to obtain linear polymers.

We designed three types of copolymers which were found to be thermoplastic and they could be used for casing of the surface of paper.

1. Degraded polyamide 66-PLA-PEG 6000
2. Degraded polyamide 66-PLA-TDI-PEG 4000
3. Degraded polyamide 6-PLA-TDI-PEG 4000

The structure of these copolymers was proved with IR-spectroscopy. The molecular weight was determined with SEC-chromatography.

OP-22

Formation of an Interpenetrating Network by Crosslinking of UF-Resins with Blocked IsocyanatesViktar Shadurka^{1,3}, Wolfgang H. Binder^{1*}, Manfred Dunky², Wolfgang Kantner²

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Blocked isocyanates are widely used as latent crosslinking agents for different thermosetting resins[1]. We have introduced a new application mode of these compounds by using them for the crosslinking of the UF-resins aiming at the improvement of the hydrolytic stability and the mechanical properties of the final adhesive. The crosslinking is expected to occur via a covalent bonding of isocyanate onto methylol- or/and urea groups within the UF-resin. This crosslinking process is competed by the reaction of isocyanate with water under formation of polyurea, which does not lead to the covalent crosslinking. Our research[2] concentrates on the elucidation of the main reaction pathways between blocked isocyanates and aqueous UF-resins together with a decisive proof of the crosslinking reaction under formation of an interpenetrating network.

We have used blocked isocyanates on basis of 2,4-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate and various blocking groups, which were synthesized and mixed with UF-resins producing stable and homogeneous dispersions. The stability and the deblocking chemistry of the compounds in pure form and in mixture with the UF-resin were investigated via DSC analysis, ¹³C-NMR-spectroscopy and dynamic ATR-IR-spectroscopy. The crosslinking of the UF-resins by the blocked isocyanates was studied by estimating the solubility of the cured resin in dimethylformamide. It was discovered that the reaction between blocked isocyanates and UF-resin occurs at a significantly lower temperature than the decomposition temperature of the respective pure compounds.

The reaction pathways as well as the covalent crosslinking were investigated by model reactions between pure or blocked phenylisocyanate and methylolated ureas. It was shown that the covalent bonding of isocyanate onto urea groups was the dominant process whereas the formation of a urethane bond by reaction with methylol groups was insignificant. The reaction pathways in the model systems were monitored via HPLC giving insight into the reaction kinetics.

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OP-23

Synthesis and Surface Characterization of Well-defined Chain-end-functionalized Polystyrenes with 2, 4, 8, 16, and 32 Perfluorooctyl Groups

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A series of well-defined chain-end-functionalized polystyrenes with 2, 4, 8, 16, and 32 perfluorooctyl (C₈F₁₇) groups of dendritic skeleton were synthesized *via* living anionic polymerization, in conjugation with iterative coupling reaction, and transformation reaction. Polystyrenes functionalized with plural benzyl bromide moieties were first synthesized according to our previous method.^[1] The benzyl bromide moieties were reacted with 1,1-diphenylalkyl anion prepared from 1,1-bis(*tert*-butyldimethylsilyloxyphenyl)ethylene and *sec*-butyllithium to give the polymer with doubled number of *tert*-butyldimethylsilyloxyphenyl groups. After deprotection of silyl groups, the polystyrene functionalized with a definite number of hydroxyl groups was, thus, synthesized. C₈F₁₇ groups were then introduced by two different reactions of the hydroxyl groups with perfluoroalkylated compounds. Williamson reaction with C₈F₁₇(CH₂)₃Br / NaH and esterification with C₈F₁₇COCl gave the polymers functionalized with C₈F₁₇(CH₂)₃OPh- and C₈F₁₇COOPh-, respectively. It should be emphasized that the resulting polymers always possessed predictable molecular weights, very narrow molecular weight distributions, and a definite number of functional groups. The resulting polymers were cast from their benzene solutions onto cover glasses to prepare film samples. After annealing at 110 °C for 2 h, the film samples were used for XPS and contact angle measurement to characterize their surface structures. Obviously, the C₈F₁₇ groups are enriched at outermost surface and hydro- and oleophobic surface are formed. Expectedly, the degree of enrichment of C₈F₁₇ group increased with increasing a number of C₈F₁₇ groups as in the previous samples reported by our group.^[2,3] However, the fluorine atomic percent of the polymers bearing with C₈F₁₇ groups of dendritic structure is lower than those of corresponding polymers with C₈F₁₇ groups of linear structure. Tentatively, it is supposed that the orientation of C₈F₁₇ groups at outermost surface may be slightly disordered because of a steric hindrance of dendritic C₈F₁₇ groups. Moreover, the fluorine atomic percent of the polymer with C₈F₁₇(CH₂)₃OPh- groups is always higher than that with C₈F₁₇COOPh- groups, suggesting that the linkage between polymer chain and C₈F₁₇ group affects the fluorine enrichment

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OP-24

Microhardness of quenched Polypropylene

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Quenching of PP leads to a so-called smectic or mesomorphic morphology, which is described and discussed in several works.[1-5] If the quenched form of PP is annealed at elevated temperatures, ordering and recrystallization occur. Because of the development and increasing of crystallinity the mechanical properties of the quenched and annealed materials vary to a large extent. Indentation testing, which is a good tool for the characterization of polymeric materials [6], is suitable to show the influence of annealing because microhardness is very sensitive to morphological changes. In the presentation the influence of molecular weight on the microhardness of quenched and subsequently annealed PP will be shown. A clear dependence of microhardness on molecular weight and annealing temperature was detected. Some examples deal with the influence of annealing time.

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OP-25

Fatigue of Glass-Fiber Reinforced Polypropylene (PP-GF)

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Fatigue properties are an integral part of material comparison and selection but they are also important for component design. While fatigue crack propagation (FCP) tests are a common method for material selection, S-N-curves are a widely spread method for component design although they just deliver life times for given stresses but no information about stress-strain-relationships. A new evaluation method for fatigue data are isocyclic stress-strain-diagrams (ISSD). In such diagrams, pairs of maximum stress and associated strain are plotted for each 10ⁿ cycle. If tests are performed for different stress levels the isocyclic stress-strain-curves are generated, which are comparable to isochronous stress-strain-curves for monotonic tensile tests.

In this work ISSD and FCP methods are applied to polypropylene model compounds reinforced with 30 m% short or with 30 m% long glass fibers (PP-SGF30 and PP-LGF30), both with the same and lower molar mass matrix PP, as well as to PP(hp)-SGF35, a high performance short glass fiber reinforced compound with a higher molar mass matrix. As shown in Fig. 1a the ranking of stiffness and resistance to creep induced by middle stress is PP-LGF30 and PP-SGF30 which is the same as for resistance to FCP as shown in Fig. 1b. Of major importance, the ranking in terms of FCP data for these two materials types corresponds to the shifts in the ISSD with increasing cycle number. Also compared in Fig. 1b is the PP(hp)-SGF35 grade with higher molar mass of the matrix polymer, which exhibits a significantly improved FCP resistance over the lower molar mass PP-SGF30 grade. In fact, the PP(hp)-SGF35 grade is superior in its FCP resistance to the PP-LGF grade.

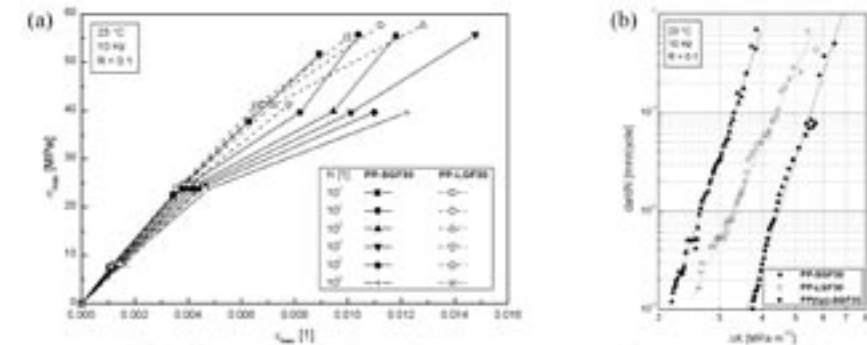


Fig. 1: Fatigue of glass-fiber reinforced polypropylene: (a) isocyclic stress-strain-diagram and (b) crack propagation behavior by linear elastic fracture mechanics

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OP-26

Molecular dynamics simulations of the first steps of the formation of polysiloxane layers at a zinc oxide surface

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The present study is motivated by the increasing use of polysiloxane layers for corrosion protection of metal(oxide) surfaces[1] by the industry and the associated need for an improved understanding of the formation of polymer layers at such surfaces from its monomers, i.e. single silane molecules. Therefore, physical properties of various dissolved silane molecules adsorbed at a ZnO surface are studied via constant temperature molecular dynamics simulations. A metal oxide surface instead of a pure metal surface is chosen to account for the fact that in contact with air many metals (like zinc, which is used for a cathodic corrosion protection of steel) are forming a thin metal oxide surface. As a first step a single dissolved silane molecule in contact with ZnO was studied[2]; in the present communication the calculations are extended to the adsorption of a whole layer consisting of a large number of silane molecules. In both studies the influence of the solvent (i.e. isopropanol) is explicitly taken into account. The adsorbed single silane molecules exhibit a different behavior depending on the chemical nature of their tail[2]: Octyltrihydroxysilane molecules with their rather unpolar tail show a statistically favored orthogonal orientations at the polar metal oxide surface with all the three polar hydroxide groups of the head being in contact with polar ZnO surface and the unpolar tail remaining in the isopropanol phase. On the contrary, due to their highly polar tail aminopropyltrihydroxysilane molecules show a more less parallel orientation at the surface. Apart from some minor fluctuations two hydroxide groups as well as the amino group of the tail are in contact with the surface. The behavior of the thiolpropyltrihydroxysilane molecules is somehow located in between – the thiol group is not polar enough to exhibit such a strong attraction to the polar surface to force permanent contact. Therefore, the molecules show two different orientations (orthogonal and parallel) though the one similar to that of aminopropyltrihydroxysilane is slightly preferred. Most of these results obtained for single adsorbed silanes can also be transferred to whole monolayers consisting of many adsorbed silane molecules thus paving the way to a better understanding of the formation of such layers.

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OP-27

Numerical studies of n-renormalized Rouse theories of polymer dynamics

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A new microscopic approach adopted as n-renormalized Rouse theory for describing of dynamical properties of entangled polymer melts, was recently presented [1,2]. It is based on the Zwanzig-Mori projection operator techniques. The following nonlinear Generalized Langevin Equation (GLE) for autocorrelation functions of probe polymer chain relaxation mode included in the polymer matrix is used in this approach:

$$\frac{\partial C_p(t)}{\partial t} + \int_0^t \Gamma_p(t-\tau) \frac{\partial C_p(\tau)}{\partial \tau} d\tau = -\frac{p^2}{N^2 \tau_p} C_p(t) \quad (1)$$

where τ_p - relaxation time of the Kuhn's segment, p - the relaxation mode number, N - the number of Kuhn's segment per chain. The memory function $\Gamma_p(t)$ includes the whole of intermolecular interactions arising in polymer melt and evaluates in accordance with projected instead of real Hamilton dynamics.

Asymptotical solution of GLE was recently carried out in the frame of renormalized and twice renormalized Rouse theories in Makovian approximation for infinitely long polymer chains [2] and the aspects of further n-renormalized Rouse approach development were denoted [3].

In our present study the solution of the GLE (1) is obtaining by combining various numerical methods for n-renormalized Rouse theories. It is showing that solution of GLE (1) for some intermediate relaxation mode $1 < p \ll N$ is strongly non-Markovian or nonexponential and can be fitted by so-called stretched-exponent [4]:

$$C_p(t) = C_p(0) \exp\left(-\left(\frac{t}{\tau_p}\right)^\alpha\right) \quad (2)$$

Effects of finite length of polymer chains and nonexponential form (2) of autocorrelation functions on mean-squared segment displacement, diffusion coefficient and spin-lattice relaxation time are studying.

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OP-28

Properties of confined star-branched polymer chains

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We considered two simple models of star-branched polymers near impenetrable surfaces. The model chains were constructed on a simple cubic lattice. Each star polymer consisted of $f = 3$ arms of equal length and the total number of segments was up to $N = 799$. The excluded volume effect was included into the model and therefore the system was studied at good solvent conditions. In the first model chains were terminally attached with one arm to the surface. The grafted arm could slide along the surface. In the second model the star-branched chain was adsorbed on the surface.[1] The grafting density and the strength of adsorption were varied. The simulations were performed using the dynamic Monte Carlo method with local changes of chain conformations.[2] The influence of the grafting density on static and dynamic properties of the system was studied. The internal and local structure of a formed polymer layer was determined. The lateral diffusion and internal mobility of star-branched chains were studied as a function of the strength of adsorption and the grafting density. The differences in chain behavior in both cases were pointed out. It was shown that the behavior of grafted and weakly adsorbed chains was similar to that of a free three-dimensional polymer. The dynamic behavior of structural chain's elements (tails, loops and trains) was also studied.

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OP-29

Biopolymers: A Challenge for GPC Characterization

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Naturally occurring Biopolymers[1] are renewable resources of interest to many industries.[2] Biopolymers show a wide variety of molecular structures as well as different biological degradation and biocompatibility, all of interest for their industrial application. Inherent to the nature of Biopolymers is their ability to have strong interactions with surfaces or other molecules. Here starts the challenge for producers of GPC materials, as GPC requires a separation mechanism without interactions. Additionally, the separation of high molecular monodisperse polymers like proteins requires a high resolution column that often antagonize with polydisperse samples (see fig. 1). Nucleic acids and Proteins are normally molecular monodisperse and all molecules have the same composition (number and kind of monomers and their monomer sequence). However polysaccharides appear as Homopolymer, Copolymer, branched Homopolymer or branched Copolymer, and they are normally molecular polydisperse (present a molecular weight distribution, fig 2).

GPC applications of Biopolymers that will highlight the requirements for the successful measurement of molecular weight, molecular weight distribution and structure are presented. The branching degree, by-products and agglomeration information is possible through coupling with light scattering and viscometry, and the chemical composition through FTIR coupling.

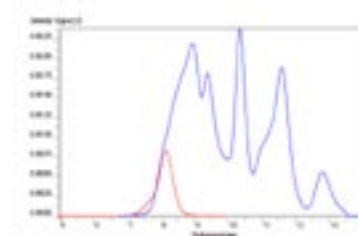


Fig. 1: Measurement of protein hydrolysates together with the protein source

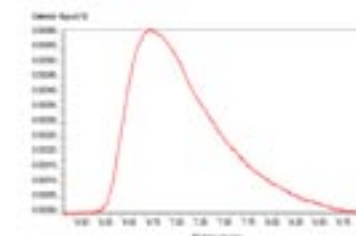


Fig. 2: Measurement of high molecular weight hyaluronic acid

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[2] Food, Pharmaceutical, Biotechnology, Biochemistry, Paper, Textile and Chemical.

OP-30

An experimentally fast and straightforward method for the direct determination of axial dispersion σ_{ad} as occurring in size exclusion chromatography**Irene Schnöll-Bitai**Institut f. Phys. Chemie, Währinger Str. 42, A-1090 Wien, Austria
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The method can be used with (a) monodisperse samples, (b) Poisson distributions (commercially available polymer standards) or (c) narrow distributions which are the weighted sum of Poisson distributions (e.g. prepared by free radical polymerisation under pseudostationary or quenched instationary conditions). The location of the points of inflection i_p define the relative peak width $\delta (= i_{p,high}/i_{p,low})$ which is an invariant quantity with respect to the number, molar mass and the so called hyper distribution [1,2] and consequently the type of detector.

$$2\sigma_{SEC} = V_{i_{low}} - V_{i_{high}} = \frac{1}{k} \{ \lg M_{i_{high}} - \lg M_{i_{low}} \} = \frac{1}{k} \lg \frac{i_{p,high}}{i_{p,low}} = \frac{1}{k} \lg \delta_{SEC} \quad (1)$$

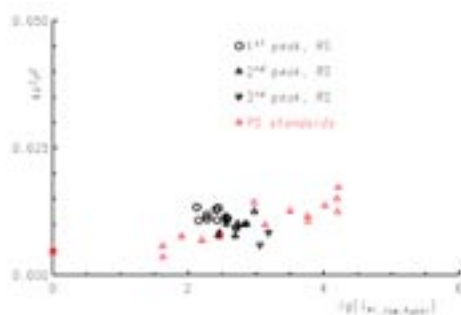
(k = slope of the linear calibration). As the method is based on the validity of the additive contributions of axial dispersion and the (ideal) peak variance σ_{peak}^2 to the experimental peak variance, $\sigma_{SEC}^2 = \sigma_{peak}^2 + \sigma_{ad}^2$, the knowledge of σ_{SEC} and σ_{peak} suffices for the direct determination of σ_{ad} :

$$\sigma_{ad} = \sqrt{\sigma_{SEC}^2 - \sigma_{peak}^2} = \frac{1}{2k} \sqrt{(\lg \delta_{SEC})^2 - (\lg \delta_{peak})^2} \quad (2)$$

For monodisperse samples (a) is $\delta = 1$, for Poisson distribution (b) δ depends on the value of the peak maximum i_{max} and for type (c) distributions the duration of the initiation t_n and dark period t_0 is essential ($j=1,2,3,\dots$ is the number of the peak)

$$\delta_{peak} = \frac{i_{max} + \sqrt{i_{max}}}{i_{max} - \sqrt{i_{max}}} \quad (3b)$$

$$\delta_{peak,j} = \frac{j(t_n + t_0)}{(j-1)(t_n + t_0) + t_0} \quad (3c)$$



The good agreement between the σ_{ad} values determined with polystyrene standards (PSS) and polystyrene prepared by rotating sector polymerisation in microemulsion (light to dark ratio 1:5) can be seen.

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OP-31

Hyaluronic Acid and other Biopolysaccharides: Characterization by GPC/SEC using Low Angle Light Scattering and Viscosity Detection**G. Heinzmann**Viscotek GmbH, Durlacher Str. 2, 76356 Weingarten; Tel.: (+49)7244-722550, Fax: (+49)7244-706554,
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GPC (Gel Permeation Chromatography), also known as SEC (Size Exclusion Chromatography), is a well known technique for the characterization of synthetic and biological polymers. However, conventional GPC measurements yield only relative molecular weight distributions, because it is necessary to calibrate the GPC separation columns with a set of polymer standards of known molecular weight. To increase the amount of information that can be obtained from GPC measurements, light scattering and viscosity detectors have been introduced. The signals of these instruments depend on the molecular weight (and size) of the polymeric samples, in contrast to concentration detectors like RI or UV.

The technique of Triple Detection GPC/SEC including Low Angle Light Scattering (LALS) is used for the characterization of hyaluronic acid and other biopolysaccharides. Within the family of biopolysaccharides, completely different structures are observed, although the chemical composition of the different biopolysaccharides is very similar to each other.

As one very interesting example for biopolysaccharides, hyaluronic acid is extensively used in the field of cosmetic surgery and other areas. It is produced using natural sources and by synthetic routes. Due to the rigid structure of hyaluronic acid and its unusual physical properties, the characterization of hyaluronic acid is a difficult application in the field of GPC/SEC. This presentation shows a method to produce reproducible and accurate data for molecular weight and structures of hyaluronic acid samples.

Furthermore, the GPC/SEC-characterization of other biopolysaccharides like nitrocellulose and maltodextrins is discussed.

Keywords: GPC/SEC, Hyaluronic Acid, Maltodextrins, Nitrocellulose, Intrinsic Viscosity, Low Angle Light Scattering, Molecular Weight

OP-32

New Chromophores for Photoinitiators

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OP-33

Synthesis of Hyperbranched Polysaccharide by Ring-Opening Polymerization of 1,6-Anhydrohexopyranose using Thermally Induced Cationic Initiator

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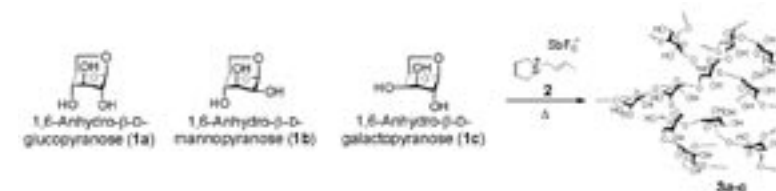
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The ring-opening polymerizations of 1,6-anhydro- β -D-glucopyranose (1a), 1,6-anhydro- β -D-mannopyranose (1b), and 1,6-anhydro- β -D-galactopyranose (1c) as latent cyclic AB₄ monomers were carried out using 2-butenyl-tetramethylenesulfonium hexafluoroantimonate (2) as a thermally induced cationic initiator. The polymerization in propylene carbonate proceeded without gelation to produce hyperbranched polysaccharides, 3a-c, and their molecular weights could be controlled. Polysaccharide 3 was completely soluble in water, dimethyl sulfoxide, and 1,3-dimethyl-2-imidazolidinone, slightly soluble in pyridine, and insoluble in toluene, chloroform, acetone and methanol. The weight-average molecular weights (Mw,SLS) values measured by static light scattering (SLS) varied in the range of 2.9×10^4 to 6.2×10^4 for 3a, 6.5×10^3 to 5.7×10^5 for 3b, and 1.3×10^4 to 1.1×10^5 for 3c, which were significantly higher than the weight-average molecular weight (Mw,SEC) values by size exclusion chromatography (SEC).

The solution viscosity of 3a-c was very low, and the intrinsic viscosities were from 3.2×10^{-3} to $4.7 \times 10^{-3} \text{ L} \cdot \text{g}^{-1}$. The structural analysis indicated that 3a-c consisted of many kinds of α - and β -D-linked hexopyranosyl repeating units including a slight amount of D-hexofuranosyl repeating units and numerous nonreducing D-hexopyranosyl terminal units. The degree of branching (DB), estimated by the methylation analysis of 3a-c, was in the range of 0.36 - 0.38 for 3a, 0.38 - 0.44 for 3b, 0.45 - 0.50 for 3c.[1] In conclusion, the thermally induced cationic polymerizations of 1a-c using 2 were facile method leading to the hyperbranched polysaccharide with high DB value.



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OP-34

Polymer Brushes by Surface-Initiated Polymerization - Structuring on the Micro- and Nanometer ScaleUrsula Schmelmer^(a), Anne Paul^(b), Alexander Küller^(b), Rainer Jordan^{*(a,c)}, Wolfgang Eck^(b),Armin Götzhäuser^{*(b,d)}, Michael Grunze^(b), Abraham Ulman^(c)*(a) Lehrstuhl für Makromolekulare Stoffe, TU München, Lichtenbergstr. 4, 85747 Garching**(b) Lehrstuhl für Angewandte Physikalische Chemie, Im Neuenheimer Feld 253, Universität Heidelberg, 69120 Heidelberg.**(c) Department of Chemistry, Chemical Engineering and Materials Science, 6 Metrotech Center, Polytechnic University, Brooklyn NY 11201, USA.**(d) Institut für Physikalische Chemie, Hans Meerwein Str., Philipps-Universität Marburg, 35032 Marburg*
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The concept of surface-initiated polymerization (SIP) to prepare dense and well defined polymer brush systems on solids has been demonstrated for all types of polymerization [1] such as the (controlled) radical, living cationic [2] and anionic polymerization.[3] One advantage of using ordered and well-defined SAMs as initiator systems for the SIP is that the locus of the initiator sites and therefore, the features of the resulting polymer brushes can be directly controlled. Here, we present the SIP of vinyl monomers using a SAM of an asymmetric azo-initiator. The bonded initiator is prepared at surface areas which were locally predefined by the so-called chemical lithography.[5] The synthesized initiator proved to be suitable for thermal as well as photochemical initiation of the radical SIP. Results for both initiation types will be presented and discussed. Structuring of the SAMs can be performed by irradiation through a lithographic mask or by direct writing with a focused e-beam. While the first enables a parallel and thus faster structuring, the latter allows the fabrication of individually 'written' surface patterns. The capabilities of the chemical lithography, in combination with the SIP for surface pattern enhancement will be outlined. The currently smallest line width prepared by 'direct-writing' of the primary pattern using a focused e-beam is approximately 40-45 nm. Acknowledgements: This project is financially supported by the Deutsche Forschungsgemeinschaft (GR 625/50-1 and JO 287/2-1).

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OP-35

Silylation of WoodG. Weichslberger^[1,2], S.Knaus^[2], H.Gruber^[2], M. Schwanninger^[3]*1) Wood Competence Center, Wood K-Plus, St. Peterstr. 25, 4020 Linz, Austria**2) Vienna University of Technology, Institute of applied synthetic chemistry, Getreidemarkt 9/163 MC, 1060 Vienna, Austria**3) Vienna University of Agricultural Sciences, Institute of chemistry, Muthgasse 18, 1190 Vienna, Austria**E-mail: weichslberger@otech7.tuwien.ac.at*

Chemical modification of wood has been extensively studied for the last decades in order to influence properties such as for example wettability, dimensional stability, biological resistance or adhesion. The processes involved, rely essentially upon forming covalent bonding between the hydroxyl groups of wood and some chemical reagent leading to modification of the basic chemistry of the cell walls. Many studies in this area have been focused either on etherification or esterification reactions, with a particular attention on acetylation with acetic acid anhydride.

We investigated the chemical modification of spruce cellulose, spruce wood meal and solid spruce wood with organosilicon compounds (OSC) such as trimethylchlorosilane (TMCS), N,O-bis-trimethylsilylacetamide (BSA) and hexamethyldisilazane (HMDS) respectively, in liquid phase. Taking advantage of the high reactivity of TMCS, a procedure was developed, to determine the amount of water which cannot be removed from the wood by drying, so called bound water or non freezing water. To make clear, whether (a) bond formation between OSC and the wood has taken place, (b) how much of the OSC had been incorporated and (c) which parts of the wood cells reacted, proper analytical methods were developed. Bond formation between OSC and wood was confirmed by IR spectroscopy and solid state NMR spectroscopy. A simple method was established to quantify the extent of silylation by IR spectroscopy, replacing the time consuming wet decomposition method. Furthermore, scanning electron microscopy with EDX detection was applied to gain information about the Si-distribution at a microscopic level. Some selected properties of silylated wood were also investigated, the results thereof are part of the poster.

OP-36

Thermal stability of LGF Polypropylen

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The lecture shows the results for the thermal long-term behaviour of long glass fibre reinforced polypropylene (PP LGF). The properties of PP LGF become more and more important for using this kind of materials for technical parts. Long glass fibres allow a significant increase of mechanical properties. Especially the rigidity/toughness ratio becomes much better. For injection moulded technical parts it is very important to obtain a sufficient mean fibre length, which is significantly longer than in case of short glass fibres reinforcement. During development of components it is necessary to consider specific guidelines on part design, mould design and machinery set up. Following these steps the significant mean fibre length will be obtained. To get sufficient information about the long-term performance of technical parts it is necessary to check out the thermooxidative long-term stability. During research projects at IB STEINER, based on LGF materials, the thermooxidative stability was measured by isothermal long-term DSC (Differential Scanning Calorimetry). Literature and experience show that this method is a very reliable instrument to estimate the thermooxidative long-term stability of polyolefines.

A lot of measurements were carried out on granulate and tensile bars, which contained different amounts of thermal stabiliser systems. These thermal stabiliser systems were compared. Additionally mechanical tests were carried out to verify the results.

OP-37

Cellulose Fibre Reinforced Composites: New Challenges and Opportunities

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Now a days, ecological concern has resulted in a renewed interest in natural materials and therefore issues such as recyclability and environmental safety are becoming increasingly important for the introduction of new materials and products. Natural fibres like flax, hemp, kenaf, jute and sisal do have a number of techno-economical & ecological advantages over E-glass fibres. The combination of interesting mechanical and physical properties together with their environmentally friendly character has triggered a number of industrial sectors, notably the automotive industry, to consider these fibres as potential candidates to replace glass fibres in environmentally safe products. In fact, car manufacturers are aiming to make every component recyclable or biodegradable, which does not leave much scope for glass fibre reinforced composites. An important aspect with respect to optimal mechanical performance of fibre reinforced composites in general and durability in particular is the optimization of the interfacial bond between fibre and polymer matrix. This paper discusses the important challenges and opportunities for cellulose fibre reinforced polymer composites.

OP-38

The role of Plastics in a sustainable Development

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Sustainable Development is regarded as a joint development of ecological, economical and social criteria. Most plastic products are produced from oil and gas, so called non renewable resources (NRR). Use of products made from plastics thus is contributing to demand of scarce NRR and to emissions of greenhouse gases, mainly CO₂. Therefore products made from renewable resources (RR) often score better in these two environmental categories. Plastic products in the contrary are often advantageous due to lower economic life cycle cost (LCC). Today no method exists to compare such ecological disadvantages combined with economical advantages of products from NRR with products from RR. We have developed such a method [1]. We use all or part of these economical advantages for ecological sensitive improvements. E.g. we do finance with this money thermal insulation of house walls, thus sparing heating energy and connected emissions. Results for different examples show that in this way low cost products (even from NRR) can contribute to Sustainable Development more efficiently than higher cost products made from RR. We discuss other methods in this connection, the impact of internalisation of external cost etc.

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OP-39

Carbon-Nanofiber-Composites for Medical Applications

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Carbon nanofibers and nanotubes promise to revolutionize several fields in material science and open the way nanotechnology into medical applications. Market development will depend on material availability at reasonable prices. Our developmental partner has achieved bulk production capacities of high purity carbon nanofibers (CNFs) at low cost by catalytic chemical vapor deposition. Polymer composites have been prepared by intensive shear mixing and dispersing of CNFs into polymer matrices via extrusion. These compounds contain carbon nanofibers that are thousands of times smaller than conventional carbon fibers, which leads to extremely high aspect ratios (length:tube diameter), giving improved properties at very low loadings. In polypropylene the application of less than 10 % wt. CNFs reduced the volume resistivity from >10¹³ Ohmcm to a value of <10⁵ Ohmcm. Achieving similar conductivity using traditional additives such as carbon fiber or carbon black requires higher loadings that may affect properties such as strength and toughness/impact, processing, and surface finish.

Deeper understanding of the chemistry driving the formation and the interfacial matrix-fiber behaviour of these nanocomposites enabled us to discover practical methods of production of these materials for medical applications where the enhancements required are mechanical in nature with a strong focus on biomedical compatibility. Traditional fillers are far too large to provide homogenous compounds suitable for these thin sections. Especially advanced medical procedures may involve devices such as catheters and stent-delivery balloons, which require extraordinarily thin walls and smooth surfaces. We are focussing on the development and volume production of technical polymers incorporating performance-enhancing nanofillers, which provide properties not possible with ordinary polymers or traditional fillers alone like improved bending stiffness, tensile strength, elongation, or torque. With these newly, innovative developments we try to demonstrate unique improvements in material properties and barrier characteristics and offering the potential for biomedical compatibility.

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OP-40

**Electrospinning P(LLA-CL) Nanofiber:
A Biomimetic Extracellular Matrix for Cardiovascular Tissue Engineering****Xiumei Mo, H.-J. Weber, Chengyu Xu*, S. Ramakrishna****Laboratory for Cardiovascular Engineering, Division Jülich, Aachen University of Applied Sciences, Ginsterweg 1, D-52428, Germany*** Biomaterials Lab. Bioengineering division, National University of Singapore, 9 Engineering Drive 1, Singapore 117576
e-mail: xiumeiMo865@msn.com***Introduction**

To face the new stages of tissue engineering, a biomimetic extra cellular matrix (ECM) is expected, which should have similar nanofibrous structure as that of natural collagen in a native tissue. This native ECM acts as a scaffold to bring cells together and to form a tissue, to control the tissue structure and regulate the cell phenotype. In this paper electrospinning method has been used for the fabrication of nanofibrous ECM for cardiovascular tissue engineering, targeting to built a small diameter biodegradable blood vessel scaffold.

Experimental Materials:

Poly(L-lactid-co-caprolactone) [P(LLA-CL)] (75:25) copolymer was obtained from Japan. Human coronary artery endothelial cells (EC) and smooth muscle cells (SMC) were obtained from American Type Culture Collection (ATCC; Arlington, VA).

Tube nanofiber scaffolding:

P(LLA-CL) acetone solution was electrospun in nanofiber through a nozzle at the action of 12KV high electrostatic voltage. A rotating mandrel with a Teflon tube collector was placed under the spinning nozzle at a distance of 80mm, below the mandrel is a parallel aluminum grid with sharp edge, which guided the fiber aligning on Teflon tube. Tubular nanofiber scaffold was thus collected on the Teflon tube.

Characterization of nanofiber:

SEM (Jeol JSM-5800LV), x-ray diffractometer (Lab-X, XRD-6000, Shimadzu) and DSC (Pyris 6, Perkin Elmer) were used to test the morphology, crystal structure and thermal behavior of nanofiber. Nanofiber mesh on coverslip were seeded with SMC and EC cells and cultured in an incubator. DMEM medium with serum and growth factors was changed every 3 days. Cells attachment and proliferation on the nanofiber were observed under SEM.

Results and discussion:

Tube nanofiber scaffolds with different fiber aligning angles to the longitude direction have been prepared by putting the aluminum grid in different angle with the Teflon tube. The strength of nanofiber tube scaffold could be enhanced by laying the nanofiber on the tube with different angle. Nanofiber showed different thermal behavior and crystal structure with as-used material. During electrospinning the higher electrostatic voltage coursed the orientation of molecular chains along the fiber direction. But only the molecular sequences which have lower glass transition point than room temperature could crystallize during electrospinning. Electrospinning P(LLA-CL) nanofiber showed good biocompatibility. Both SMC and EC cells attached and proliferated well on the nanofiber.

OP-41

Biopolymer Nanofiber Scaffolds for Biomedical Applications**Benjamin S. Hsiao***, Benjamin Chu*, Dufei Fang, Steven Zong, Kwang-Sok Kim*Departments of Chemistry and of Biomedical Engineering, State University of New York at Stony Brook, Stony Brook, NY 11794-3400**E-mail: bhsiao@notes.cc.sunysb.edu*

An innovative multi-jet electrospinning technology (esJets™) has recently been developed by us at Stony Brook [1-7]. The prototype multi-jet electrospinning apparatus demonstrated mass production potential to fabricate cost-effective non-woven membranes containing nanofibers of biopolymers. The unique features of the esJets™ technology include multiple drug loading capability (antibiotics, anesthetics, anti-inflammatory agents, proteins, DNAs), pattern formation, layer-by-layer processing and hybrid nanoparticle/nanofiber composites. Our current research activities of this technology focus on two biomedical applications: (1) barrier membranes to prevent surgery-induced adhesions, and (2) novel scaffolds for tissue engineering. For anti-adhesion applications, the unique multiple-jet electrospinning process enabled us to load antibiotics into the membranes with controlled drug release rate and biodegradation time. These medicated membranes offer several advantages over commercial products: (1) they can completely prevent the surgery-induced adhesions, (2) the membranes provide better handling ability, (3) they leave fewer scars after the application. Potential applications of this membrane in the clinical arena include the prevention of adhesions after abdominal surgery, open gynecologic pelvic procedures as well as cardiac or thoracic surgery. For tissue engineering applications, electrospinning offers a unique means to manufacture nanostructured scaffolds containing non-woven nanofibers for various tissue engineering applications, the uniqueness of electrospun scaffolds are several: (1) the fiber anisotropy can be controlled, allowing the generation of directed cell growth, (2) DNAs, growth factors and proteins can be incorporated into the nanofiber scaffold using a proprietary approach, which can be controlled released in vivo or in vitro, (3) the biological affinity and the degradation rate of the scaffold can be finely adjusted, (4) the porosity of the scaffolds can be controlled.

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OP-42

Polymer Properties as a Function of repeated Instrument Processing

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Medical Device Manufacturers have a responsibility to demonstrate the integrity of a medical device over its claimed lifetime. Accordingly information on the development of mechanical properties are needed in order to determine a device lifespan or service interval. Polymers used as/in surgery instruments degrade during service with loss of properties (appearance, mechanical properties, overall performance) due to degradation caused by the service environment or instrument processing. The effects of two ageing methods simulating instrument processing are investigated. First change in longterm mechanical properties due to two different aging methods are measured and compared. Second, the resulting changes of the material properties are assessed in relation with physical, chemical or thermal ageing phenomena or combination thereof. A standard clinical instrument processing cycle was the reference method. A clinical proofed washing/disinfection program (detergent: neodisher mediclean forte) was followed up by 18 minutes steam sterilisation at 134 °C (Process D+S). D+S was compared with just the washing/disinfection step (detergent: BORER deconex ALKA ONE), a short term test often used to verify chemical material resistance (Process D). For both methods ageing cycles were performed up to 200 times. The effects on POM, PP, PEI, PPSU-Blend and PEEK (all "medical grade") are determined. Tensile and impact tests were performed to measure mechanical properties. DSC, FTIR and several optical methods are used to determine the aging phenomena.

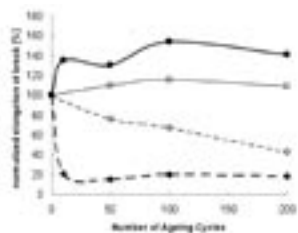


Fig-1: Elongation at break of PP and PEEK for different aging methods (values normalized to 100 %)

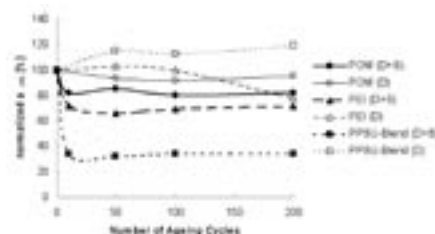


Fig-2: Charpy (notched) Impact behaviour of POM, PEI and PPSU-Blend for different aging methods (values normalized to 100 %)

Longterm mechanical properties (Fig-1 and Fig-2) exhibit a great difference concerning the ageing test method. The influence of temperature (steam sterilization) in terms of material properties is significant. Already after 10 D+S cycles mechanical properties changed in range of + 40 % to - 80 %. Aging phenomena for POM (thermal), PP (thermal), PEI (chemical, thermal), PPSU-Blend (chemical) and PEEK (thermal) had been founded and are described. The influence of cleaning agent composition regarding material properties (PPSU-Blend) is described. The results reveal that predicting of longterm mechanical properties regarding instrument processing cannot sufficiently be described by neglecting either the chemical (washing/disinfection) or thermal (sterilization) influence. Therefore future investigation should include a clinical relevant aging method (chemical resistance, sterilization) in order to determine material properties relating to longterm product design parameters and biocompatibility.

OP-43

Werner Kuhn - A pioneer of polymer research
In memory of the 40th anniversary of his death

W.G.Pohl

Austrian Chemical Society, Vienna, Austria

Werner Kuhn was born in 1899. He received his Ph D in physical chemistry from the Uiversity of Zürich. For two years he worked in the Institute for Theoretical Physics of Kopenhagen with Niels Bohr. After his "Habilitation" in Zürich he moved to Heidelberg, working there with Karl Freudenberg and for some months in the laboratory of Ernest Rutherford in Cambridge. In 1930 he became associate professor at the Technische Hochschule Karlsruhe and 1936 full professor at the University of Kiel. In 1939 he received a call to the University of Basel, where he stayed as the director of the Institute for Physical Chemistry until his untimely death on the 27. august 1963. The author was the last student who was accepted as a Ph D student by Werner Kuhn. He wants to give a survey of the scientific accomplishments of his teacher and remind of his admirable methods of research and modest personality. Original letters of Hermann Mark to Werner Kuhn and the answer of Kuhn will be presented. From Kuhn's research the presentation will focus on his theory of hydrodynamics of chain polymers. In this field he layed foundations which where later used by Paul Flory on his way to the Nobel prize. Secondly the author will give a survey of Kuhn's work on "artificial muscles". He made his PhD thesis in this area studying the conversion of chemical energy into mechanical work and vice versa.

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OP-44**Die Abformung funktioneller Mikrostrukturen für die Medizintechnik im Spritzgießverfahren**Christian Gornik*Battenfeld Kunststoffmaschinen GmbH
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Man unterscheidet grundsätzlich zwischen drei verschiedenen Arten von „Mikroteilen“. Das Mikrospritzgießteil hat ein Teilgewicht von kleiner 1g. Die zweite Art von „Mikroteilen“ sind Spritzgießteile mit Toleranzen im µm-Bereich, also sog. Mikropräzisionsformteile. Die dritte Art von Mikroteilen sind Spritzgießteile mit makroskopischen Abmessungen, also im Milli- bis Zentimeterbereich und darüber, auf deren Oberfläche sich Mikrostrukturen befinden. [1,2] Das Ziel bei der Herstellung dieser auch als m2M-Teilen (micro-to-macro) bezeichneten Teilen ist, die Oberflächenstruktur so auszubilden, dass sie für bestimmte Funktionen verwendet werden kann. Als lab-on-the-chip-Systeme („Labor auf der Chipkarte“) sind mikrostrukturierte Teile bereits heute in den Bereichen Medizin- und Biotechnologie in Verwendung, da ein zunehmender Bedarf an miniaturisierten Reaktoren und Analysatoren besteht[3]. Spritzgusskunststoffteile eignen sich für die Anwendungen in der Medizin besonders gut, da sie kostengünstig und in großen Stückzahlen für derartige Einwegartikel hergestellt werden können.

Zur Herstellung von m2M-Teilen im Spritzgießprozeß ist neben der erhöhten Präzision der Maschine eine spezielle Prozessführung, der sog. Variotherm-Prozeß, notwendig. Ziel dabei ist es, die Erstarrung der Randschicht bei Einspritzen ins Werkzeug zu verhindern und so eine vollständige Füllung von Mikrovertiefungen zu gewährleisten. Vor dem Entformen muss die Temperatur des Teiles unter der Einfrieretemperatur liegen, um die notwendige mechanische Stabilität zu erhalten. Durch unterschiedliche Methoden des Beheizens und Kühlens konnten deutliche Verringerungen der bisher üblicherweise extrem langen Zykluszeiten erreicht werden. Das Spritzgießen von mikro- und nanostrukturierten Kunststoffteilen verdrängt aufgrund der hohen Produktivität zunehmend das Heißprägen sowie das Ätzen der Strukturen in Gläser.

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PO-1

Polymer Characterization – Tailoring a GPC System to Meet the Demands of the Application

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In GPC a size separation can be converted to a molecular weight distribution through column calibration using a series of well characterized standards. When operated in this mode, a simple differential refractometer (DRI) concentration detector is employed, the operation of the instrument and the data handling are relatively easy to automate but the molecular weight distribution obtained is relative to the polymer standards used for calibration. This set up would be ideal for a routine quality control method where the polymerisation mechanism in question may result in small changes in the molecular weight distribution of the polymer but not its architecture. In this scenario the repeatability of the system is paramount so that small variations in the measured parameters can be truly associated with changes in the polymer.

If the polymerisation conditions are likely to affect both the molecular weight distribution and the architecture of the polymer (e.g. degree of long chain branching), the GPC system must be designed to include additional detectors which are sensitive to such changes. This usually means light scattering, viscosity or a combination of both detectors as well as the regular DRI. Whilst the operation of the instrument can still be automated, the data handling requirements in this case are more rigorous and usually require more manual intervention.

This poster will outline strategies for these two different approaches and show typical examples of a regular GPC method applied to quality control and a multi-detector method for determination of branching for both organic and aqueous soluble polymers.

POSTER PRESENTATIONS

Session: Monday, September 15th 2003, 16.30 - 17.30

PO-2

**Gel Permeation Chromatography with Fourier Transform
Infra-Red Detection**Greg Saunders, Elizabeth Meehan, Steve O'Donohue and Alan Brookes*Polymer laboratories Ltd, Essex road, Church Stretton, Shropshire SY6 6AX UK
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Fourier transform infra-red (FTIR) spectroscopy is a well-established technique of the analytical laboratory. Typically, FTIR is used in 'batch mode' operation to determine the vibration absorption bands of materials and the 'fingerprinting' of compounds. The use of FTIR as a liquid-flow detector is far less widespread due to historical limitations in the sensitivity of FTIR, however, with the development of new detector and software, the coupling of FTIR detection with liquid chromatographic techniques has become possible.

FTIR has many favorable characteristics for use as a GPC detection technique. Many polymers exhibit relatively simple absorption spectra and can be readily identified by comparison to library data. Furthermore, time-resolved spectral acquisition can be used to monitor the relative intensities of individual absorption bands as a function of elution volume. By careful selection of appropriate absorption bands this allows intensity-based chromatograms to be generated for individual components of blends and copolymers. Quantitation is possible through calibration of detector response allowing compositional information to be generated. These benefits greatly enhance the information available from the GPC experiment.

FTIR detection can also be used in the high temperature analysis of polyethylene. Monitoring the C-H stretching frequencies allows the relative proportions of CH₃ and CH₂ groups in the polymer to be assessed. Using chemometric methods this information can be compared to a model to estimate the level of short chain branching (SCB) in polyethylene, information that is not readily available from traditional multi-detector GPC methods.

This presentation outlines the use of an FTIR spectrometer as a detector for gel permeation chromatography, both for room and high temperature applications. Coupling to the detector is describe using the PL-HTGPC/FTIR interface, a temperature controlled FTIR cell and heated transfer line that can be interfaced with and standard GPC instrumentation.

PO-3

**Partial and Common Regularities of Macromolecular Self-Diffusion
in Dendrimer Solutions**Alexandr Sagidullin^{a)}, Aziz M. Muzafarov^{b)}, Bernd Fritzing^{c)}, Ulrich Scheler^{c)}, Alexander N. Ozerin^{b)}, Mikhail A. Krykin^{b)}, and Vladimir D. Skirda^{a)}*a)-Dept. of Molecular Physics, Kazan State University, Kremlevskaya Str., 18, 420008 Kazan, Russia;
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The results of experimental NMR study of various dendrimer solutions have been reported. The macromolecular self-diffusion coefficients (D) and NM relaxation times (T₁, T₂) of poly(butylcarbosilane) - PBCS - and poly(amidoamine) with hydroxyl surface groups - PAMAM-OH - have been measured, and the concentration dependences D(ϕ), T₁(ϕ), and T₂(ϕ) were obtained. The molecular weight range of the dendrimers studied was from 4 299 up to 72 537 g·mole⁻¹; the range of the dendrimer volume fraction was from 0.001 up to 0.68.

It was shown that experimental concentration dependences D(ϕ) can be reduced to a general curve - to the generalized concentration dependence of reduced macromolecular diffusion coefficients. The obtained curve coincides with the generalized dependence for poly(allylcarbosilane) dendrimers[1]. This result proves the existence of the common law of the dendrimer diffusivity for macromolecules with different chemical nature. Furthermore, the generalized concentration dependence of self-diffusion coefficients of dendrimers does not depend on the chemical-physical properties of solvents. The analysis of the generalized dependence of the dendrimer D on their concentration shows that this curve tends to the analogous dependence for polymers[2] at the limits of extremely dilute and concentrated solutions only. In the intermediate range of ϕ , these curves are considerably different, that proves the sufficient difference of the diffusion behavior of polymeric and dendritic macromolecules in solutions. It should be also noted that the generalized concentration dependence of D for PAMAM-OH dendrimers coincides with analogous dependence for globular proteins in the aqueous solutions over the whole examined concentration range[3]. The last result allows us to state that the diffusion of proteins and dendrimers are generally similar.

This work was supported by US CRDF REC-007, INTAS YSF-00-134, UR.05.01.034, and Integration IO-807.

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PO-4

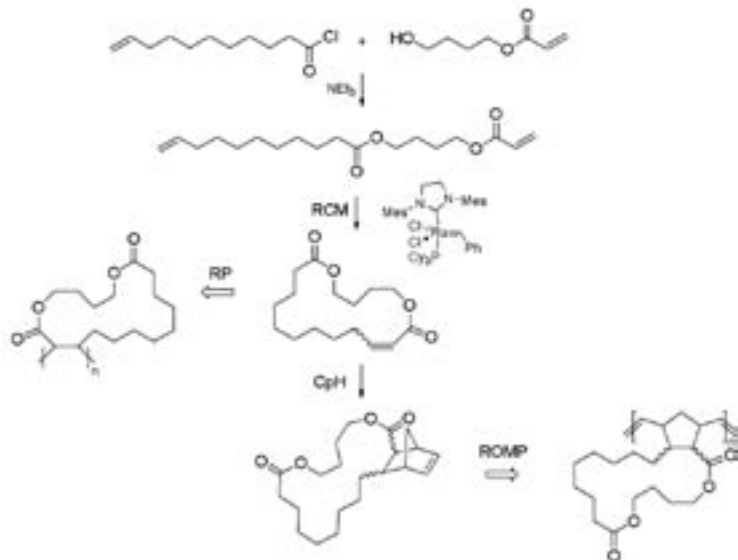
Polymers with Pendant Macrocycles

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Control over macromolecular architecture is a central goal of polymer chemistry. Efforts along these lines have been directed towards developing new synthetic methodologies whereby precise placement of chemical functionality can be achieved. We herein report a concept to prepare polymers containing pendant macrocycles. A concrete example is depicted in the figure below.



Key step is in all cases a ring closing metathesis reaction (RCM). The obtained macrocycles include an acrylate functionality, which can be exploited either for radical polymerisation (RP) or for a Diels Alder reaction yielding the corresponding norbornene derivative. The latter ones can than be polymerised by ring opening metathesis polymerisation (ROMP). The synthesis of such polymers and their characterisation will be presented.

PO-5

Examination of residual vulcanization accelerators in NR latex films

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Latex-products (e.g. gloves and condoms) contain substances which may cause skin sensitization [1]. Sensitization can be due to proteins, which are contained in natural rubber and to vulcanization accelerators used during the vulcanization of rubber. In the present investigation, we focused on the problem of allergenic vulcanization accelerators [2]. We investigated a new vulcanization system containing carbamates and xanthogenates. Carbamates were chosen such that they were extractable only to a small content and had a small ability to penetrate skin. Xanthogenates proved advantageous since they undergo decomposition reactions during vulcanization and thus are not present in the final product. The concentrations of the accelerators in NR latex were optimized with respect to speed of cure and the mechanical properties of the cured latex films. In addition, residual amounts of the accelerators in the latex films after curing were determined.

Gas chromatography (GC) and HPLC - the most common methods for the analysis of rubber chemicals [3] - proved time consuming and complicated because of the need of derivatization prior to chromatographic separation. Therefore two new analytical methods were developed:

1. An infrared (FTIR) method for quantification of residual accelerators in extracts from latex films.
2. An infrared (FTIR) method for the in-line determination of accelerators in latex films.

The results of the FTIR analyses were cross-checked with standard chromatographic procedures. It was evidenced that FTIR analysis yields results comparable to those obtained with GC. Using FTIR, detection limits below 0,01 phr (parts per hundred parts of rubber) were demonstrated for different vulcanization accelerators. After NR latex vulcanization under appropriate conditions, only low amounts of carbamate were extractable. Xanthogenates were no more detectable in the vulcanized NR films and in the extracts prepared therefrom. The low amounts of residual accelerators both in the NR latex films and extracts therefrom suggest that the optimized vulcanization system should possess a significantly lower allergenic potential than conventional systems.

The investigations were performed within a project of the Polymer Competence Center Leoben GmbH (PCCL).

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PO-6

Discrete polymerisable lumophores

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In general, oligomers possess more predictable and reproducible properties than polymeric materials and additionally they can be carefully purified. Nevertheless polymeric materials obtain a superior morphological stability against crystallization and they are more easy to process. Consequently, advantages of monodisperse lumophores and polymers can be combined by introducing the lumophore into a polymer, either as a side chain or a part of the polymer backbone. Especially polymers prepared by ring opening metathesis polymerization (ROMP) of exo/endo-2-substituted norbornenes, because they are amorphous since the polymer contains both exo and endo substituents, cis and trans double bonds, and head to tail, tail to tail, and head to head monomer relationships in the polymer backbone. Furthermore, ROMP: especially with the latest initiator generation provides complete initiation, extraordinary functional group tolerance and high activity, opening up the way for a rational design of block copolymers consisting of e.g. blue or red light emitting lumophores as exemplified by the figure below.

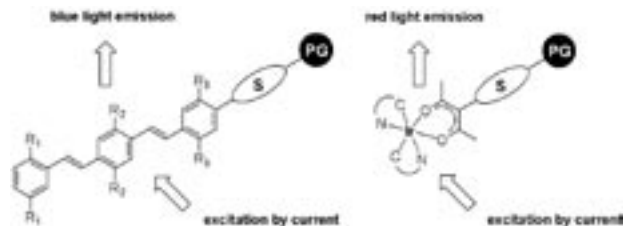


Fig.: S (spacer), PG (polymerisable group)

A strategy to incorporate PPV-derivatives and IR-complexes into ROM-Polymers will be presented.

PO-7

Discrete Oligo-phenylene-vinylene-Derivatives

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Alternating para- and meta-linked poly(phenylene-vinylene) are a potentially interesting class of materials for optoelectronic applications. The meta-linkages introduced into the conjugated backbone increases the bandgap[1], and making blue light emission from soluble PPV-derivatives possible. Recently, research on monodisperse conjugated oligomers has dramatically grown and expanded. Monodisperse conjugated oligomers, on the one hand, serve as model systems to directly generate useful and predictable structure-property relationships to rationalize the properties of the parent polydisperse polymeric materials[2]. On the other hand, oligomer materials with defined length and construction have become a subject of its own.

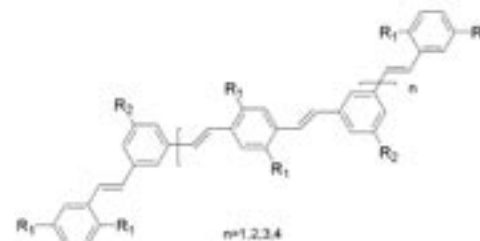


Fig.: Oligo-PPV-Derivative

A strategy of a stepwise synthesis for the preparation of precisely defined oligo(*m,p*-phenylene-vinylene)s will be described, and a comparison of correlated quantum chemical simulation and measurement results of absorption and emission properties of these systems will be presented.

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PO-8

Semicontinuous Emulsion Copolymerization of Vinyl Acetate and Butyl Acrylate Using Different Initiator and Different Chain Length EmulsifierAyfer Sarac*Yildiz Technical University, Faculty of Sciences and Arts, Davutpasa Campus, Department of Chemistry, 34010 Esenler-Istanbul, Turkey**E-mail: ayfersarac2002@yahoo.com*

Vinyl acetate and butyl acrylate copolymers are used besides adhesive industry especially in paint and coating industries as binder. Vinyl acetate-co-butyl acrylate latexes were synthesized in the presence of non-ionic emulsifiers which have different chain length, protective colloid and different initiators (ammonium persulfate and potassium persulfate). Vinyl acetate/butyl acrylate monomer ratio was determined as 85/15 based on previous studies [1-3]. In this study, copolymerizations were done at the high solid content by similar in industrial practice and all chemicals were used as received. Two latex series were synthesized in those studies; in the first serie ammonium persulfate was used as initiator and the ethoxylation degree of non-ionic emulsifiers (the different chain length of non-ionic emulsifiers) were changed from 10 to 40. Potassium persulfate was used as initiator in synthesizing of the second serie copolymers and the different chain length of non-ionic emulsifiers as emulsifier. Copolymer latexes were characterized by measuring Brookfield viscosity, molecular weights (Mn, Mw, Mv) and surface tension of dried latex film.

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PO-9

Determination of Thermodynamical Interaction Parameter and Rate of Crystalline of Polycaprolactone with Some Solvents by Gas ChromatographyAyfer Sarac, Özlem Cankurtaran*, Ferdane Yilmaz*Yildiz Technical University, Faculty of Sciences and Arts, Davutpasa Campus, Department of Chemistry, 34010 Esenler-Istanbul, Turkey**E-mail: ayfersarac2002@yahoo.com, kurtaran90@yahoo.com, fyilmaz@yildiz.edu.tr*

Polycaprolactone is one of semicrystalline aliphatic polyesters[1,2]. Solubility condition of the polymer is related its rate of crystalline. Inverse gas chromatography is very useful technique for the determination polymer-solvent interaction and crystallinity rate of polymers[3,4].

In this study the retention diagram of polycaprolactone for the tert-butyl acetate was obtained by inverse gas chromatography method in the temperature range 40-140 °C. Rate of crystalline was determined between 35.89 and 39.06 in the temperature range 40-53 °C. Thermodynamic interactions was determined for cyclopentane, cyclohexane, tetrahydrofuran, 1,4-dioxane and tert-butyl acetate with polycaprolactone between 70-140 °C. Specific retention volume V_g° , Flory Huggins polymer-solvent interaction parameters, χ_{12}° , equation of state polymer-solvent interaction parameters, χ_{12}^* , the weight fraction activity coefficients, Ω_1° , effective exchange energy parameters, X_{12} , partial molar heat of sorption, $\Delta H_{1,sorp}$, the partial molar heat of mixing, $\Delta H_{1,m}$ were determined.

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PO-10

Synthesizing of New Silicon-Based Surfactants and Determination of Their Surface PropertiesAyfer Sarac¹, Thomas Nennadal², Simone Knaus², Heinrich Gruber^{2*}¹ Yildiz Technical University, Faculty of Sciences and Arts, Davutpasa Campus, Department of Chemistry, 34010 Esenler, Istanbul, Turkey² Institute of Applied Synthetic Chemistry Division of Macromolecular Chemistry Getreidemarkt 9, A-1060 Wien-AUSTRIA
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Silicones are widely used in industry and consumer products such as fluids, resins, room temperature vulcanizing rubber and heat-cured rubbers. They are further used as new engineering materials such as silicon surfactants[1]. Silicon surfactants are structurally derived from polydi-methylsiloxane, in which the methyl groups are partly substituted by lipophilic or hydrophilic non-ionic or ionic moieties. The unique properties of silicone surfactants are because of their lyophobic silicone part[2,3]. In this study, a series of allyl ethers of polyols and monosaccharides with trimethylsilyl, diisopropylidene, and acetyl protective groups were synthesized using different multi-step reaction pathways. Characterization of these molecules was achieved by ¹H-NMR, ¹³C-NMR, FTIR and melting point analysis. In addition, some modified siloxanes were synthesized by hydrosilylation of these unsaturated reaction components with various H-Si functional siloxanes to yield a first series of silicone surfactants, and different siloxane components were used for varying the length of the siloxane backbone. All obtained products were analyzed by surface tension measurements to characterize the surface properties.

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PO-11

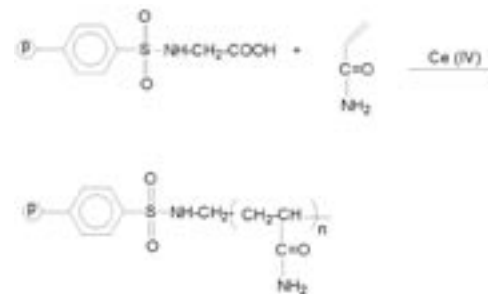
Poly (acrylamide) Grafts on Spherical Polymeric Sulfonamide Based Resin for Selectively Removal of Mercury Ions from Aqueous Solutions

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The use of polymer-bonded ligands in selective mercury removal has been the many research articles.[1,2] Linear polymers grafted onto crosslinked polymer resin particles offer numerous potential applications due to the combination of resin insolubility and the flexibility of the graft polymer. Grafted polymer was prepared in three steps; starting from styrene-DVB (divinyl benzene) (10%) copolymer beads of 420-590 µm particle size: Chlorosulfonation; sulfamidation with glycine ; grafting of acrylamide from the amino acids by cerium ammonium nitrate oxidant.



The resulting polymer resin with 250 % of grafting polyacrylamide has been demonstrated to be an efficient mercury-specific solvent which is able to remove Hg (II) from solutions. In neutral conditions, mercury loading capacity was found 2.9 mmol.gram resin.

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PO-12

Hyperbranched Polystyrenes by carbocationic Self-Grafting

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One of the interesting approaches for the preparation of randomly hyperbranched polymers is grafting of macromolecules onto polymer chains in several steps[1]. This approach is based on preparing polymers having an active group at one end able to react with its own side groups. Two new different strategies developed by us for preparing hyperbranched polymers by this way will be presented:

1) a one-pot procedure with two simultaneous reactions: chain growing of styrene, and grafting by the polystyryl cation onto the pendant phenyl rings at the same time under quasiliving carbocationic polymerization conditions.

2) a two-step reaction in which polystyrene with narrow molecular weight distribution containing 1-chloro-1-phenylethyl terminal group obtained by quasiliving atom transfer radical polymerization (ATRP) was used as self-alkylating polymer under conditions analogue to carbocationic polymerization.

The resulting products were analyzed by a GPC system equipped with continuous RI and viscosity detectors (Viscotek model 200) using THF as eluent. The drastic decrease of the observed alpha parameter in the Mark-Houwink-Sakurada equation of the products compared to that of linear polystyrene indicates that highly branched polymers were formed. These results were also supported by ¹H NMR spectroscopy. These analyses proved that our new synthetic process easily yielded hyperbranched polystyrenes.

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PO-13

New amphiphilic Co-Networks based on Poly(dimethylsiloxane) Macromolecules

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Amphiphilic conetworks (APCN) are crosslinked polymer structures consisting of covalently bonded hydrophilic and hydrophobic polymer chains, and thus they swell in both hydrophilic and hydrophobic solvents. Due to the advantageous properties which are the result of their unique structure, APCNs may be applied in a variety of advanced technologies and fields, and they have been widely investigated worldwide in recent years. APCNs are synthesized by free radical copolymerization of telechelic hydrophobic macromonomers and hydrophilic monomers (or vice versa). Among other polymers, various modified poly-siloxanes, polyisobutylenes, polybutadienes etc. have been used as hydrophobic segments in APCNs until now.

In this presentation, we report on the synthesis of poly(N,N-dimethyl acrylamide)-l-poly(dimethylsiloxane) (PDMAAm-l-PDMS) amphiphilic conetworks, in which the hydrophilic poly(N,N-dimethyl acrylamide) chains are linked by hydrophobic poly-(dimethylsiloxane). Methacrylate-telechelic PDMS (MA-PDMS-MA) with higher molecular weight (Mn=10,000) was purchased, whereas MA-PDMS-MA with lower molecular weight was prepared by quantitative chain end modification of hydroxyl-telechelic PDMS obtained by cationic ring opening polymerization. The synthesis of the conetworks was carried out by free radical copolymerization of N,N-dimethyl acrylamide and methacrylate-telechelic poly(dimethylsiloxane) macromonomer initiated by 2,2'-azobisisobutyronitrile (AIBN) in THF common solvent at 60 °C. After 3 days reaction time, the conetworks were purified, and then analyzed by elemental analysis and DSC. The amphiphilic nature of these new materials has been investigated by swelling in various hydrophilic and hydrophobic solvents.

PO-14

Terminal Modification of Polystyrenes through Carbocationic IntermediatesTamás Fónagy¹, Béla Iván¹, Ulrich Schulze², Jürgen Pionteck²¹ Department of Polymer Chemistry and Material Science, Institute of Material and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, Pusztaszeri u. 59-67, P. O. Box 17, Hungary;² Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

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Quasiliving polymerizations[1] are suitable for the preparation of a wide variety of well-defined polymers. One of the most studied processes in polymer chemistry has been the atom transfer radical polymerization (ATRP) in recent years. This technique is very useful for the synthesis of numerous well-defined polymer architectures. However, lots of advantageous functionalities cannot be prepared by direct synthesis, thus polymer modification by postpolymerization reactions is often desired. Since all the polymers prepared by ATRP contain terminal halogen atom one of the most obvious methods is the nucleophilic substitution for attaching desired endgroups.

During processing and application of polymers with labile halogen atom the elimination of hydrogen halogenides may cause corrosion, thus the removal or replacement of the halogen should be solved. One possibility for 2-halogen-2-phenyl-ethyl-ended polystyrene (PSt-X) was developed by us. This involves the reaction of PSt-X with trimethyl aluminum. The reagent results in the substitution of halogen atom to methyl groups through carbocationic intermediate.

The polystyryl carbocation can also be generated by TiCl₄ and reacted with a variety of other reagents. For example, in the presence of allyltrimethylsilane (ATMS) the allylation of chain ends was expected in dichloromethane solution. Monitored by ¹H NMR spectroscopy the disappearance of methine protons neighboring with chlorine atom and the appearance of signals corresponding to allyl groups (at 4.8 and 5.5 ppm) were observed. The lack of signal at 3.3-3.5 ppm assigned to methine protons with two neighboring phenyl rings indicated the domination of the reaction with ATMS over Friedel-Crafts alkylation. Thus, allyl-terminated polystyrene (PSt-allyl) without detectable side reactions was formed. Since the PSt-allyl can be regarded as a substituted propylene, the copolymerization of this macromonomer with olefins by metallocene catalysis was expected to result in new graft copolymers. Thus a systematic investigation was carried out by us on the influence of synthesis conditions on the structure of poly(propylene-g-styrene) (PP-g-PSt) graft copolymer obtained by the copolymerization of propylene with PSt-allyl[2]. ¹H NMR spectra of the resulting copolymers show that PSt-allyl partly incorporated into the polypropylene backbone. Analytical results showed that the increasing temperature had the most significant effect on PSt content of the resulting graft copolymers, i. e. PSt content significantly increases with increasing polymerization temperature. The resulting PP-g-PSt graft copolymers were tested as blending agents for PP and PSt. These investigations led to some unexpected results on the effect of PSt chain length on the blending efficiency.

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PO-15

Polyisobutylene Star Polymers by quasi-living carbocationic Polymerization initiated from a hyperbranched polymeric Core

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Star polymers are of great interest due to their unique properties such as low viscosity, the capability to encapsulate low molecular weight molecules acting as one molecule micelle or network precursors providing new network structures. Using polyisobutylene as building block in these structures is even more encouraged when a biostable, biocompatible and elastic polymer is needed with high physical and chemical stability. Hyperbranched polycumyl-chlorides (PCC) are a novel type of macroinitiators synthesized from isopropenyl-dicumyl-chloride (IDCE) inimer by self-condensing carbocationic polymerization. Several synthesis strategies were examined including the batch process the slow monomer addition and initiator-based procedures. It was found that these techniques greatly influenced the properties of the PCC hyperbranched polymers. The hyperbranched PCC has many initiating sites which can be converted to PIB arms by the quasiliving carbocationic polymerization of isobutylene in a one-pot reaction. The quasiliving nature of the polymerization is demonstrated, which allows several chain end modification reactions or multiblock copolymer (TPE) synthesis with new possibilities for designed star polymer structures. The resulting polymers have been investigated by GPC, ¹H NMR and DSC. The star polymers have relatively narrow MWD. Polymers with different MW (20x10³-200x10³ g/mol) and arm functionality (10-100) have been synthesized by varying the conditions of the core forming reaction.

PO-16

Poly(ethylene oxide)-Polyisobutylene amphiphilic Co-Networks

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Amphiphilic conetworks are crosslinked polymers consisting of covalently bonded otherwise immiscible hydrophilic and hydrophobic macromolecules. Amphiphilic conetworks (APCNs) containing hydrophilic polyethyleneoxide (PEO) and hydrophobic polyisobutylene (PIB) have been synthesized by chain end coupling of the corresponding hydroxyl-telechelic PEO and three-arm star PIB with a diisocyanate. In another approach, a highly ordered alternating structure was synthesized using the same polymers as building blocks but having different curing conditions. This synthesis strategy resulted in a structurally new generation of APCNs with different topology and characteristics compared to APCNs prepared by previously applied synthetic methods.

The optimal reaction conditions were determined for preparing PEO-PIB APCNs, and it was found that well-defined PEO-PIB conetworks with designed compositions can be obtained by reacting stoichiometric amounts of PEO with different molecular weights (400, 1000, 1450) and three-arm star PIB with $M_n = 1800$, $M_w/M_n = 1.08$ and $F_n = 3.0$. High gel fractions were observed at high overall polymer concentrations with a limiting 30 % since phase separation occurs above this value in common solvents like toluene. Swelling studies of the prepared samples confirmed the amphiphilic nature of these new materials. DSC measurements indicate that the PEO-PIB APCNs have phase separated structure, and crystallization of PEO is either significantly or completely suppressed in these conetworks. When present, PEO melting points appear at lower temperatures than in the starting materials.

PO-17

Carbocationic Modifications of PVC and Poly(vinylchloride-co-2-chloropropene) Copolymer

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Poly(vinyl chloride) (PVC) next to polyolefins is one of the most common and cheapest thermoplastic polymers used in a wide range of applications worldwide. In addition to its advantageous properties, PVC has also some negative characteristics. The most important are: low thermal, thermooxidative and photo stability during processing and use at elevated temperatures [1]. It is widely accepted that chain defects like labile (reactive) allylic and tertiary chlorines play an important role in the initiation of degradation processes. However, reactive sites along the PVC chain are suitable for its modifications. A recent study [2] indicates that allyl groups can be attached to PVC by carbocationic modification of labile chlorines. The concentration of allyl and/or tertiary chlorines is very low (usually less than 0.1 mol%) in commercial PVCs. As a consequence only low amounts of functional groups can be attached this way to the polymer chain.

Poly(vinyl chloride) (PVC) and poly(vinyl chloride-co-2-chloropropene) copolymer (PVC(T)) were synthesized by radical polymerization in solution at Borsodchem Ltd. (Hungary). The PVC(T) copolymer contained approximately 1 mol % tertiary chlorine atoms. Both PVC and PVC (T) were treated with allyltrimethylsilane in the presence of $TiCl_4$ in 1% w/v solution in dichloromethane (DCM) under nitrogen atmosphere at -78 °C. This carbocationic modification reaction replaced the tertiary chlorines by allyl groups quantitatively.

The thermal and thermooxidative stability of the initial polymers and the modified PVCs were also studied. Degradation experiments were carried out in an inert solvent, 1,2,4-trichlorobenzene (TCB) at 200 °C. The changes of molecular weight of PVCs during thermooxidative degradation were followed by gel permeation chromatography (GPC). Thermogravimetric analysis (TGA) was also used to assess thermal stability. HCl evolution was measured by conductivity measurements. It was found that the modified materials possess improved thermal and thermooxidative stabilities indicating efficient carbocationic allylation is.

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PO-18

Carbocationic Polymerization of Isobutylene in Benzotrifluoride, an Environment friendly fluorosolventPéter W. Groh¹, Béla Iván¹, Feike de Jong² and Teun Graafland²¹ Department of Polymer Chemistry and Material Science, Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, Pusztaszeri u. 59-67, P. O. Box 17, Hungary² Shell International Chemicals B.V., Postbus 38000, 1030 BN Amsterdam, The Netherlands

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In recent years, as an outcome of intensive evolution in quasiling polymerizations[1], significant developments have also been occurred in the field of macromolecular syntheses of polymers with well-defined molecular weight and architecture. Polyisobutylene (PIB) is an important chain segment in such polymer structures due to its remarkable chemical and physical properties[2]. PIBs with exact microstructure can only be prepared by quasiling carbocationic polymerization (QLCCP) of isobutylene, which is usually carried out in a solvent mixture containing a nonpolar hydrocarbon and a polar chlorohydrocarbon components. This latter is usually CH₂Cl₂ or CH₂Cl₂/DCM both possessing low boiling point and high vapor pressure. In addition, these compounds can decompose O₃ if their vapor reaches the stratosphere. Benzotrifluoride, (BTF or trifluoromethylbenzene) has been recently reported as an environmentally safe alternative solvent for replacing DCM in certain organic reactions[3]. Based on this observation, we have carried out systematic investigations of carbocationic polymerization (CCP) of isobutylene in BTF.

CCP of isobutylene was carried out by the 2-chloro-2,4,4-trimethylpentane (TMPCl)/TiCl₄ initiating system in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA)[4,5] in differently purified BTFs in the temperature range of -20...0 °C. The resulting polymers were analyzed by GPC and ¹H NMR. The stability of the growing species was monitored by applying long periods of monomerless conditions and subsequent monomer addition. Fast polymerizations were observed. The molecular weights (MW) were close to target MWs in conjunction with unimodal, relatively narrow molecular weight distributions (MWD). These observations indicate that unlike in DCM-hexane mixtures, no chain transfer to monomer occurred in BTF at these elevated temperatures. However, in some cases, proton abstraction occurred on a fraction of the chain ends after the consumption of the monomer yielding terminal double bonds. These double bond terminated chains coupled during long (1-3 hours) monomerless periods, resulting in chain end deactivation. This event limits the livingness of the polymerization in BTF. The different solvent purification techniques played no significant effect on the results of the polymerizations. According to ¹H NMR spectra, there was no sign of alkylation of the aromatic rings of the BTF molecules by the growing carbocations. It can be concluded that CCP of isobutylene can successfully be carried out in BTF, a chlorinated solvent substitute, yielding unimodal and narrow MWD and well-defined molecular weights in the temperature range of -20...0 °C.

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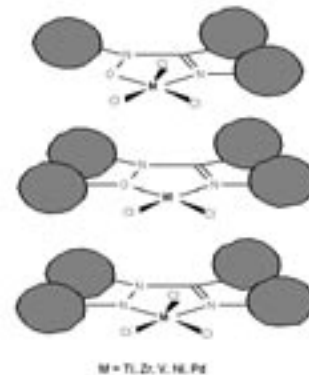
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PO-19

New ethylene polymerization catalysts based on iminohydroxamate early to late transition metal complexesBenno Bildstein,^a Alexander Krajete,^a Holger Kopacka,^a Klaus Wurst,^a Peter Preishuber-Pflügl,^b Marc O. Kristenc^a University of Innsbruck; Institute of General, Inorganic and Theoretical Chemistry, 6020 Innsbruck, Austria.^b BASF AG, 67056 Ludwigshafen, Germany.^c Basell Polyolefins, 67056 Ludwigshafen, Germany.

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The development of new non-metallocene olefin polymerization catalysts is an active research topic in academic and industrial laboratories.[1] Here we report on a "next generation" of non-cyclopentadienyl metal complexes for the insertion polymerization of olefins, based on novel ligand families derived from 5-ring chelating iminohydroxamates containing sterically bulky peripheral substituents. Most notably, neutral [N,O] iminohydroxamate Ni complexes show high activities rivaling those of the best known non-metallocene catalytic systems. Catalyst design strategies and structure-activity-relationships will be presented.

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PO-20

Thermal Switchable Initiators for ROMP

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The design of switchable initiators for metathesis polymerisation is an important goal. Switchable initiators start the polymerisation after a certain event like irradiation with UV-light or heating. One important advantage of such initiator systems is that monomers and the initiator can be stored together and the mixture of both can be manipulated without a concomitant unwanted polymerisation. The commonly used design motives for initiators fulfilling these requirements are depicted in the scheme below.



The first strategy (example a) is to use a ligand M which is inert, but becomes labile upon irradiation or heating. This prerequisite is hard to meet, because even ligands which are known to form strong and inert bonds to ruthenium(II) centres seem to be too labile in this special ligand environment. A way to overcome this problem is to take advantage of the chelate effect (example b and c). Thus ligand M is either attached to the carbene (b) or to via X (X = e.g. oxygen) to the ruthenium in a way that 5- or 6-membered rings are formed.[1] Another possibility is to employ Fischer carbenes (example d) instead of Schrock carbenes as the initiators.[1] Our approach to meet this challenge follows the route b. Different hemilabile ligands had been prepared and the corresponding complexes isolated and tested in model reactions.[2]

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PO-21

Benzophenone based Ynones as Photoinitiators

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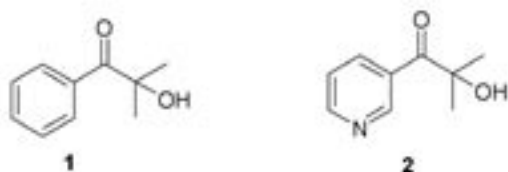
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PO-22

Laser Flash Photolysis of Pyridine Ketones

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Until now most Type I photoinitiators for free radical polymerization are based on the phenyl moiety.[1] We have found that this chromophore is replaceable by electron-poor heterocyclic structures such as pyridines which exhibit similar activity compared to the reference initiator 1.[2] Photo-DSC measurements under nitrogen atmosphere using 3-substituted derivative 2 in laurylacrylate gave results comparable to those with 1.



Surprisingly measurements under air indicated significantly decreased sensitivity towards oxygen quenching reactions. Since there's only less known on the photochemistry of pyridine ketones it was of interest to investigate the new photoinitiators by Laser Flash Photolysis and Steady State Photolysis. By the latter method α -cleavage reaction could be clearly identified by quenching reactions with the stabile radical TEMPO. By Laser Flash Photolysis decreased rates for oxygen quenching reactions have been found for the pyridine carbonyl radical in comparison to the benzoylradical formed from 1.

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PO-23

Synthesis of Chelator - endfunctionalized Polyisobutylenes

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Polyisobutylenes (PIB) are used as supramolecular building blocks due to their easy synthetic approach by living cationic polymerization. This enables the synthesis of controlled polymerarchitectures with low polydispersities and adjustable molecular weights, as well as the introduction of a broad spectrum of functional endgroups. Herein we report the quantitative formation of an chelator-endfunctionalized PIB that carries a multiple donor-acceptor-system. Association constants for complementing ligands, such as substituted cyanuric [1] or barbituric [2] acids, are reported to be as high as 108 thus presenting a valuable system in approaching nano-structural order within polymer blends. Allyl-terminated PIB (1) was prepared by a direct quench of living polyisobutylene with allyltrimethylsilane [3]. Hydroboration of the double bond using 9-BBN and oxidation with m-chloro-peroxy-benzoic acid [4] yielded the hydroxy-terminated moiety which was readily converted to the bromine analogon (2) via the Appel reaction [5]. Subsequent etherification with dimethyl 5-hydroxyisophthalate was carried out in THF/K₂CO₃ using 18-crown-6 as a catalytic agent. Direct amidation of the isophthalic esters with 2,6-diamino-pyridine and butyllithium followed by acylation of the second amino-group using butyryl chloride 1 yielded the multiple donor-acceptor functionalized PIB (3).

The purity of the PIB and the conversion of the endgroups was monitored via ¹H- and ¹³C-spectroscopy, as well as GPC-analysis.



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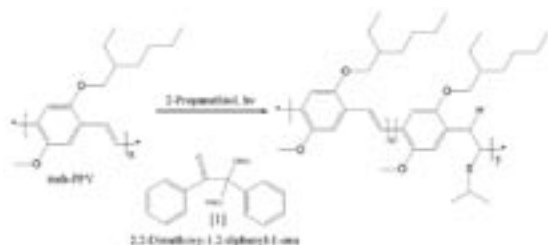
PO-24

Atmospheric Pressure Ion Deposition (APID) as novel technique for the structured surface modification of polymer films

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The surface of thin films of MEH-PPV can be modified in a thiol-atmosphere by irradiation with UV-light as outlined below. The reaction, which destroys the conjugated system of MEH-PPV and consequently the absorption/emission behavior of the polymer, can be accelerated with photoinitiators (e.g. 2,2-Dimethoxy-1,2-diphenyl-1-one 1) that react much faster with UV-light than the thiol. The amount of photoinitiator added into a polymer film can be used to control the degree of modification. Consequently, patterned illumination of thin films of MEH-PPV that contain a photoinitiator can be used for structured surface modification. However, in this case unreacted photoinitiator remains in the not illuminated parts of the polymer film, what usually causes instability of the products.



To overcome this problem APID was used for the structured deposition of photoinitiator 1 on thin films of MEH-PPV, what subsequently allowed structured surface modification by illumination with UV light under a thiol-atmosphere. Results will be presented that show that both the degree of modification and the region on the polymer film can be well controlled by experimental parameters of the APID process. The financial support by the Austrian Science Fund (SFB Electroactive Materials, Project P13962) is gratefully acknowledged.

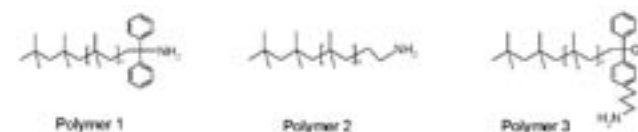
PO-25

Amino functionalized Polyisobutylenes

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Living polymerizations that proceed in the absence of chain transfer and termination are valuable techniques in polymer synthesis providing uniform polymers of defined architecture and functionalization [1]. The living cationic polymerization of polyisobutylene (PIB), initially developed by Kennedy et al. [2], allows efficient control of chain length and endgroup functionalization by a quasiliving polymerization mechanism. Our investigations are directed to develop simple routes to amino-functionalized PIB due to its wide chemical reactivity in nucleophilic coupling reactions, allowing an easy coupling reaction of PIB yielding block-copolymers. We have developed three different protocols for the synthesis of PIB functionalized with primary amino-groups. A quantitative one-pot synthesis of amino-telechelic PIB was achieved by quenching diphenylethylene (DPE) capped PIB with liquid ammonia yielding polymer 1 [3,4]. The resulting amino-functional PIB however is sterically hindered due to the presence of two aromatic rings limiting its reactivity towards future coupling reactions. Therefore another approach via a post-polymerization process was studied. Hydroboration of an allyl-terminated PIB followed by alkaline hydrogen peroxide oxidation yielded a PIB-CH₂OH, functionalized with a primary alcohol [5], from which PIB-CH₂Br were obtained by the Appel-reaction [6]. Starting from PIB-CH₂Br a new nucleophilic displacement reaction using trimethylsilyl azide (TMSN₃) and tetrabutylammoniumfluorid (TBAF) furnished the corresponding azido-telechelic polyisobutylene, which was finally reduced into the primary amine in high yields (polymer 2). Another aminofunctional PIB (polymer 3) was obtained by a direct quenching reaction with a bromoterminated 1,1-diphenylethylene (DPE) derivative [7] via the alkylbromo terminated PIB.

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PO-26

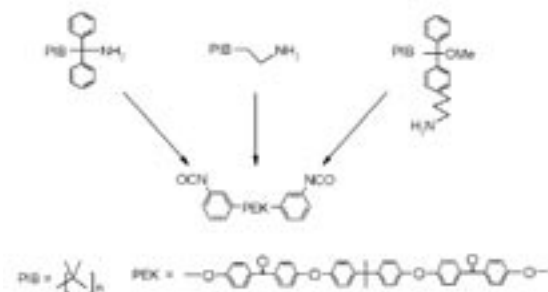
Synthesis of Polyetherketone-Polyisobutylene block Copolymers

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Block copolymers are an important class of materials due to the possibilities to combine polymers with largely differing properties. Since the block segments are covalently bonded, microphase separation occurs leading to various phase morphologies and interesting physical properties such as thermoplastic elastomeric behavior. Thus polyisobutylene (PIB) that combine its excellent elastomeric properties with the outstanding thermal, oxidative and hydrolytic stability of high performance polymers would be an extremely useful building block for high performance thermoplastic elastomers.

We have combined polyetherketone (PEK)-polymers with PIB yielding new types of block copolymers. The end-functionalization of PIB or PEK-polymers with suitable nucleophiles namely olefin-, bromide-, hydroxyl- and amino-moieties is described [1,2,3]. PEK telechelic polymers were prepared by the endcapping of preformed arylfluoride telechelic PEK with a protected triarylimin-group followed by acidic deprotection [4]. The following amino-functional PEK macromer yielded in isocyanat functional PEK by treating the polymer with diphosgen. The combination of the telechelic PEK- and PIB-blocks was then achieved by condensation of isocyanate-telechelic polyetherketones (PEK) with amino-telechelic PIB. Product formation was proven by ¹H-, ¹³C- NMR as well as via GPC-measurements and demonstrates for the first time the combination of PIB with PEK in one block copolymer.



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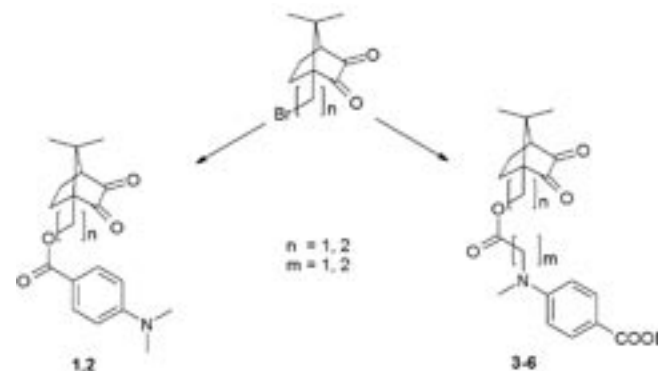
PO-27

Synthesis and Photoactivity of new Camphorquinone Derivatives

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Visible light photoinitiators (PI) based on the camphorquinone-amine systems are state of the art for radical polymerization of dimethacrylates in dental filling materials.[1] These Type II PIs belong to bimolecular systems and are therefore limited in their reactivity due to diffusion controlled processes.[2] The aim of this project was to increase the reactivity of the camphorquinone/amine system by covalently bonded aromatic amines using intramolecular activation.[3] Therefore two precursors, 10-bromocamphorquinone and 10-bromomethylcamphorquinone, were prepared which allow selective modification of these initiators. By using cesium carbonate coupling reactions under mild conditions various new covalently bonded initiators (1-6) were prepared.



UV-absorption spectroscopy revealed similar behavior compared to the physical mixture. The activity of these systems has been measured by differential scanning photocalorimetry (Photo-DSC) using lauryl acrylate as model monomer. By variation of the PI concentration, increased activity and therefore the effect of intramolecular activation has especially been found at low initiator concentrations. Additionally, the effect of the close vicinity of the amine to the diketone in the different new PIs will be discussed.

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PO-28

Pseudostationary Polymerization: Improving the determination of the rate constant of propagation

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Polymerization started by pulsed-laser initiation (PLP) with subsequent analysis of the chain length distribution (CLD) by size exclusion chromatography (SEC) of the polymer formed directly yields the propagation constant k_p from the position of the "extra-peaks" appearing in the CLD which arise because of the correlation between the initiation of radical chains (within the narrow time interval of the laser flash) and their termination (by the increased concentration of radicals produced in subsequent flashes). Introduced 16 years ago[1] it is meanwhile a IUPAC recommended standard procedure. Theoretical distribution curves which neglect the fluctuation of propagation (assuming a strict proportionality between chain length l and growth time t of a radical chain) exhibit discontinuities in form of edges at the position of $L_0^{(n)} = n \cdot k_p [M] t_0$, $n = 1, 2, \dots, ([M]$ being the monomer concentration and t_0 the time interval between two successive laser pulses). Considering this fluctuation Poisson broadening replaces these edges by peaks (consisting of a superposition of Poisson peaks) whose points of inflection (PI) on the low molecular weight side of the peaks are located near to $L_0^{(n)}$. More precisely, they are shifted to values slightly below $L_0^{(n)}$ the extent of the shift depending on the experimental conditions chosen. Further broadening (accompanied by a further shift) arises due to the axial dispersion during SEC analysis. Based on simulated distribution curves[2] with a reasonable extent of axial dispersion it appears that the error introduced by using the positions of the points of inflection as approximations for $L_0^{(n)}$ results in an error of approximately 10–20% in evaluated values of k_p which is rather small compared with methods for k_p determination by combining stationary and instationary data. Nevertheless, the method may be substantially improved (at least in principle) if a quantitative relation between experimental conditions and the shift of the position of the PIs would be available. A detailed analysis of the extra peaks making use of an experimental peak width δ (defined as the ratio of the PIs at the high and low molecular weight side[3]) in comparison with a theoretically defined δ value based on the properties of a Poisson peak in addition considering axial dispersion yielded several types of master functions for a correction reducing the expected relative error by more than a factor 10!

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PO-29

Physical relationships between the surface topography and the optical properties of transparent polymer filmsG. Wallner^{1*}, K. Resch², R.W. Lang^{1,2}, C. Teichert³^{1) Institute of Materials Science and Testing of Plastics, University of Leoben, Franz-Josef-Straße 18, A-8700 Leoben}^{2) Polymer Competence Center Leoben GmbH, Parkstraße 11, A-8700 Leoben}^{3) Institute of Physics, University of Leoben, Franz-Josef-Straße 18, A-8700 Leoben}*E-mail: wallner@unileoben.ac.at*

Both, amorphous and semi-crystalline films from different polymer types and thicknesses ranging from 12 to 150 μm were characterized as to their relevant solar optical properties [1, 4]. In the solar wavelength range (300 to 2500 nm) the direct and diffuse transmittance and reflectance were measured at normal or near normal incidence with a Perkin-Elmer integrating sphere spectrophotometer. Treating the polymer films as being opaque, the spectral data were averaged using a weighting factor equal to the solar spectrum for air mass 1.5. Under the assumption of isotropic scattering the effective extinction coefficients were modeled by the four-flux radiative transfer model of Maheu [2]. In this manner appropriate optical data were generated for a large number of technically relevant films. The photometric characterisation in the solar range and the calculation of non-spectral, solar-optical film properties using models for scattering-absorbing media have shown, that the solar extinction is dominated by scattering. In particular it is the supramolecular structure of the polymer films which is of great importance in the solar range. While the amorphous polymer films exhibit isotropic scattering occurring mainly at the surface, for many of the semi-crystalline polymers forward scattering was found. For 50 μm thick semi-crystalline films the volume fraction of scattering was about 0,5. Apart from the semi-crystalline fluoropolymer and polyethyleneterephthalate films, which compare well with amorphous polymer films, the semi-crystalline polymer films in general reveal a higher degree of scattering. Investigations using atomic force microscopy in an appropriate bandpass were performed to study the influence of geometrical surface characteristics on the solar scattering coefficient of transparent polymer films [3, 4]. A good correlation between root mean square roughness (rms-roughness) of the film surface and the dimensionless solar scattering coefficient was found.

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PO-30

Design and Synthesis of Donor/Acceptor-substituted PPV Copolymers via the Polycondensation Route. New Materials for Solid-State Lasers and Photovoltaics.H.-H. Hörhold^a, H. Tillmann^a, C. Badera, W. Holzer^b, A. Penzkofer^b, S.A. Carter^c,A.J. Breeze^d^a Institut für Organische Chemie und Makromolekulare Chemie, Univ. Jena, Germany^b Institut II – Experimentelle und Angewandte Physik, Univ. Regensburg, Germany^c Physics Department, Univ. of California, Santa Cruz, USA^d National Renewable Energy Laboratory, Golden, Colorado, USA

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The synthesis of PPV copolymers via the polycondensation route is reviewed. Applying the PO-activated carbonyl olefination (Horner-reaction) we have synthesized dialkoxy-phenylene vinylene based photonic materials, including the polycondensation-type MEH-PPV (strictly linear and fully conjugated) and a series of alternating copolymer and terpolymer combinations with 2,5-dialkoxy-phenylenevinylene (M3EH-PPV, DMO-DO18-PPV), arylamine-vinylene (TPA-MEH-PPV, TPD-MEH-PPV, TPD-MEH-M3EH-PPV) and thianthrene-vinylene (Thianthrene-DOO-PPV, Thian-threne-MEH-M3EH-PPV) subunits [1]. Patents claiming the general formula, EL application and synthesis of alternating copolymers and ordered terpolymers are being held [2]. Acceptor-substituted PPV copolymers (CN-Ether-PPV) have been synthesized through repetitive Knoevenagel-reaction [3].

Here travelling-wave lasing (TWL) is demonstrated. Upon pumping thin films with laser pulses (Exc. 347 nm, 35 ps) low threshold lasing occurs (laser threshold < 10 μJ/cm², laser linewidth ~ 10 nm) with reasonable high laser output [4]. The polymers also work well as DFB-lasers exhibiting very small laser linewidths (< 0.3 nm) [5].



Further, we demonstrate that these PPV-derived condensation polymers are good materials for photovoltaic cells. The materials that make the best solar cells are M3EH-PPV, M3EH-PPV:CN-Ether-PPV blends, and perylene benzimidazole (PBI) / M3EH-PPV bilayers [6]. QE values and photovoltaic action spectra have been studied. The devices reach peak quantum efficiencies of 8, 23, and 18 %, respectively. The M3EH-PPV:CN-Ether-PPV blend devices have achieved short circuit current densities of J_{SC} = 3.3 mA/cm² and open circuit voltages of V_{OC} = -0.65 V, leading to overall power efficiency of 0.6 - 0.8 % with ITO/TiO₂/Au as electrodes. Thin-film PBI / M3EH-PPV bilayer cells (ITO/bilayer/Au) exhibit power conversion efficiencies of 0.71 % under 80 mW/cm² white light illumination (J_{SC} = 1.96 mA/cm², V_{OC} = -0.63 V and fill factor ff = 46 %).

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PO-31

Existence of Dislocations in melt-crystallised and plastically deformed PolypropyleneH. Wilhelm^{1*}, A. Paris¹, E. Schafler¹, S. Bernstorff², J. Bonarski³, T. Ungar⁴,
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The aim of this work was the proof of dislocations in melt-crystallised polypropylene and the investigation of the development of the density of dislocations during plastic deformation. In contrast to metals by polymers the knowledge of fundamental mechanisms during plastic deformation are not very advanced. One reason is that classic methods like electron microscopy by polymers not suitable for all samples. It's possible to prove the existence of dislocations in solution grown single crystals, but for melt-crystallised spherulites is no preparation method available to detect dislocations. For this purpose a new multiple X-ray profile analysis (MXPA) [1,2] has been applied for the first time to deformed samples of isotactic polypropylene. The proof of the presence of dislocations has been done by evaluation of the width of the profiles (FWHM analysis) in the modified Williamson-Hall-plot. Therefore must with the application of a contrast factor C the peak width ΔK linear increase with CK^2 . The dislocation density and other micro structural parameters were determined by the Multiple Whole Profile Analysis (MWP). Samples of isotactic polypropylene with high degree of crystallinity and pure α -phase have been investigated. One series was deformed by rolling, and one by uniaxial compression. Deformations of true strains up to 50 % have been achieved. The measurements were carried out at the SAXS beamline of Synchrotron ELETTRA in Trieste.

The analysis of the profiles required a particular algorithm, because many parameters had to be fitted simultaneously. Reliable evaluations were possible only by means of automatic determination of the starting values in a pre-fit. It has been shown that dislocations are present in polymers and that their density increases with plastic deformation. Dislocation densities from 2×10^{16} to $5 \times 10^{17} \text{ m}^{-2}$ have been determined. These values are much higher than those usually found in metals. They are consistent with the assumption that the mean free path of dislocations just equals the lamella thickness. However, there may exist uncorrelated lattice defects (e. g. in the interface between crystalline and amorphous phase) which also induce peak broadening and therefore might lead to an overestimation of the dislocations density.

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PO-32

Synthesis of Star-shaped Polystyrene with Glucose in the Chain-End

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Three-dimensional polymeric architectures with functional groups have potential to offer an attractive material, which possesses active sites inside or outside the compact structures. We report here the synthesis of functionalized star-shaped polystyrenes with glucose via 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated radical polymerization. In the first step, we prepared two types of arm-polymers. Styrene (St) was polymerized with 4-[1'-(2'',2'',6'',6'')-tetramethyl-1''-piperidinyloxy]-ethylphenyl 2,3,4,6-tetra-O-acetyl- β -D-glucopyranoside (**1**) at 120 °C to afford a functionalized arm-polymer, i.e., an end-functionalized polystyrene with acetylated glucose (**2**). Similarly, St was polymerized with 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane (**3**) to obtain an unfunctionalized arm-polymer, i.e., polystyrene (**4**). In the second step, the reactions of the arm-polymers with divinylbenzene (DVB) were performed in *m*-xylene at 138 °C, followed by purification using preparative SEC to provide several types of star-shaped polystyrenes with acetylated glucose. For example, the reaction of **2** with DVB afforded a star-shaped polystyrene with acetylated glucose in the chain-end (**5**). In addition, the reaction of **4** with DVB in the presence of **1** afforded a star-shaped polystyrene with acetylated glucose in the core (**6**). A dynamic laser light scattering (DLS) measurement in toluene indicated that **5** and **6** existed as the particles with the diameters of 17.4 and 25.6 nm, respectively. The weight-average molecular weights determined by a static laser light scattering (SLS) measurement gave the arm-numbers of **5** and **6** with 13 and 21, respectively. The number of the glucose units in the core of **6** was found to be 37, which was determined from specific rotation ($[\alpha]_{D}^{25}$). Finally, **5** and **6** were modified by deacetylation using sodium methoxide to produce star-shaped polystyrenes with glucose in the chain-end and the core (**7** and **8**, respectively). We present here amphiphilic properties of the final architectures.

PO-33

Synthesis and Characterization of Novel POPAM-PAMAM (POMAM) Hybrid Dendrimers as Reactive Modules for Biologic Nanodevice Construction

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Dendritic polymers are recognized as the fourth and most recent new major macromolecular architecture. Dendrimers are a subclass of nanoscale, core-shell type dendritic polymers. They may be precisely and systematically controlled as a function of (a) size – number of shells (generations) surrounding the core, (b) shape (determined by core) and (c) surface chemistry (functional groups on the last shell). Presently, over 50 different interior compositions and over 200 different surface modifications of these polymers have been reported. As such, they are versatile nanoscale building blocks although somewhat less well known than the fullerenes and nanotubes.

In this presentation, we wish to report the synthesis and characterization of a new class of dendrimers based on the synthetic hybridization of an interior composition derived from a commercially available dendrimer poly(propyleneimine) (PPI or POPAM) dendrimers (DSM) with the subsequent addition of poly(amidoamine) (PAMAM) dendrimer structure. The synthesis was accomplished by a divergent reiterating method involving a Michel addition and amidation reactions. These molecules have been extensively characterized using NMR, HPLC, AFM, GPC and potentiometric titration. The resulting "dendrimer copolymers" have been demonstrated to consist of POPAM cores surrounded by PAMAM shells. These structures are controlled nanoscale modules manifesting new properties distinct from either POPAM or PAMAM dendrimers.

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PO-34

Application of a new class of ruthenium catalysts for metathesis reactions

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The development of new homogeneous ruthenium metathesis catalysts and their application to various types of metathesis reactions such as RCM (ring closing metathesis) and metathesis based polymerization reactions are described. (SIMES)Cl₂Ru=CH-o-O/PrC₆H₄[1], SIMES=1,3-bis-Mes-4,5-dihydroimidazol-2-ylidene, was used as precursor complex. We will show that our new catalysts rival or exceed their precursors in reactivity and that they catalyze reactions that have so far only known to be catalyzed by Schrock-type initiators [2,3] Furthermore, we will show a simple access to a heterogenized analogous compound. Polystyrene as well as ROMP based monolithic supports were used as heterogeneous supports. RCM of several monomers was used to benchmark the systems. A Poly(2-oxazoline) was used as amphiphilic support and polymerizations were performed in aqueous media. The synthesis of the new catalysts, their heterogenization as well as selected examples for RCM and polymer reactions will be presented.

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PO-35

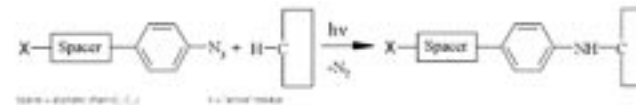
Photochemical immobilization of functional azides onto polypropylene surface

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Due to the extremely high reactivity of nitrenes, photomodification of surfaces using aryl azide represents a very general surface modification method which is applicable to a wide range of surfaces such as for example polystyrene, poly(etherurethane), polyacrylonitrile, glass, cellulose, poly(vinyl alcohol), polyimide and polyethylene. The suitability of aryl azides for surface modification of polypropylene has already been proven in previous work of our group. Enhanced wettability^[1] and light stability^[2] were achieved by covalent bonding of carbohydrate residues and hindered amine light stabilizers respectively. The aim of the present work was to study the effect of "tailoring" the azides by introduction of a hydrophobic spacer, which should increase the affinity to the top layer of the PP surface and the solubility in the surface-near layers of the bulk, and to investigate the influence of process parameters such as azide concentration, immersion time and irradiation intensity.



In addition, first results of synthesis and photografting of a functional azide containing a long-chain aliphatic spacer and metal-bonding "active" residue will be presented.

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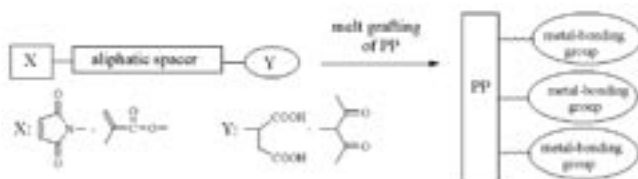
PO-36

Synthesis and Melt Free-Radical Grafting of Novel Monomers Containing Chelating Moieties

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Several monomers containing functional groups capable of chemisorption of palladium, which is a determinant step in electroless metallization of polymers [1,2], were prepared. A long-chain aliphatic spacer was introduced to increase the solubility of the monomers in the polymer melt and to enhance the compatibility of grafted side chains and homopolymers with PP. PP was functionalized by reactive extrusion [3-5] and injection molding, respectively, and some properties of the modified polymer were investigated.

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PO-37

Estimation of Slow Crack Growth Behavior in PE by means of Modified Stepwise Isothermal Segregation TechniqueM. Haager¹*, G. Pinter^{1,2}, R.W. Lang^{1,2}¹ *Polymer Competence Center Leoben, Parkstraße 11, 8700 Leoben,*² *Department of Materials Science and Testing of Plastics, University of Leoben, Franz-Josef-Straße 18, 8700 Leoben*
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Polyethylene (PE) has been used successfully in pipe applications for almost 40 years. Typically a service life of 50 years is required and lately even 100 years are proposed. To ensure this, time consuming internal pressure tests are carried out on pipe samples. To evaluate the performance of new materials, it is necessary to develop new test methods and strong efforts were made in finding new and shorter tests based on slow crack growth (SCG). Furthermore scientist are trying to gain understanding of those parameters that control the fracture behavior of PE. Today it is generally believed that the lifetime is influenced by a large number of structural and morphological parameters. The primary of these are molecular mass and its distribution, number, type and distribution of short chain branches, degree of crystallinity and lamella thickness. With this knowledge it should be possible to estimate the performance of new pipe materials by analyzing their structure [1].

10 years ago Adison et al. [2] came forward with a new method to characterize the structure of PE by Stepwise Isothermal Segregation (SIS) using differential scanning calorimetry. The technique consists of a sequenced multiple-stage stepwise thermal treatment of the sample allowing separation of the macromolecules with respect to their length-to-branching content and distribution. It is assumed that such a separation process gives an image of specific crystallizable species which are responsible for slow crack growth resistance of PE. Later a modified SIS was suggested to refine the method, and a drift molecular parameter was calculated from the crystallization data at 114 °C and 119 °C to assess the SCG behavior of PE [3, 4].

In the current research project several commercially used PE pipe resins were evaluated with modified SIS technique. It was possible to rank the materials according to their SCG resistance. Additionally structural changes, that influence the lifetime of PE pipes, could be detected.

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PO-38

Influence of Talc and SEBS on PP/talc/SEBS Composites under the Gamma Irradiation Sterilization Conditions

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Among thermoplastics the polypropylene is outstanding with respect to its attractive combination of low cost, low weight, heat distortion temperature above 100°C, and extraordinary versatility in terms of properties and applications. With the appropriate modification it is possible to improve the existing properties of the PP, or even obtain the new ones. As a result of its originally superior properties, the PP is commonly used in medical purposes, where it has to undergo the process of sterilization beforehand. The sterilization of the PP in medicine is most often being carried out with low dose of gamma irradiation, which can influence the changes of properties of both the polymeric matrix and modifiers. Therefore the purpose of our research work was to determine the structure-mechanical properties relationships of unirradiated and gamma irradiated PP composites with talc filler and poly(styrene- β -ethylene-co-butylene- β -styrene) block copolymer (SEBS) or SEBS grafted with maleic anhydride (SEBS- γ -MA) as elastomeric modifiers, as well as of corresponding binary composites and blends. Unirradiated and gamma irradiated composites and blends were characterized by wide-angle X-ray diffraction, optical microscopy, scanning electron microscopy, FTIR spectroscopy, tensile measurements and measurements of notched impact strength. The effects of composition and gamma irradiation on the properties of the PP composites and blends are discussed with emphasis on the study of the stabilizing effect of talc in irradiated PP composites.

PO-39

Effect of chemical Modification on cure, mechanical and swelling Characteristics of Sisal / Oil Palm Hybrid Fiber Reinforced Natural Rubber Composites.

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The effects of chemical modification of fiber surface in sisal/oil palm hybrid fiber reinforced natural rubber composites have been studied. Composites were prepared using fibers treated with varying concentrations of sodium hydroxide solution and different silane coupling agents. The vulcanisation parameters, processability characteristics, tensile properties and swelling characteristics of these composites were analysed. The rubber / fiber interface was improved by the addition of a resorcinol-hexamethylene tetramine bonding system. The reinforcing property of the chemically treated fiber was compared with that of untreated fiber. The extent of fiber alignment and strength of fiber-rubber interface adhesion were analysed from the swelling measurements. The fracture mechanism of treated and untreated fiber reinforced rubber composites was analysed from SEM studies.

PO-40

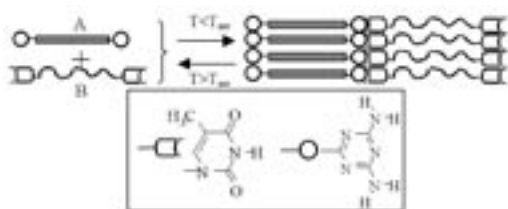
Studies on Supramolecular functionalized Polyetherketones and Polyisobutylenes

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Supramolecular polymers are a new generation of materials, where directed non covalent forces determine the material properties to a high extend.[1] Hydrogen bonds, dipol-dipol interactions, π - π stacking and charge-charge interactions can be used to generate chains with tuneable molecular weights as well as dendritic architecture and weakly crosslinked networks in solution. Therefrom new materials with tuneable properties such as modulative mechanical and rheological properties as well as tuneable and switchable nanostructures can be designed.[2]

We report the formation of supramolecular polymers derived from an α,ω -thymine-functionalized telechelic polyisobutylenes (PIB-thymine) and the complementing α,ω -2,4-diamino-1,3,5-triazine-functionalized telechelic polyetherketones (PEK-triazine) [3]. Both structures interact by complementing hydrogen bonding units present at their respective chain ends reminiscent of the triple hydrogen bonding in DNA. The structure of the PEK-triazines and the PIB-thymines are proven by ¹³C-NMR-spectroscopy, GPC and MALDI-spectroscopy. When the triazine PEKs are mixed as a 1:1 complex in solution with PIB-thymine, the short triazine-PEK's show a temperature dependent association behavior visible by dynamic NMR-spectroscopy. A strong shift of the central NH-bond of the PIB-thymine from 8.8 ppm (solution in CDCl₃) towards 12.4 ppm in the 1:1 complex can be seen. Additional proof of the formation of a supramolecular, hydrogen bonded network is derived from temperature resolved liquid NMR-spectroscopy, solid state NMR-spectroscopy as well thermal- and rheological investigations.[4]



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PO-41

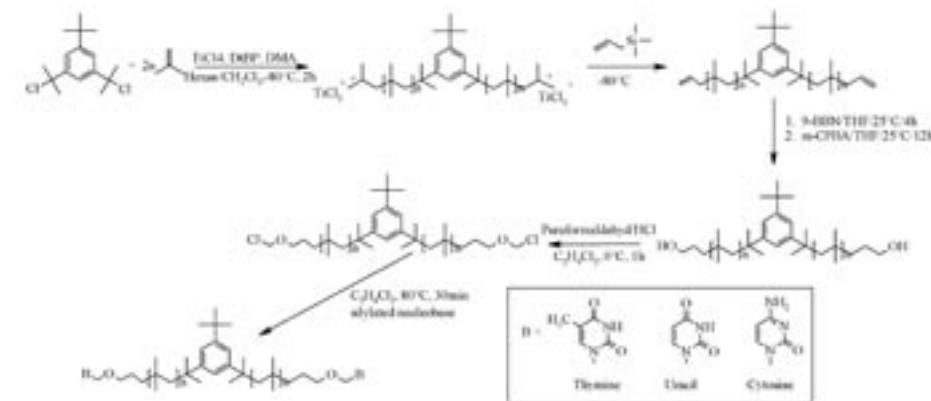
Syntheses of Nucleobase-telechelic Polyisobutylenes

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Polyisobutylenes (PIB) are widely applicable polymers which can be easily prepared by a quasilinging cationic polymerization-reaction. This technique allows an efficient control of the chain length and a narrow molecular weight distribution due to the absence of chain transfer reactions.[1] The termination of PIB with nucleobases such as thymine, uracile or cytosine opens the opportunities for the formation of multi-hydrogen bonds with complementing functionalities such as 2,4-diamino-1,3,5-triazines or adenine.

We have developed a protocol for the quantitative preparation of nucleobase terminated PIB. As a first step allyl-terminated PIB is prepared by a direct quench of the living polyisobutylene with allyltrimethylsilane.[2] This allyl-terminated PIB can then be converted to hydroxyl-terminated PIB by addition of 9-BBN and oxidation with hydrogen peroxide [3] or 3-chloroperoxybenzoic acid. In order to achieve a quantitative termination of PIB with nucleobases, highly reactive electrophiles within the coupling step are needed. We use chloromethylethers, which can be obtained from the corresponding hydroxy-moiety by conversion with paraformaldehyd and HCl. This chloromethylether-terminated PIB reacts with silylated nucleobases such as thymine, uracile or cytosine to yield the corresponding PIB in quantitative yield. Thus a variety of hydrogen donor-acceptor-donor PIB's can be prepared in which the endgroup can be characterized by high resolution ¹H- and ¹³C- NMR spectroscopy.



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PO-42

Transition metal complexes with new N-heterocyclic carbene ligands that give access to polymer bound catalystsMonika Mayr¹, Klaus Wurst², Michael R. Buchmeiser^{1*}¹ Institut für Analytische Chemie und Radiochemie, Universität Innsbruck, Austria² Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Austria

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During the last years, transition-metal complexes bearing N-heterocyclic carbene (NHC) ligands have been extensively studied due to their excellent features in homogeneous catalysis. [1] The most common NHCs used are imidazolin-2-ylidene derivatives. [2] They both activate and stabilize the catalytically active metal center. In our work we focused on the synthesis of heterogeneous catalysts where the catalyst is heterogenized via the NHC ligand [3]. In course of our investigations, we prepared a different class of nucleophilic carbenes where the NHC is part of a six membered ring. The synthesis of the corresponding precursors, 3,4,5,6-tetrahydropyrimidinium salts, is shown. For heterogenization, we synthesized NHC-precursors with pendant OH groups respectively polymerizable functional groups linked via an ester function. We will present the synthesis of various metal complexes (e. g. Rh, Ir, Pd, Ru) based on these new ligands, outline the possibilities for heterogenization and give some illustrative examples for catalysis.

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PO-43

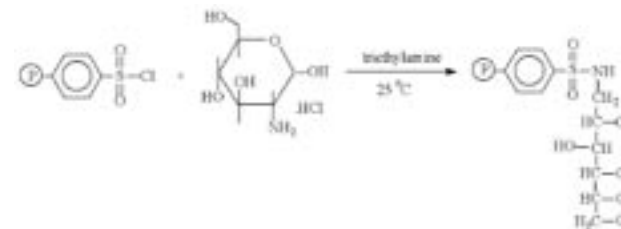
Modification of Crosslinked Polystyrene based Polymers for Boron-specific Extraction

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Extraction of trace boric acid and borates using crosslinked polymer resins [1] is of special importance due to the plant-stunting effect of boron when present in irrigation water even in trace quantities as low as 4 ppm. The effect is extremely drastic in the regions of boron-mining in west Anatolia [2]. In this study a boron specific resin with glucose amide has been prepared starting from Styrene-DVB (10%) copolymer beads with particle size of 420-590 μm (scheme).



Resulting bead polymer has been demonstrated to be efficient in removal of trace quantities of boron from aqueous boric acid or borate solutions. Boron sorptions were assigned by analysis of residual boron contents of treated solutions. The results indicate that boron uptake capacity of bead polymer is around 0.5 m.mol.g⁻¹. Recycling of the polymer resin can be achieved by acid-base treatments.

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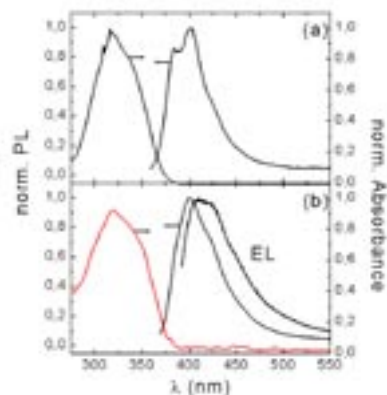
PO-44

Synthesis of a new polymer containing blue light emitting oligomers
via ROMP

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A new well-defined conjugated oligomer based on the fluorene-carbazol-fluorene triad was synthesized in good yield by palladium-catalyzed Suzuki cross coupling reaction [1]. This chromophore was attached to a norbornene and the obtained monomer polymerized by Ring Opening Metathesis Polymerisation (ROMP) with the 3rd generation Grubbs catalyst ($H_2IMes)(3\text{-bromo-pyridine})_2(Cl)_2Ru=CHPh$ ($H_2IMes = N,N\text{-bis(mesityl) 4,5-dihydroimidazol-2-ylidene}$). [2] The novel polymer was characterized by means of NMR, IR, WAXS and GPC. Furthermore, the thermal, electrochemical, and optical properties of the amorphous polymer were examined. The polymer emitted strong deep blue luminance around 400 nm with vibronic replicas spaced by ca. 0.16 eV in thin film or in solution. The onset of luminescence in simple layer device structures was approximately 7 V. These optical, thermal und electrical properties promise a great potential of these material for light emitting devices.



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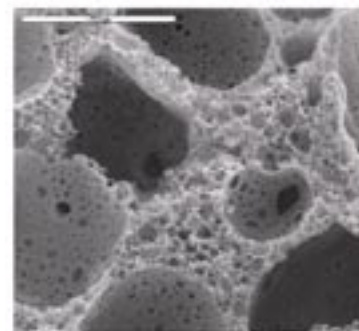
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PO-45

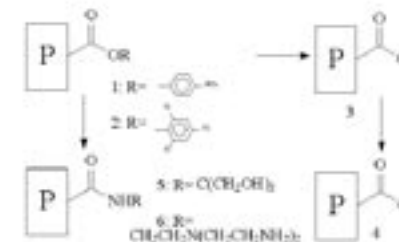
Arylacrylate based monolithic porous polymer supports by emulsion
polymerisationPeter Krajnc^{*a}, Nermina Dreca^a, Jane F. Brown^b, Neil R. Cameron^ba) Univerza v Mariboru, Fakulteta za kemijo in kemijsko tehnologijo, Smetanova 17, 2000 Maribor, Slovenija
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Arylacrylates have already been used as reactive monomers in the synthesis of polymer beads by suspension polymerisation.[1] For some applications, especially in a flow through reaction systems, monolithic polymer supports have proven to outperform beads-filled columns, mostly due to better efficiency and a lower back pressure.[2] Some acrylate monolithic supports have been commercialised and utilised among other for peptide synthesis and screening for peptide affinity ligands.[3] We have used 4-nitrophenylacrylate and 2,4,6-trichlorophenylacrylate together with styrene and divinylbenzene incorporated in emulsions with various ratios of water to oil volume, up to high internal phase emulsions [4] to produce reactive porous monolithic supports with open cellular structure (see Figure). Materials were studied by scanning electron microscopy, FTIR spectroscopy, mercury porosimetry and N_2 adsorption/desorption methods. We also tested novel materials for reactivity towards nucleophilic substitutions (see Scheme) and successfully obtained high loading tris(2-aminoethyl)amino derivative type scavenger and tris(hydroxymethyl)aminomethane derivative type linker.

Figure:
SEM of 4-nitrophenylacrylate PolyHIPE (90% PV)



Scheme



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PO-46

Modification of recycled polymer blends with activated natural zeolite

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The growing interest in natural zeolite is based on some specific peculiarities of its structure, which after dehydration enables adsorption processes of polymer molecules and/or segments on the zeolite surface to take place. The main goal of the study is to investigate the effect of dehydrated zeolite on the flow behaviour, mechanical properties and morphology of immiscible blends from unsorted polymer wastes. A tetra-component blend consisting of 40 wt.% polypropylene (PP), 40 wt.% high-density polyethylene (HDPE), 15 wt.% low-density polyethylene (LDPE) and 5 wt.% polystyrene (PS), was studied as a model system of commingled plastic wastes. Zeolite, clinoptilolite - (K₂,Na₂,Ca)Al₆Si₃₀O₇₂·x23H₂O, micro milled (particle size < 40 μm) and dehydrated at 350°C for 3 hours, was used. Compositions from recycled blend and dehydrated zeolite in a wide concentration range (from 0 to 20 wt. %) were prepared using a twin-screw extruder Brabender DSE 35/17D in the temperature range from 140 to 190°C. The compositions were characterized by capillary rheometry, Charpy impact strength test, differential scanning calorimetry (DSC) and site-resolved wide-angle X-ray scattering (WAXS). The results show a compatibilizing effect of dehydrated zeolite at low concentration levels (1-2 wt.%), expressed by improvement of flowability and impact strength. Zeolite changes the parameters of non-isothermal phase transitions and exhibits different influence on PP and PE due to their different nucleation ability. WAXS measurements on cross-sections of injection-molded specimens provide information about the distribution of crystallite modifications, orientation of PP and PE crystallites and zeolite particles, crystallite dimensions and crystallinity. The results of this study can open wide possibilities for utilization of dehydrated zeolite in recycling of unsorted polymer wastes.

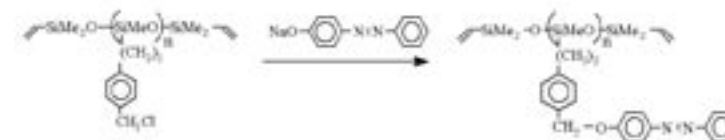
PO-47

Azo-group containing polysiloxanes with conformational photo-control

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Taking into account the different domains of application (optical information storage, holographic technology, liquid crystals etc.) in the last period the polymers containing azo-groups were carefully studied [1-4]. This paper presents synthesis and characterization of polysiloxanes containing different pendant substituents possessing azo-group. The synthesis involves the reaction of polysiloxanes containing pendant chlorobenzyl groups with different azo-phenol, an example being presented in following scheme:



The following azo-phenols were used: 4-(2,4-dinitro-phenylazo)-phenol, 2-(4-hydroxy-phenylazo)-antraquinone, 4-(9-ethyl-9H-carbazol-3-ylazo)-phenol and 4-phenylazo-phenol. The reactions were performed in DMSO, in the presence of tetrabutylammonium hydrogensulphate as catalyst (85 °C, 5 hours). The polymers were characterized by ¹H-NMR, thermo-optical microscopy in polarized light and thermogravimetry. For evidencing the conformational modification of the polymer chain, due to the trans/cis isomerization of the pendant azo-groups during the UV irradiation, viscosimetric studies were effectuated. The polymers' substitution degree is a function of the azophenol type and it is situated between 95 % (4-phenylazo-phenol) and 50 % [4-(9-ethyl-9H-carbazol-3-ylazo)-phenol]. If the substitution degree is above 60 % the polymers are solid products.

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PO-48

Poly(siloxane-g-styrene) and poly(siloxane-g-methylmethacrylate) by CuCl or Cu(0) catalyzed ATRP from benzyl chloride derivatized polysiloxanesL. Petraru¹, E. Taran², B. Donose³, K. Higashitani³, A. D. Asandei⁴, G. Sauvet⁵ and N. Hurduc^{2*}

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The recent development of atom-transfer radical polymerization (ATRP) techniques opened up new avenues for the preparation of well-defined polymers with predetermined molecular weights, low polydispersities, functional groups, and various architectures under relatively mild reaction conditions[1-4]. We are presenting herein the CuCl/2,2'-bpy or Cu(0)/2,2'-bpy catalyzed synthesis of poly(siloxane-g-styrene) and poly(siloxane-g-methylmethacrylate) graft copolymers prepared by ATRP from benzyl chloride derivatized polysiloxanes in toluene.



The polymers were characterized by GPC and ¹H-NMR. Atomic Force Microscopy (AFM) was used to investigate the effect of the polymerization on the Cu(0) surface. Previously studies have shown that polysiloxane initiators and CuCl/byp catalysis afford good yields and polydispersities for the corresponding graft or star polymers[5]. With Cu(0)/byp however, we obtained Mw/Mn of about 2.5, probably due to an insufficient amount of persistent radicals. Benzyl chloride were used as a model initiator in the presence of Cu(0). The AFM investigation of the copper surface showed the deposition of a layer after the reaction. This layer is not soluble in toluene, THF or other solvents but can be washed away by water. The chemical structure of this layer is currently under investigation.

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PO-49

Computer simulations of grafted amphiphilic polymer chains

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We designed a simple model of a polymer layer formed by many chains. Each chain was built on a flexible [310] lattice.[1] All chains were terminally attached to an impenetrable surface and the lateral motion of the entire chain was enabled. The force field used consisted of the long-range contact potential between polymer segments with the excluded volume. It was assumed that the chains were built of hydrophilic and hydrophobic segments. The Monte Carlo simulations of this model were carried out using the Metropolis algorithm[2]. The influence of the grafting density, the length of the chain, and the sequence of the chain (homopolymer chain, amphiphilic chain, block copolymers) on the static and dynamic properties of the system were studied and discussed. The size, shape and structure of the polymer film formed near the surface were determined. The low temperature structures formed by the brush were described and compared for all sequences under consideration. The dependence of the lateral diffusion of chains on the grafting density, chain length and the sequence was studied. The scaling dependencies were established for the size and diffusion coefficient.

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PO-50

The Gas transport Studies of Natural Rubber (NR) and Carboxylated Styrene Butadiene Rubber (XSBR) Latex Membranes**Stephen Ranimol** and Thomas Sabu**School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India -686 560
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The gas permeability of polymers is an important factor for various applications including barrier materials and membranes for gas separation. The relevance of permeation studies wide spread in the industrial zones of food packaging, encapsulation of electronic circuits, protective coatings such as paints, and varnishes, biomedical devices etc. The wide application of membranes for gas separation has been attracted many polymer technologists to synthesis new polymeric membranes with good permeability and selectivity. The present paper deals with the gas permeability studies of natural rubber (NR) and carboxylated styrene butadiene rubber (NR/XSBR) latex blend membranes with special reference to blend ratio, pressure and nature of permeants using oxygen and nitrogen gas. Natural rubber (NR) shows the highest permeability than carboxylated styrene butadiene rubber latex films. The experimentally determined values have been theoretically correlated using Maxwell, Bruggeman, and Bottcher models. The oxygen- to- nitrogen selectivity decreases with increase in XSBR content.

PO-51

Untersuchungen über die Wechselwirkungskräfte in glasfaserverstärkten Polymerverbunden**Robert Schinner**, Rosemarie Plonka, Alla Synytska, Anja Caspari, Cornelia Bellmann, Karina Grundke*Institut für Polymerforschung Dresden e.V.*

Das mechanische Verhalten glasfaserverstärkter Verbundmaterialien wird durch die Eigenschaften der Verstärkungsfasern, der polymeren Matrix und der Grenzschicht zwischen Faser und Matrix bestimmt. Die Matrix wird nur dann ausreichend durch die Faser verstärkt, wenn die Adhäsionsverbindung zwischen Glasfaser und Matrix eine so hohe Festigkeit aufweisen, daß sie bei Krafteintrag nicht zuerst zerstört wird [1]. Adhäsionsphänomene in technischen Prozessen werden immer noch weitgehend empirisch betrachtet. Es sind nicht nur thermodynamische Größen, wie die Ober- bzw. Grenzflächenenergien für die Höhe von Haftkräften verantwortlich, sondern es haben auch mechanische und chemische Eigenschaften einen Einfluß auf die Wechselwirkungskräfte in einer Grenzschicht. Eine notwendige Voraussetzung zur Verbundbildung ist eine optimale Benetzung der Verstärkungsfasern, so daß Fehlstellen im Material ausgeschlossen werden können. Außerdem geht man davon aus, daß neben dispersen Wechselwirkungskräften vor allem auch polare und darunter Säure-Base-Wechselwirkungskräfte die Haftfestigkeit der beiden Verbundpartner positiv beeinflussen [2, 3]. Das wird mit dem Einsatz unterschiedlicher Schichtsysteme, die Haftvermittler mit auf das Matrixsystem abgestimmten funktionellen Gruppen enthalten, ausgenutzt. Zur Abschätzung der Benetzbarkeit und möglicher Wechselwirkungskräfte in der Phasengrenze müssen die Oberflächen der Haftpartner näher charakterisiert werden. Das erfolgt mittels elektrokinetischer und Benetzungsmessungen. Eine weitere Charakterisierung reaktiver Systeme geschieht mittels Tropfenprofilanalyse und die direkte Untersuchung der Benetzung von Glasfasern durch diese reaktiven Harzsysteme.

Mit den derzeitigen zur Verfügung stehenden Methoden zur Bestimmung von oberflächenenergetischen Größen kann eine sehr umfassende und gründliche Charakterisierung der Einflußgrößen auf die Benetzung von Glasfasern durch entsprechende polymere Systeme durchgeführt werden. Mit der Kombination unterschiedlicher oberflächenchemischer Methoden erhält man genauere Informationen über die Auswirkung unterschiedlicher Modifizierungsverfahren. So konnte nur mit Hilfe elektrokinetischer Messungen die Änderung der Funktionalität der Faseroberflächen durch die eingesetzte Schichte ermittelt werden. Die Autoren bedanken sich bei der DFG Sta 324/12-1 und dem BMBF für die Unterstützung ihrer Forschungsarbeiten.

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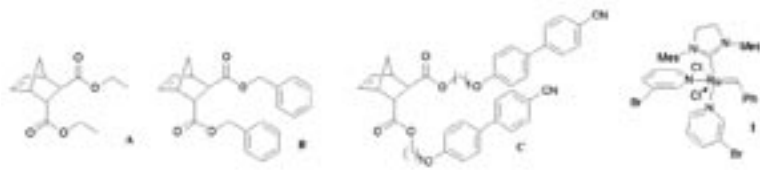
PO-52

ABC Triblock Cooligomers - prepared by Ring Opening Metathesis Polymerisation - Results of MALDI TOF MS

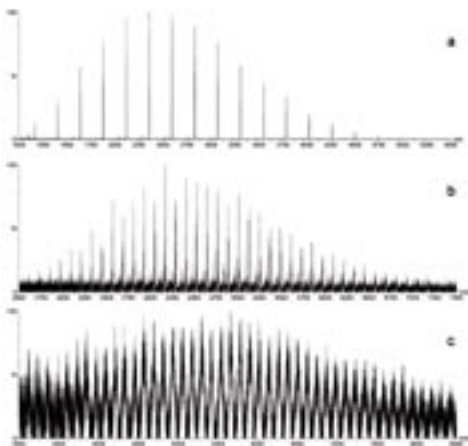
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Ring opening metathesis polymerisation (ROMP) is a powerful tool to prepare well defined and highly functionalised polymers.[1] 3rd generation Grubbs' initiator (H₂Mes)₃(3-bromo-pyridine)₂(Cl)₂Ru=CHPh (1) (H₂Mes= N,N'-bis(mesityl)-4,5-dihydroimidazol-2-ylidene) accomplishes living oligomerisation of norbornene monomers with different substituents.[2] A combination of MALDI-TOF MS, GPC and ¹H-NMR was used to investigate the synthesis of blockcopolymers. This contribution focuses on the results obtained by MALDI-TOF MS.



The results showed that complete initiation for the oligomerisation of monomers A, B and C can be achieved with initiator 1. Analytic details of these oligomerisations, such as identity of end-groups, polydispersity indices, and number average (MN) as well as weight average (MW) molecular weights will be presented. As an important fact for future applications, rational design of various well defined ABC triblock cooligomers and copolymers is possible. To proof our theory cooligomers of A, AB, and ABC were prepared and analysed (see figure below).



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PO-53

Banana Fibre Reinforced Phenolformaldehyde Composites

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Potential of banana fibre as reinforcement in Phenol Formaldehyde resin has been investigated. Specific strength and modulus values of the banana fibre reinforced composites were found to be comparable with that of glass fibre composites. Static and dynamic mechanical properties of the composites were found to increase with increasing glass fibre addition. Incorporating small volumes of glass fibres further improved the mechanical properties of the composites. The fibre-layering pattern is also having an influence in the overall performance of the composites where maximum properties were obtained in intimate mixture of both the fibres. To improve the fibre/matrix adhesion and the resistance to moisture absorption the banana fibre surface were given different chemical modifications which include different silanes, latex treatment heat treatment ,acetylation,cyanoethylation and mercerisation. The role of interfacial adhesion on mechanical and dynamic mechanical properties of the composites was analysed. Finally, the properties of the composites were compared with that of theoretical preictions.

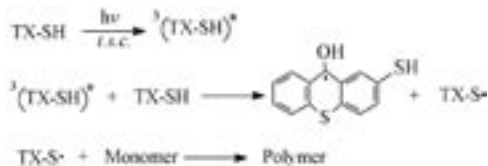
PO-54

The Investigation of Photoinitiated Free Radical Polymerization of Methylmethacrylate with Thioxanthone Derivatives under Magnetic Field Effect

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Photoinitiated free radical polymerization is used widely in various applications and preferred for the production of polymers and copolymers with high molecular weights. It is well known that radicals are active species in radicalic polymerization reactions. Magnetic field produces singlet-triplet transitions in electronic states of radicals by different kinds of mechanisms.



In this study, the photoinitiated polymerization reactions of methylmethacrylate with thioxanthone derivatives are proposed in the presence and absence of magnetic field effect. Finally, the effect of photoinitiator, magnetic field, and molecular weights of polymers were determined.

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PO-55

Influence of the Specimen Shape on Physical Testing Results of Polyoxymethylene (POM) Exposed to Thermooxidative StressesS. Lüftl¹*, V.-M. Archodoulaki¹, S. Seidler¹, M. Glantschnig²¹ *Vienna University of Technology, Institute of Materials Science and Testing, Favoritenstraße 9-11, A-1040 Vienna*² *SFS Intec GmbH, Korneuburg**E-mail: lueftl@mail.zserv.tuwien.ac.at*

Polyoxymethylene (POM) belongs to the group of engineering polymers, it is commonly used in technical parts of the automotive, electric and electronic industry[1]. The material is known e.g. for its good friction properties as well as for its glossy surface on one hand and for its tendency of degradation during processing accompanied with the release of gaseous formaldehyde on the other hand. In practice, two possibilities to enhance the degradation stability of POM-Material are used: One method is to transform the degradation sensitive hydroxyl groups at the ends of the polymer chain into acetate groups (POM-Homopolymer)[1,2], the other method consists in the copolymerization of Trioxane with cyclic ethers to get a POM-Copolymer. In that case the degradation is interrupted when the process arrives at the statistically distributed ether group[1,3]. In further investigations on the thermooxidative degradation behaviour of POM[4,5] a commercially available copolymer was tested, that is used for automotive parts. Tensile testing specimens were produced by injection moulding and exposed to thermooxidative stresses by oven storage at 140 °C for 2, 3, 5 and 8 weeks. After that period different physical tests like tensile test, MVR and thermal analysis (DSC and TGA) were performed. To determine the correlation between the data obtained on tensile test specimens and structural parts used in practice, loudspeaker grids of the same material which were also produced by injection moulding are tested. Loudspeaker grids were treated similar to the tensile test specimens. The same physical tests were performed after a storage time of 3 and 5 weeks in the circulating oven. The test results obtained with the loudspeaker grids were more or less different from those found for the tensile test specimens depending on the applied test method. Therefore physical data determined on standard test specimens with comparably thick walls (e.g. tensile test specimens) do not always correlate with data obtained from practical structural elements, especially when their wall thickness is relative small compared to that of tensile test specimens.

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PO-56

Kinetics of non-isothermal melting and crystallization of gamma Irradiated Isotactic Polypropylene

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The total rate of the non-isothermal melting and crystallization are estimated according to Atanasov et al. [1,2]. The non-isothermal crystallization is based on the equations of Turnbull et al. [3] and Hoffman's theory [4]. The thermodynamic parameters: the lamellar thickness, the transport energy through the phase boundary and the free surface energy are determined [5]. The melting rates of the samples increase with different doses at the same temperature. The gamma rays cause the scission and crosslinking, which lead on the alpha-gamma phase transition. The triclinic gamma phase is more imperfect than monoclinic ones. It melts at the lower temperatures. The higher rate of melting is due to the triclinic crystallites. The lamellar thickness during the melting decreases because of the great number of defects. The free surface energy and the energy of activation during the phase boundary crystal-melt decrease as well. The rate of non-isothermal crystallization increases exponential with the doses.

The lamellar thickness and the free surface energy remain nearly constantly with the doses. At the low doses the growing crystals are in monoclinic or mixed modification. Mainly triclinic crystallites grow at the high doses. These changes are resulted from the intrinsic mass transport from the crystal to the amorphous regions. The start temperatures of crystallization, as well as the whole temperature interval are shifted to the lower temperature because of the irradiation. These results well corresponded with the spherulitic morphology of iPP. The content of gamma phase and lamellar defects sharply increase with increasing of the doses. It is formed a lot of alpha-gamma and gamma-gamma twins. The obtained results confirm the hypotheses for the radiation annealing and the radiation melting.

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PO-57

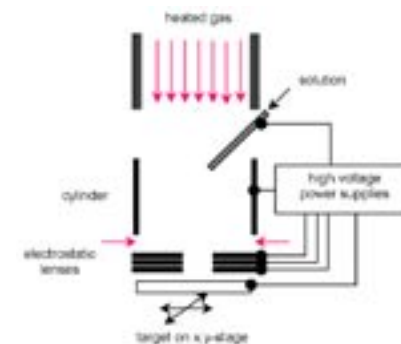
On the experimental setup and the control of Atmospheric Pressure Ion Deposition (APID)T. E. Hamedinger^{1*}, T. Steindl¹, G. Hayn¹, S. Mayer¹, D. Sandholzer¹, J. Albering², J. O. Besenhard², R. Saf^{1*}

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Ion beam techniques are very flexible tools being used in material research, biology and medicine, microelectronics and micromechanics, optics, analysis and basic research [1]. Some of the key technologies in this field of science are ion beam assisted deposition facilities. Within this contribution details of the experimental setup of APID (compare scheme), a deposition technique based on the electrospray process, will be presented. The method uses the phenomenon that solutions of various materials (e.g. polymers, oligomers, biomolecules) can be dispersed into a charged aerosol by electrostatic forces [2]. After dispersion gas phase ions are produced by desolvation of the droplets. Subsequently electrostatic lenses are used to collect/focus these ions towards a target. Various experimental parameters (e.g. applied voltages, concentration of solution injected) determine the morphology of the deposited product (e.g. film or micro/nano structured particles). The influence of several parameters will be presented, software used for continuous monitoring of operating conditions included. The results of analytical investigations (AFM, UV/VIS spectra) of the products will be discussed in correlation to the operating parameters used during the processing. The financial support by the Austrian Science Fund (SFB Electroactive Materials) is gratefully acknowledged.

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PO-58

Influence of crystallization temperature and annealing on the microhardness of α - and β - phases of iPP and E/P-copolymerT. Koch*, S. Seidler*Vienna University of Technology, Institute of Materials Science and Testing, Favoritenstraße 9-11, A-1040 Vienna
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Besides the most common α - modification after polymer processing an amount of β - modification of Polypropylene can often be found, which influences the mechanical properties. The material becomes tougher [1], which is the reason for adding special β - nucleating agents.

Microhardness measurements, which are a useful tool for the characterization of polymers [2], were done on different PP materials. In a high molecular weight iPP and a random E/P copolymer the microhardness of sporadically developed β - spherulites was compared with the hardness of neighbouring α - spherulites. The influence of the crystallization temperature and of annealing was shown. For comparison of creep behaviour indentation creep tests were realized on an α - and a β - nucleated material.

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PO-59

Experiments towards three-dimensionally controlled deposition of functional materials by Atmospheric Pressure Ion Deposition (APID)T. Steindl¹, T. E. Hamedinger¹, G. Hayn¹, S. Mayer¹, D. Sandholzer¹, A. Gupper², P. Wilhelm², R. Saf¹*1) Institute for Chemistry and Technology of Organic Materials, Graz University of Technology, Stremayrgasse 16/1, A-8010 Graz;**2) Research Institute for Electron Microscopy, Steyrergasse 17, A-8010 Graz,
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Functional materials represent a class of materials that exhibit special properties. But for many applications the way how these materials are processed is as important as the chemical structure, especially when several materials are combined to achieve novel properties. A still challenging problem is the processing to thin films that contain different materials at different locations. Theoretically Atmospheric Pressure Ion Deposition is a technique that offers several unique features that could open the way to thin films with three dimensionally controllable chemical composition. One of the most important advantages of the method is, that it's an extremely soft technique where usually no decomposition has to be considered during the processing. This is true even for rather sensitive materials. Furthermore, the method allows the sequential or even simultaneous processing of chemically rather different materials, what's interesting from various different points of view in materials science. Within this presentation latest results concerning the application of APID as technology for the x, y, z controlled deposition of materials will be presented. A crucial point for this aim is the design of the APID ion sources, which was continuously improved by theoretical simulations based on Simion© 7.0. Selected examples of these simulations will be presented. Furthermore structured films that were produced with different experimental setups will be shown. The examples will include ultrathin films with continuously increasing thickness into x and/or y direction, logos of the institute etc. Characterisation of the films by several analytical techniques will be included. The financial support of the FWF (SFB Electroactive Materials) is gratefully acknowledged.

PO-60

Polymer multilayers prepared by APID (Atmospheric Pressure Ion Deposition)

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The interest in thin and ultra thin organic films has continuously increased in the last years. Today the most common method that is used to make thin films is spincoating. This technique however shows a few limitations. (e.g. the area that can be coated is limited, and the use of solvents often make the assembly of multilayered systems impossible). Other often used methods like CVD (Chemical Vapour Deposition) can only process low molecular weight materials. Macromolecules therefore show a too low volatility. But Tailor-made functional polymers can often show their specific properties only after suitable processing. This is the reason why the development of new techniques that allow processing of functional polymers is a very important field.

The latest results in the fabrication of thin electroactive polymer layers with the APID technique will be presented. The technique works under atmospheric pressure. In the first step a beam of single or multiple charged pseudo molecules is formed by drying of micro-droplets that were produced by electrospray ionisation (ESI)[1,2], an ionisation technique well known in mass spectrometry. In a second step a system of electrostatic lenses is used to direct this ion beam towards a target. The investigation of light emitting devices (LED) based on a multilayered structure prepared by APID will be presented. It will be shown that APID is a promising technology for the processing of functional polymers.

The financial support of the FWF (SFB Electroactive materials) is gratefully acknowledged.

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PO-61

Surface modification of polyimides for electric motor manufacture

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PO-62

New amphiphilic polymer supports for transition metal catalyzed reactions in water

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By cationic ring-opening polymerization of 2-oxazolines followed by a simple hydrolysis reaction we have synthesized amphiphilic block copolymers bearing carboxyl or hydroxyl groups on the side chains. Functionalized ligands and metal complexes can be coupled efficiently under mild conditions to these versatile polymer supports, as demonstrate realized applications for enantioselective hydrogenation [1], hydroformylation [3] and metathesis [4] in micellar media. As an example the enantioselective hydrogenation of (Z)-methyl α -acetamidocinnamate is presented in more detail. Compared to previously described water-soluble supports, our amphiphilic system shows a significant increase in activity and enantioselectivity.

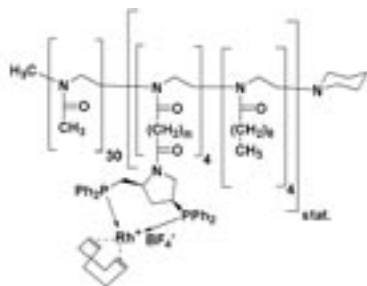


Figure: Polymer supported catalyst for enantioselective hydrogenation

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PO-63

What you should avoid in the application of polymer thermal analysis (a day in a thermoanalytic laboratory)

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Thermal characterisation of polymeric materials covers many aspects of material science, chemical engineering, organic chemistry, analytical chemistry and physical chemistry. TGA (thermogravimetric analysis) is often used to characterize the decomposition and thermal stability of polymers under different conditions like atmosphere (oxygen, nitrogen or air) or heating rate. DSC (differential scanning calorimetry) is widely in use for the basic characterisation (glass-transition temperature, melting point) of polymers. The most important factors that produce deviations between individual measured results are: (i) the operator, (ii) the equipment and the instruments, (iii) the calibration of the instruments and (iv) the environmental effects during the test procedure. In practice there are many parameters known to have an influence on the results measured by the TGA and DSC [1] especially for the points (ii) and (iii) such as sample weight, atmosphere, calibration frequency etc. in order to minimize the influence of the factor (i). The examples of this presentation demonstrate that there is a substantial variation in the measured values even though we considered this points and we would like to provide support for day-to-day work in thermoanalytic laboratories.

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PO-64

Effect of styrene/ethylene/butylene/styrene block copolymer on dynamic mechanical behaviour and processability of high impact polystyreneVesna Rek¹, Tamara H.Grgurić¹ and Želimir Jelčić²,¹) Department of Polymer Engineering and Organic Chemical Technology, Faculty of Chemical Engineering and Technology, University of Zagreb, Maruličev trg 19 10000 Zagreb, Croatia²) INA Polymers, Žitnjak b.b., 10000 Zagreb, Croatia

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Blends of high impact polystyrene (PS-HI) and styrene/ethylene/butylene/styrene block copolymer (SEBS) are systematically investigated to determine the effect of the rubber on the polymer properties. Four compositions on the complete range of blend compositions are analyzed. The processing behavior of the PS-HI + SEBS blends are analyzed and the dynamic mechanical behavior of the processed blends are examined. Rheological behavior of prepared blends during processing was followed by measuring the torque vs. time in the extruder Haake Record 90. Dynamical mechanical analysis, the primary viscoelastic functions are obtained in temperature range -150°C to 160°C. The blends were also investigated in creep-fatigue regime and relaxations were obtained at temperatures 25,35,45,55 and 65°C. The master curves for the reference temperature 25°C were created by time-temperature correspondence principle. The results show the changes of blends processability and dynamic mechanical behavior with increasing of the elastomer, SEBS. The correlation of the processing parameters and viscoelastic functions with the number of phases, their compositions and content are discussed.

PO-65

Synthesis and characterization of new adhesion promoters made from 3-substituted pyrrole derivatives^{1,2}

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For grafting polypyrrole on oxidized surfaces such as Al/Al₂O₃, Ti/TiO₂, Ta/Ta₂O₅ and Fe/Fe₂O₃, a new kind of adhesion promoter, ω-(pyrrol-3-yl alkyl) phosphonic acid, has been successfully synthesized. These new derivatives have two functional groups, phosphonic acid as the head group and pyrrole as the terminal group (polymerizable group). ω-(pyrrol-3-yl alkyl) phosphonic acids were studied for their adsorption behavior on oxide substrates and chemical or electrochemical deposition of polypyrrole over modified oxide surface or electrodes. Several analytical techniques such as contact angle measurement, surface plasmon resonance spectroscopy (SPR), UV-VIS Spectroscopy, grazing incident FTIR, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed to characterize the adsorbed layers on different substrates. SPR showed the kinetics of adsorption process, which is completed within hours. Grazing incident FTIR and angle dependent XPS showed the presence, order and orientation of these new compounds on the surface, where the phosphonic acid group is attached to the surface. CV-measurements were made to get information about the oxidation potential of these compounds. Chemical polymerization and electrochemical polymerization of terminal pyrrole moiety on the substrates modified with synthesized compounds afforded dense, homogeneous and adhesive films of polypyrrole. The conductivity of these films is enhanced as a consequence of this change in morphology. Impedance, photoluminescence and photocurrent measurements were done to study the semi-conducting properties of the grafted polymer films.

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PO-66

Preparation and characterization of microfibrillar composites based on oriented, self-compatibilizing polyester/Bisphenol-A polycarbonate blendsN. Denchev^a, M. J. Oliveira^a, O. S. Carneiro^a, T. A. Ezquerro^b, Z. Denchev^{a*}*a) IPC - Institute for Polymers and Composites, Dept. of Polymer Engineering, University of Minho, Guimarães 4800-058, Portugal**b) Institute of the Structure of the Matter, CSIC, Madrid 28006, Spain**E-mail: denchev@dep.uminho.pt*

Nanostructured composites can be obtained by blending and cold drawing of two or more properly selected immiscible polymers (at least one of them being semicrystalline) followed by annealing at certain temperatures. The major component of the blend forms an isotropic and relaxed matrix, whereas the minor one forms the reinforcing elements - semicrystalline microfibrils with dimensions in the nanometer range, imparting enhancement of the mechanical performance of the system [1,2]. The main goal of this study was to manufacture and characterize nanostructured composite materials in which the reinforcing elements are made of poly(ethylene terephthalate) (PET) or poly(ethylene naphthalate) (PEN) embedded in a matrix of Bisphenol-A polycarbonate (PC).

The preparation of these composites included: (i) melt blending in a twin-screw extruder of various amounts of PET or PEN (25 and 50% by weight) and PC (75 and 50%, respectively); (ii) extruding of oriented PC-polyester cables and (iii) cold drawing of the latter to draw ratios of 5-10. The oriented bristles so obtained were further compression-moulded at temperatures below the fusion of PET (PEN) to get films in which the PC isotropic matrix was reinforced by long longitudinal or short, chaotically oriented polyester microfibrils. PC-PET and PC-PEN films were also produced with no orientation of either phase.

The evolution of the nanostructure during the said manufacturing process was analysed by SEM and optical microscopy. The degree of transesterification between the polyester and PC phases taking place during melt blending and compression moulding stages as well as their impact on the mechanical properties of samples obtained at different processing stages were also investigated.

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PO-67

Properties of silylated wood - effects on surface wettability, Mechanical strength and dimensional stabilityG. Weichsberger^{1,3}, S. Knaus¹, H. Gruber¹, Christian Hansmann^{2,3}*1) Vienna University of Technology, Institute of Applied Synthetic Chemistry, Getreidemarkt 9/163 MC, 1060 Vienna, Austria**2) University of Agricultural Sciences (BOKU), A-1190 Vienna, Austria**3) Competence Centre for Wood Composites and Wood Chemistry (WOOD K plus), St. Peter Straße 25, A-4020 Linz, Austria**E-mail: weichsberger@otech7.tuwien.ac.at*

Although wood in general is a raw material with an outstanding broad spectrum of applications, several of its basic properties also restrain its range of appliance. One main disadvantage of wood is its swelling and shrinking behaviour due to water uptake and loss of water, respectively, as it might happen during a change in climate conditions. As up to 60% of spruce wood consists of cellulose- and hemicellulosic material, which is highly hygroscopic because of its numerous polar hydroxyl groups, this rather undesired wood property can be influenced by manipulating the "natural" hygroscopy of the wood cell wall components. The use of organosilicon compounds for hydrophobisation of cellulose is an already established method, used in textile finishing or for water repellent coatings. In wood chemistry, so far, only little is known about the suitability of silylation [1-3] as a proper tool to introduce hydrophobicity into wood cell walls or wood constituents. The present study deals with the characterisation and properties of silylated wood meal and solid wood samples, respectively, synthesized by reaction with trimethylchlorosilane, N,O-bis trimethylsilylacetamide, hexamethyldisilazane and γ -aminopropyl triethoxysilane. The influence of silyl residues on wood properties such as mechanical stability, surface hydrophobicity and dimensional stability was investigated.

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PO-68

Effect of high-energy radiation and alkali treatment on the properties of cotton-celluloseCsilla M. Földváry^{a*}, Erzsébet Takács^a, László Wojnárovits^a, István Sajó^b^aInstitute of Isotopes and Surface Chemistry, CRC, HAS, Budapest^bInstitute of Chemistry, CRC, HAS, Budapest

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The sorption, physical and chemical properties of the cellulose of different origin are very important in the textile industry, because these characteristics influence the efficiency of the dyeing process and other chemical treatments. The natural cellulose contains ordered crystalline fraction, named cellulose I and amorphous cellulose fraction. The irradiation causes chain-breaks and oxidative degradation of cellulose. In the work reported here the samples were irradiated with γ -rays of Co-isotope or with 2 and 6 MeV electrons of an electron accelerator in the 100-1500 kGy dose range. Similarly to the industrial practice the supermolecular structure of cellulose was modified after irradiation by swelling in 3-6 mol dm⁻³ sodium-hydroxide or in 3-3,75 mol dm⁻³ tetramethyl-ammonium-hydroxide (TMAH). This treatment was combined with irradiation. Due to irradiation induced degradation the degree of polymerization was found to decrease as shown by viscosity measurements. During the irradiation the amount of the carbonyl-groups noticeable increases, these groups are later transformed to carboxyl-groups during the alkali treatment determined by FTIR measurements at 1730 cm⁻¹ and 1640 cm⁻¹, respectively. During NaOH treatment considerable mass loss was observed. This mass loss was also shown by the increased absorbance of the solutions in the UV region, due to the dissolved cellulose. The X-ray diffraction results showed the transformation of the crystalline structure from cellulose I to cellulose II. The percentage of transformation increased either with the increase in the absorbed dose or the concentration of the alkali solution.

PO-69

The Influence of Mechanical Stress and Thermal Treatment on Conductivity of Carbon Black Filled Elastomers

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Conductive rubbers have been a subject of the research activities for a long time. Recently interest has been growing in rubber-based electrically conductive polymer composites in connection with their applications as electronic equipments, pressure sensitive switches, important strategic materials such as EMI shielding, floor heating elements, or materials for dissipation of electrostatic charge[1]. The conductive rubber composites can be easily prepared by mixing a rubber matrix with conductive filler. Carbon black, graphite, carbon fibres, metal-coated inorganic oxide particles and metal powder are frequently used as the conductive fillers[2-3]. The effect of mechanical deformation on the intensity of electric current was investigated in the system EPDM and SBR filled with carbon black. The deformation of the material in tensile mode leads to a destruction of conductive paths formed by the filler particles, resulting in to a drop of current. Consequent relaxation of electrical conductivity after the stress release was detected. After stress release a sudden decrease of the current was observed followed by an increase of the current within 20-40 min. due to relaxation and partial reconstruction of the conductive paths. The composites exhibit excellent stability of the electrical conductivity. Stability of electrical conductivity was tested in heating/cooling cycles in the temperature range from 16°C to 145°C. Conductivity was measured by the four-point van der Pauw method. A significant increase of conductivity was found in the composites during whole thermal treatment. The effect can be explained by the transformation of the conducting paths in the testing samples during heating.

Acknowledgement

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PO-70

Nonconventional Modification of Polarity of Polyethylene through Blending with Oxidized Fischer-Tropsch ParaffinIgor Novák^{*1}, Igor Krupa¹, Adriaan S. Luyt²¹ Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia² School of Chemical Sciences, University of the Free State, Private Bag X13, Phuthaditjhaba, 9866, South Africa

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Polyethylene (PE) has diverse useful applications due to its good mechanical properties and chemical resistance. Various methods have been used for improving of PE adhesive properties, e.g. corona discharge or plasma surface modification, as well as chemical surface etching. Another way of increasing the PE adhesive properties is its modification in the bulk by addition of a low amount of polar polymers or low-molecular weights additives [1, 2]. Easy modification of polarity of PE through blending with oxidized Fischer-Tropsch paraffin investigated. It was found that 10-wt.% of the oxidized paraffin increases considerably the polar component of the surface free energy. Modification of low-density PE with oxidized paraffin significantly improved the strength of the adhesive joint between low-density PE and an epoxy based-substrate. This behaviour was not observed for high-density PE. The conservation of good mechanical properties of PE was observed. The paraffin content has only a moderate influence on the mechanical properties, dependent on the degree of crystallinity. The degree of crystallinity of Fischer-Tropsch paraffin was found to be lower than that of high-density PE, but higher than that of low-density PE. Differential scanning calorimetry measurements indicated miscibility of PE with oxidized Fischer-Tropsch paraffin in the investigated concentration range, in both the solid and the molten state.

Acknowledgement

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PO-71

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Electrically conductive adhesives (ECAs) have attracted great attention because of their adhesive and electrical properties and numerous potential applications. [1, 2] A growing interest is observed in the potential of electrically conductive metal-loaded polymer adhesives for solder replacement in surface mount technology and other microelectronic application in cases when soldering is difficult or impossible because of low thermal stability. An adhesive joining has to have either better properties or more simple technology compared to a traditional soldering. Electrical conductivity and elongation at break of epoxy resin filled with electroconductive carbon black, graphite or with silver-coated basalt particles or fibres were investigated. Percolation concentrations were determined to be 14-volume % for epoxy/carbon black composites, 22-volume % for epoxy/graphite composites and 28 - 29-volume % for both epoxy/Ag-coated basalt particles and fibres. The steepest increase in electrical conductivity and the most pronounced decrease in elongation at break occurs at similar filler concentration range for all investigated systems. A good correlation between phenomenological model, introduced in and experimental data for all investigated systems was observed.

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