

ISPAC-2010

23rd International Symposium on Polymer Analysis and Characterization

31 May - 2 June 2010



POSTECH

Pohang University of Science and Technology
Pohang, Republic of Korea

23rd International Symposium on Polymer Analysis and Characterization

Social Events

Welcoming Reception (May 30, Sunday 18:00~20:00) will be at D'medley of POSCO International Center.

Lunch (May 31~ June 1) will be provided at the lobby of POSCO International Center during the poster session.

Banquet (June 1, 18:00~) will be held at Grand Ballroom of POSCO International Center

We are accepting reservations for the tour of Pohang Accelerator Laboratory (May 31, Monday 17:00~18:00) and for the excursion to Gyeongju (June 2, 13:00~). Registration will take place in Lobby of POSCO International Center.

Please wear your badges at all time during the events.

Dining Facilities on Campus

D'medley (Buffet), 2F POSCO International Center

Phoenix (Chinese), 5F POSCO International Center

Wisdom (Cafeteria), 2F Jigok Community Center

Breakfast 08:30~10:30 / Lunch 11:50~13:20 / Dinner 18:00~19:00

Yeon-Ji (Korean), 1F Jigok Community Center

Lunch 13:00~15:00 / Dinner 16:00~20:00

Burger King, 1F Jigok Community Center

10:00~22:00

Oasis (Snack), 1F Student Union

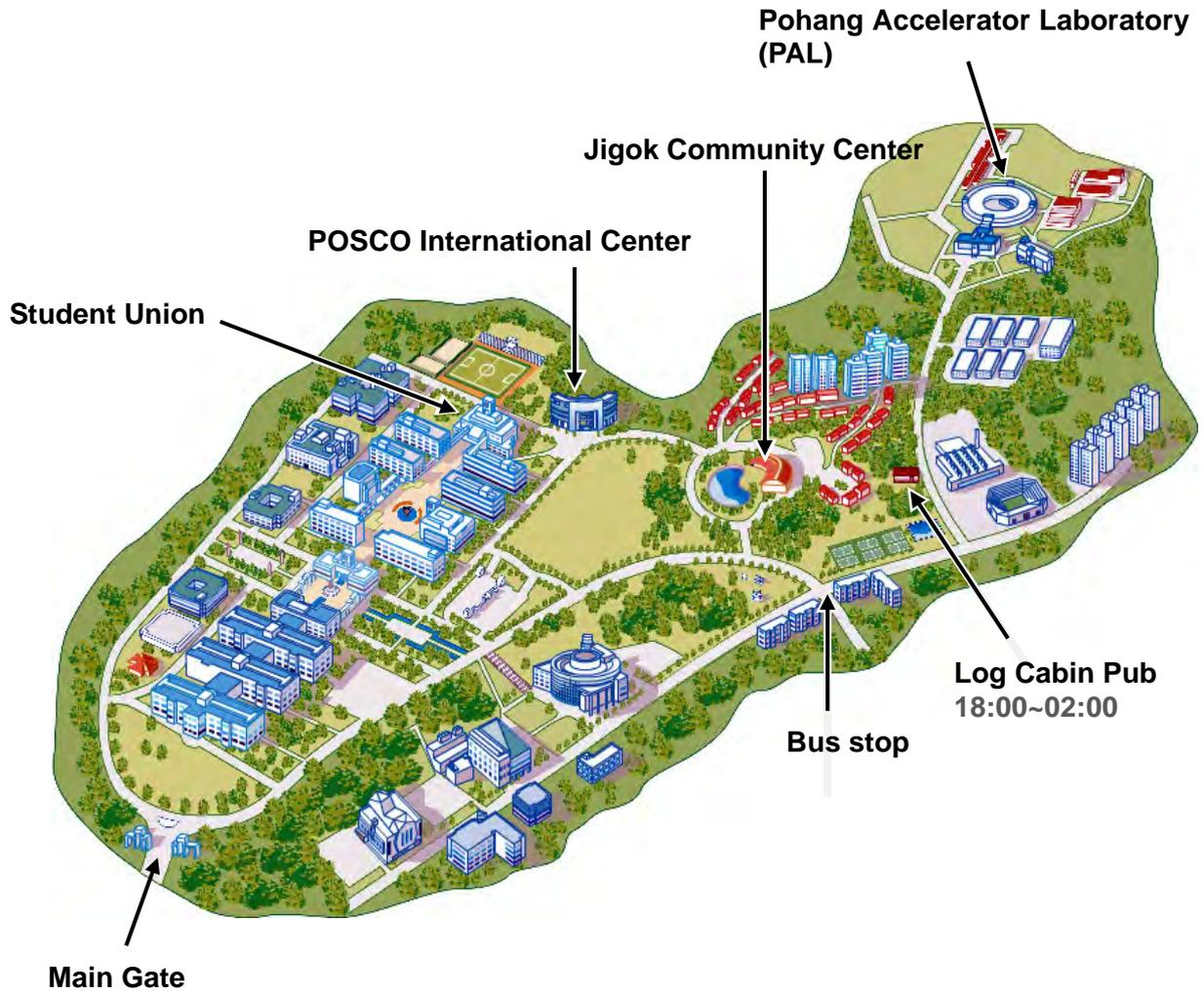
Breakfast 08:00~10:00 / Lunch 11:30~ 15:00 / Dinner 16:00~19:30

Other Facilities

Rosebud (Cafe) & Convenient Store 1F Student Union

Monet (Cafe), Crown Bakery, Souvenir Shop & Convenient Store, 1F Jigok Community Center

Locations



ISPAC Governing Board

*G.C. Berry, *Carnegie Mellon University, USA*; gcberry@andrew.cmu.edu

O. Chiantore, *University of Torino, Italy*; oscar.chiantore@unito.it

**T. Chang, *Pohang University of Science and Technology, Korea*; tc@postech.ac.kr

H.N. Cheng, *USDA Southern Regional Research Center, USA*; hnycheng100@gmail.com

A.W. deGroot, *Dow Chemical Co., USA*; adegroot@dow.com

N. Hadjichristidis, *University of Athens, Greece*; hadjichristidis@chem.uoa.gr

J. Janca, *Tomas Bata University in Zlin, Czech Republic*; jjanca@ft.utb.cz

P. Kratochvíl, *Institute of Macromolecular Chemistry, Czech Republic*; krat@imc.cas.cz

J. W. Mays, *University of Tennessee, USA*; jimmymays@utk.edu

E. Meehan, *AstraZenca, UK*; liz.meehan@astrazeneca.com

H. Pasch, *University of Stellenbosch, South Africa*; hpasch@sun.ac.za

W. F. Reed, *Tulane University, USA*; wreed@tulane.edu

M. Rinaudo, *CERMAV-CNRS, France*; rinaudo@cermav.cnrs.fr

G. J. Vancso, *University of Twente, The Netherlands*; vancso@ct.utwente.nl

* ISPAC Chair **ISPAC-2010 Chair

Emeritus Members of the Governing Board

***H.G. Barth, *DuPont Co., USA*

S.T. Balke, *University of Toronto, Canada*

J.V. Dawkins, *Loughborough University, UK*

S. Mori, *Mie University, Japan*

P. Munk, *University of Texas at Austin, USA*

*** ISPAC Founding Chair Emeritus

The International Symposium on Polymer Analysis and Characterization, ISPAC, is a non-profit scientific organization. The purpose of ISPAC is to provide an international forum for the presentation of recent advances in the field of polymer analysis and characterization methodologies. This unique Symposium brings together analytical chemists and polymers scientists involved in the analysis and characterization of polymeric materials. Meetings are held annually, rotating to venues in the USA, Europe and Asia.

Previous ISPAC Symposia

Toronto,Canada (1988); Austin, TX, USA (1989); Brno,Czechoslovakia (1990); Baltimore, MD, USA (1991); Inuyama, Japan (1992); Crete,Greece (1993); Les Diablerets, Switzerland (1994); Sanibel Island, FL, USA (1995); Oxford, UK (1996); Toronto, Canada (1997); Santa Margherita, Italy (1998); La Rochelle, France (1999); Pittsburgh, PA, USA (2000); Nagoya, Japan (2001); Univ. Twente The Netherlands (2002); Baltimore, MD, USA (2003); Heidelberg, Germany (2004); Sheffield, UK (2005); Oak Ridge, TN, USA (2006); Crete, Greece (2007); Wilmington, DE, USA (2008); Zlín, Czech Republic (2009)

Future ISPAC Symposium

2011 Torino, Italy

Publication

Papers based on the main lectures and posters presented at ISPAC-2010 may be submitted for inclusion in a special Symposium issue of the International Journal of Polymer Analysis and Characterization (IJPAC). Contributions, which will receive a peer review, will be accepted by the Editor-in-Chief of IJPAC, Josef Janca (ijpac@ft.utb.cz) exclusively as electronic files, e.g., on a floppy disk, CD, etc., or as an e-mail attachment. The special issue will be published as soon as possible, with a target in late 2010 or early 2011. The Instructions for Authors may be found in issues of IJPAC, or online at the URL: www.taylorandfrancis.com.

Contributions should not exceed 15 pages double-spaced using font Times Roman 12pt, including figures, tables, and references.

The final deadline for manuscript submission (to be considered for this symposium issue) is to be announced.



ISPAC 2010 Sponsors

It is a pleasure to thank the following sponsors of ISPAC-2010:

Basic Science Research Institute (POSTECH)

Center for Electro-Photo Behaviors in Advanced Molecular Systems (POSTECH)

BK School of Molecular Science (POSTECH)

Polymer Research Institute (POSTECH)

Pohang Accelerator Laboratory

Dow Chemical Co., Basic Plastics Characterization

Symposium Program

Sunday, May 30

Short courses (Conference Room C&D, 2F POSCO International Center)

Chair: Taihyun Chang/ Josef Janca

- 10:00-11:20 Advances in HPLC for Polymer Characterization
Harald Pasch (Univ. of Stellenbosch)
- 11:20-11:30 Break
- 11:30-12:50 Advances in NMR Spectroscopy of Polymeric Materials
H.N. Cheng (USDA)
- 12:50-14:30 Lunch
- 14:30-15:50 Tailored Synthesis and Characterization of Complex Polymers
Jimmy Mays (Univ. of Tennessee)
- 15:50-16:00 Break
- 16:00-17:20 Principles and Applications of Continuous Online Polymerization Monitoring
Wayne Reed (Tulane Univ.)/**Guy C. Berry** (Carnegie Mellon Univ.)
- 18:00-20:00 Welcome (D' medley, 2F POSCO International Center)

Monday, May 31

- 09:00-09:20 Opening (Auditorium, 1F POSCO International Center)

Session 1 Molecular Characterization

Chair: Josef Janca

- 09:20-10:00 **Myeong Hee Moon** (Yonsei Univ.)
*Field-Flow Fractionation/Multiangle Light Scattering
for Ultrahigh MW Sodium Hyaluronate*
- 10:00-10:40 **Koichi Ute** (Univ. of Tokushima)
*Characterization of Methacrylic Copolymers and Terpolymers
by DOSY and Multivariate Analysis of NMR Spectra*
- 10:40-11:00 Break
- 11:00-11:40 **Willem deGroot** (Dow Chem.)
New Tools for Polyolefin's Molecular Structure Determination

- 11:40-12:20 Discussion
- 12:20 -14:00 Lunch & **Poster session** (Lobby, 1F POSCO International Center)

Session 2 Polymer Surface and Interface

Chair: Oscar Chiantore

- 14:00-14:40 **Kilwon Cho** (POSTECH)
Structure Analysis of Functional Interfaces in Organic Electronics
- 14:40-15:20 **Atsushi Takahara** (Kyushu Univ.)
Interfacial Properties and Dynamics of Polymer Brushes
- 15:20- 15:40 Break
- 15:40-16:20 **Julius Vancso** (Twente Univ.)
Designer Surfaces by Stimulus Responsive Polymer Brushes
- 16:20-17:00 Discussion
- 17:00-18:00 **Optional PAL tour** (Bus departs at the front gate of POSCO center)

Tuesday, June 1

Session 3 Application of AFM

Chair: Julius Vancso

- 09:30-10:10 **Sangmin Jeon** (POSTECH)
Nanomechanical Thermal Analysis of Polymers Using Silicon Microcantilevers
- 10:10-10:50 **Ken Nakajima** (Tohoku Univ.)
Quantitative Mechanical Property Measurement on Polymeric Materials from a Single Polymer Chain to Nano-alloys, Nano-Composites
- 10:50-11:10 Break
- 11:10-11:50 **Rüdiger Berger** (MPI)
Electrical Modes in Scanning Probe Microscopy used for Investigation of Polymers
- 11:50-12:30 Discussion
- 12:30-14:00 Lunch & **Poster session** (Lobby, 1F POSCO International Center)

Session 4 Polymer Solution and Gel

Chair: Guy C. Berry

- 14:00-14:40 **Charles C. Han** (Chinese Academy of Sciences)
Interchain Hydrogen-Bonding and Co-nonsolvency Effect of Polymers in Aqueous or Mixed Aqueous Solvents
- 14:40-15:20 **Mitsuhiro Shibayama** (Univ. of Tokyo)
Recent Development of Neutron Scattering Methods for Structural Characterization of Polymeric Systems
- 15:20-15:40 Break
- 15:40-16:20 **Jiang Zhao** (Chinese Academy of Sciences)
Fluorescence Correlation Spectroscopy for the Physics of Polyelectrolyte Single Chains
- 16:20-17:00 Discussion
- 18:00 **Banquet** (Grand Ballroom, 2F POSCO International Center)

Wednesday, June 2

Session 5 Structural Characterization

Chair: Jimmy Mays

- 09:30-10:10 **Kookheon Char** (Seoul National Univ.)
Orientation Control of Microphase-Separated Domains of Block Copolymer Thin Films Placed on Surfaces with Tunable Interfacial Interactions and Roughness
- 10:10-10:50 **Hiroshi Jinnai** (Kyoto Inst. Tech.)
Recent Development of Electron Tomography for Polymeric Nano- and Meso-Structures
- 10:50-11:10 Break
- 11:10-11:50 **Moonhor Ree** (POSTECH)
Grazing Incidence X-Ray Scattering and Its Applications in Detailed Structure Analysis of Nanostructures.
- 11:50-12:30 Discussion
- 12:30-12:50 Closing
- 13:00-20:00 **Optional Excursion** (Bus departs on 13:00 at the front gate of POSCO center)

Lectures

Session 1 Molecular Characterization

1. Field-Flow Fractionation/Multiangle Light Scattering for Ultrahigh MW Sodium Hyaluronate

Myeong Hee Moon

2. Characterization of Methacrylic Copolymers and Terpolymers by DOSY and Multivariate Analysis of NMR Spectra

Koichi Ute

3. Advanced Tools for Polyolefins Molecular Structure Determination

A. Willem deGroot

Session 2 Polymer Surface and Interface

4. Structure Analysis of Functional Interfaces in Organic Electronics

Kilwon Cho

5. Interfacial Properties and Dynamics of Polymer Brushes

Atsushi Takahara, Y. Terayama, H. Yamaguchi, M. Kikuchi, M. Terada, M. Kobayashi, T. Koga

6. Designer Surfaces by Stimulus Responsive Polymer Brushes

G. Julius Vancso

Session 3 Application of AFM

7. Nanomechanical Thermal Analysis of Polymers Using Microcantilevers

Sangmin Jeon

8. Quantitative Mechanical Property Measurement on Polymeric Materials from a Single Polymer Chain to Nano-Alloys, Nano-Composites

Ken Nakajima, So Fujinami, Dong Wang, Hao liu, Makiko Ito, Toshio Nishi

9. Electrical Modes in Scanning Probe Microscopy used for Investigation of Polymers

Stefan A.L. Weber, M. Retschke, Niko Haberkorn, Patrick Theato, Hans-Jürgen Butt, Rüdiger Berger

Session 4 Polymer Solution and Gel

10. Interchain Hydrogen-Bonding And Co-nonsolvency Effect of Polymers in Aqueous or Mixed Aqueous Solvents

Charles C. Han, Jinkun Hao, Guangcui Yuan, He Cheng

11. Recent Development of Neutron Scattering Methods for Structural Characterization of Polymeric Systems

Mitsuhiro Shibayama

12. Fluorescence Correlation Spectroscopy for the Physics of Polyelectrolyte Single Chains

Jiang Zhao, Shengqin Wang, Pengxiang Jia

Session 5 Structural Characterization

13. Orientation Control of Microphase-Separated Domains of Block Copolymer Thin Films Placed on Surfaces with Tunable Interfacial Interactions and Roughness

Kookheon Char

14. Recent development of electron tomography for polymeric nano- and meso-structures

Hiroshi Jinnai

15. Grazing Incidence X-Ray Scattering and Its Applications in Detailed Structure Analysis of Nanostructures

Moonhor Ree, S. Jin, K. S. Jin, J. Yoon, Yecheol Rho, Byungcheol Ahn, Jungwoon Jung, Samdae Park, Jin Chul Kim, Mihee Kim, Sungmin Jung

Field-Flow Fractionation/Multiangle Light Scattering for Ultrahigh MW Sodium Hyaluronate

MOON, Myeong Hee

Department of Chemistry, Yonsei University, Seoul, 120-749, Korea

Sodium Hyaluronate (NaHA) is water soluble and ultrahigh molecular weight polymer composed of disaccharide repeating units of D-glucuronic acid and N-acetyl-D-glucosamine. NaHA is found in synovial fluid, body tissues such as joints, the vitreous humor, and skin. These days NaHA is widely being utilized in cosmetics, ophthalmic surgery, the treatment of knee joint disease, and etc. Since NaHA has different applications in practice depending on molecular weight distribution, the degradation and refinement processes of NaHA are necessary to produce desired pharmaceutical applications.

Flow field-flow fractionation (FIFFF) is an elution technique to fractionate macromolecules by hydrodynamic diameter. Since FIFFF separation is carried out in a thin unobstructed channel, it reduces or bypasses the possible adsorption of sample components on packing materials, shear degradation of large-MW polymers, or column blocking, which can occur when conventional size exclusion chromatography (SEC) is utilized. When FIFFF is combined with multiangle light scattering and differential refractive index (MALS/DRI) detection, it provides an independent measurement of molecular weight and molecular weight distribution of a broad-molecular-weight-polymer sample, along with conformational information. In this presentation, the on-line FIFFF/MALS/DRI will be introduced for characterization of molecular sizes and structure of sodium hyaluronate which has been refined by various processes such as thermal treatment, radiation exposure, and enzymatic degradation.

References

- [1] H. Lee, H. Kim, M. H. Moon, Field Programming in Frit Inlet Asymmetrical Flow Field-Flow Fractionation/Multiangle Light Scattering: Application to Sodium Hyaluronate, *J. Chromatogr. A.* 2005, *1089*, 203.
- [2] D. Shin, E. Hwang, I. Cho, M. H. Moon, Molecular Weight and Structure of Sodium Hyaluronate and its Gamma radiation Degradation Products by Flow Field-Flow Fractionation and on-line Multiangle Light Scattering, *J. Chromatography A.* 2007, *1160*, 270.
- [3] J. H. Kwon, E. Hwang, I.-H. Cho, M. H. Moon, Depolymerization Study of Sodium Hyaluronate by Flow Field-Flow Fractionation/Multiangle Light Scattering, *Anal. Bioanal. Chem.*, 2009, *395*, 519.

L2

Characterization of Methacrylic Copolymers and Terpolymers by DOSY and Multivariate Analysis of NMR Spectra

UTE, Koichi

*Department of Chemical Science and Technology, The University of Tokushima,
2-1 Minami-josanjima, Tokushima 770-8506, Japan*

E-mail: ute@chem.tokushima-u.ac.jp

Many industrial polymers have been developed to give electronic, optical and composite materials. A large part of those polymers are copolymers made up of several different kinds of monomer. Detailed analysis of their molecular structures including chemical composition, comonomer sequence, stereoregularity and the distribution of these properties within the polymer, is essential for further improvement of the polymer materials. My research group in University of Tokushima has been investigating the NMR spectroscopy methods aiming to characterize those complex multi-component copolymers in solution.

MW dependence of chemical composition measured by the DOSY method

Diffusion-ordered NMR spectroscopy (DOSY), a kind of two-dimensional NMR experiments, resolves an NMR spectrum of a complex mixture of chemical species according their diffusion coefficients (D).¹⁾ Thus, DOSY analysis of a copolymer provides information about molecular-weight (MW) dependence of microstructures (chemical composition, comonomer sequence distribution, stereoregularity, etc.) just like on-line SEC-NMR experiments.

Figure 1 shows DOSY spectra of copolymers obtained by polymerization of MMA and 2-hydroxyethyl methacrylate (HEMA) with AIBN. Because HEMA is more reactive than MMA ($r_{\text{MMA}} = 0.81 \pm 0.03$, $r_{\text{HEMA}} = 1.59 \pm 0.05$, by the Kelen-Tüdös method), the copolymer obtained at a late stage of polymerization has a MW dependence of chemical composition. DOSY analysis of this copolymer clearly showed this dependence (Figure 1b). Little dependence of chemical composition was observed for the copolymer obtained at an early stage of polymerization (Figure 1a).

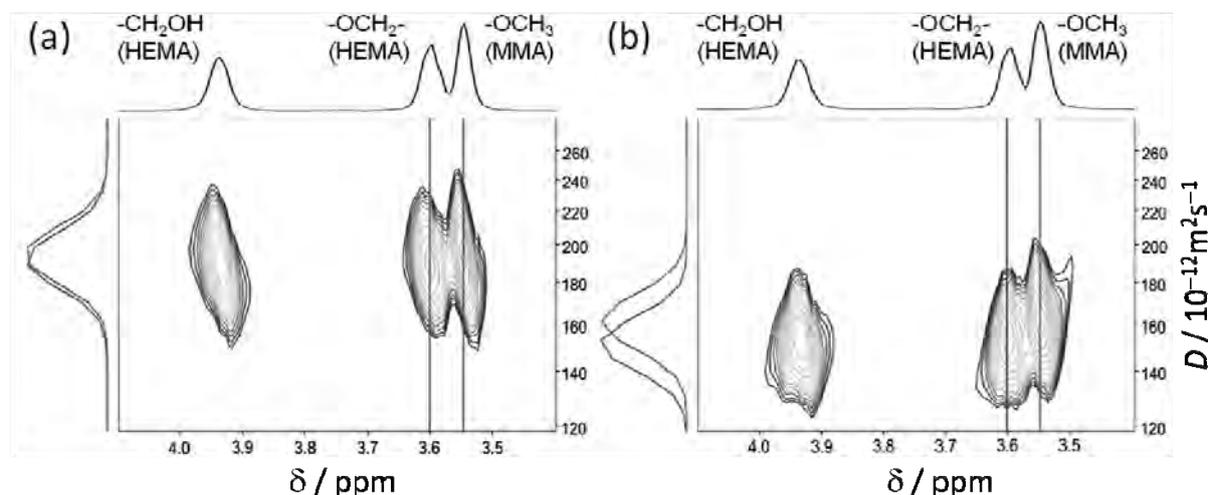


Figure 1 DOSY spectra of poly(MMA-co-HEMA)s obtained at early (a) and late (b) stages of polymerization (in DMSO- d_6 at 80 °C, 400 MHz, by maximum entropy deconvolution).
(a) M_n 25300, M_w/M_n 2.56, yield 2.2 %; (b) M_n 41400, M_w/M_n 2.91, yield 90.4 %.

Chemical composition and comonomer sequence distribution determined by the multivariate analysis of NMR spectra

NMR resonances arising from each group in copolymers often exhibit superposed splitting due to comonomer sequences and configurational sequences, and thus assignment of the individual peaks is troublesome. Recently, we reported that the methods of multivariate analysis are useful to obtain quantitative information about chemical compositions of MMA - *tert*-butyl methacrylate (TBMA) copolymers without assigning individual resonance peaks in their ^{13}C NMR spectra.²⁾

Principal component analysis (PCA) was performed for the bucket integral data sets obtained from the ^{13}C NMR spectra of PMMA, PTBMA, nine blends of the homopolymers and 16 poly(MMA-*co*-TBMA)s with various chemical compositions. Good linear relationship ($R^2 = 0.997$) was found between the first principal component (PC1) score and the chemical composition in mol % of TBMA units. The second principal component (PC2) reflected randomness of comonomer sequences. Partial least-squares regression has allowed us to propose a calibration model which predicts the fractions of the hetero dyad (MMA-TBMA) sequence (f_{MT}) from the spectrum of a given copolymer with an R^2 of 0.997 and a relative standard deviation of 7.1 % as shown in Figure 2.³⁾

This approach was successfully extended to the characterization of MMA-TBMA-HEMA terpolymers (Figure 3). PC1 and PC2 showed relationship to chemical composition whereas PC3 reflected randomness of comonomer sequence.⁴⁾

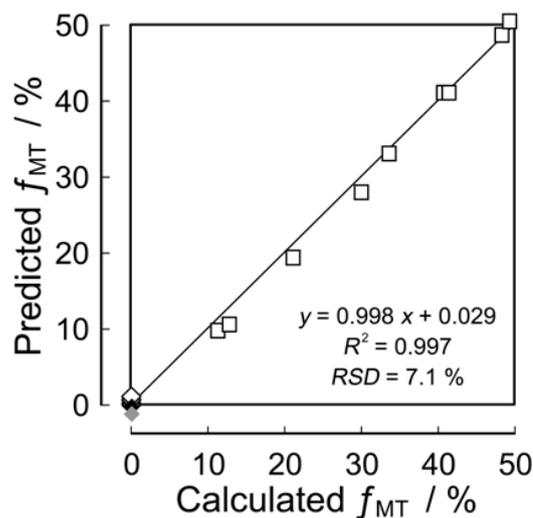


Figure 2 Partial least-squares regression analysis for predicting fractions of MMA-TBMA hetero dyad sequences from the ^{13}C NMR signals due to the carbonyl, backbone quaternary and α -methyl carbons of the poly(MMA-*co*-TBMA)s obtained at early stages of polymerization.

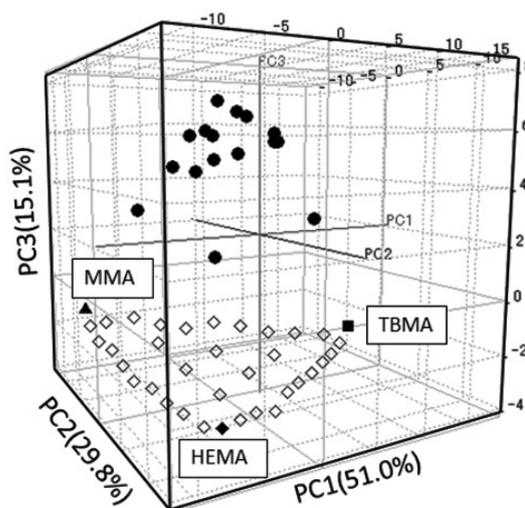


Figure 3 Principal component score plots for the ^{13}C NMR spectra of 78 samples; PMMA (\blacklozenge), PTBMA (\blacktriangle), PHEMA (\blacksquare), homopolymer blends (\diamond), poly(MMA-*co*-TBMA)s (\triangle), poly(MMA-*co*-HEMA)s (\square), poly(MMA-*co*-TBMA-*co*-HEMA)s (\bullet).

¹ Johnson, C. S. Jr, **Diffusion ordered nuclear magnetic resonance spectroscopy: principles and applications**, *Prog. NMR Spectrosc.*, **1999**, *34*, 203. ² Momose, H.; Hattori, K.; Hirano, T.; Ute, K., **Multivariate analysis of ^{13}C NMR spectra of methacrylate copolymers and homopolymer blends**, *Polymer*, **2009**, *50*, 3819. ³ Momose, H.; Maeda, T.; Hirano, T.; Ute, K., **Determination of comonomer sequence distributions of MMA-TBMA copolymers by means of multivariate analysis of ^{13}C NMR spectra**, *ISPAC-2010*. ⁴ Naono, T.; Momose, H.; Hirano, T.; Ute, K., **Characterization of methacrylate terpolymers by multivariate analysis of ^{13}C NMR spectra**, *ISPAC-2010*.

L3

Advanced Tools for Polyolefins Molecular Structure Determination

A. Willem deGroot

*The Dow Chemical Company
Technical Leader of Basic Plastics Characterization Group
2301 Brazosport Blvd.
Freeport, TX 77541
E-mail: awillem@dow.com*

“It is the simplest of polymers. It is the most complex of polymers.”: A quote from Bill Knight (Dow Scientist) paraphrased from **A Tale of Two Cities** by Charles Dickens.

Polyolefins are comprised of just carbon and hydrogen, but they still present many interesting characterization challenges for the polymer chemist. The primary molecular structural features that we pursue at The Dow Chemical Company to develop better structure property rules are molecular weight, comonomer content, long-chain branching content and their distributions.

The primary tool for molecular weight and molecular weight distribution, historically has been gel permeation chromatography (GPC). This technique was originally developed by The Dow Chemical Company almost 50 years ago¹, but it is still the best tool for obtaining this information quickly and accurately. Many improvements have been made in instrumentation, detectors and columns, but the basic principles remain the same. The primary limitation that we have tried to address here has been the ‘late elution’ phenomenon which arises when very high molecular weight polymers, typically highly branched polyolefins are analyzed. To address this we have developed high temperature, asymmetric flow field flow fractionation (HT-AF4) in collaboration with Postnova Analytics². This technique clearly shows a dramatic improvement in preserving high molecular weight species which are either shear degraded or filtered out in a typical GPC experiment.

For comonomer and comonomer distribution characterization, TREF³ has historically been the tool of choice. However, in 1994 Benjamin Monrabal developed a technique which improved the speed of analysis for comonomer distribution. He called the technique CRYSTAF⁴ and started the company now called PolymerChAR in Valencia, Spain. His latest development has been a technique which he calls Crystallization Elution Fractionation or CEF⁵. This technique improves the analysis time by almost an order of magnitude from 5 hours to approximately 30 minutes. The latest innovation in this area has been to apply interaction

chromatography to fractionate polyolefins by comonomer distribution using a graphitic column. This technique was independently developed by Harald Pasch and Tibor Mako⁶ at DKI and by Matt Miller⁷ et al at Dow. This technique offers the possibility to dramatically improve the resolution and decrease the time of analysis for comonomer distributions.

For long-chain branch detection rheology, generally considered to be the most sensitive method⁸. However, for long chain branch quantification, ¹³C NMR along with triple detector GPC⁹ are the most valuable tools. ¹³C NMR has some limitations, but triple detector GPC can be used with very high sensitivity.

In this talk I will discuss and give examples of the latest developments in characterizing these three molecular structural features of polyolefins.

References

- [1] Moore, J. C., J. Polym. Sci., A2, 835 (1964).
- [2] Mes, E. P. C., H. De Jonge, T. Klein, R. R. Welz, D. T. Gillespie, J. Chrom., A., 319-330, 1154(1-2), (2007).
- [3] L. Wild (J. Polym. Sci., Polym. Phys. Ed. (1982))
- [4] B. Monrabal (J. Appl. Sci. (1994))
- [5] B. Monrabal (Macromol. Symp. (2007))
- [6] T. Macko and H. Pasch (National ACS Meeting, Philadelphia (2008)) and (Macromolecules, 2009, 42, 6063-6067).
- [7] M. Miller et al (Macromolecules 2010, 43(8) 3710-3720.
- [8] Karjala, T. P. et al (J. Appl. Sci. in press)
- [9] Wood-Adams, P. M., J. M. Dealy, A. W. deGroot, O. D. Redwine (Macromolecules, 2000, 33, 7489-7499)

Structure Analysis of Functional Interfaces in Organic Electronics

Kilwon Cho*

Department of Chemical Engineering, Pohang University of Science and Technology,

Pohang, 790-784, Korea, E-mail: kwcho@postech.ac.kr

Control over surface induced self-assembly of electronically active pi-conjugated molecules provides great opportunities to fine-tune and optimize their electrical properties for applications in organic electronics. The design of substrates with controllable surface properties can be effectively achieved by employing functionalized self-assembled monolayers, which have become one of the most popular techniques to create well-defined functional nanostructures. By self-assembly of pi-conjugated nanostructures with strongly pi-pi interacting building blocks via surface chemistry, optimized electrical properties of organic electronic devices can be attained. In this study, with the aim of enhancing the electrical performances by promoting surface induced two-dimensional self-assembly in representative pi-conjugated molecules such as poly (3-hexylthiophene) and pentacene, we have controlled the intermolecular interaction at the interface between pi-conjugated molecules and substrates by using self-assembled monolayers functionalized with various groups. We will discuss the dependencies of self-assembled nanostructures of pi-conjugated molecules on the substrate surface and their effects on electrical performances in organic transistors. Furthermore, controlling interface properties and structures of the photoactive layer in organic photovoltaics will be presented.

Interfacial Properties and Dynamics of Polymer Brushes

A. Takahara^{1,2,3}, Y. Terayama², H. Yamaguchi², M. Kikuchi³, M. Terada³, M. Kobayashi³, T. Koga⁴

¹Institute for Materials Chemistry and Engineering, ²Graduate School of Engineering, Kyushu University,

³JST, ERATO Takahara Soft-interfaces Project, 744 Motooka, Nishi-ku, Fukuoka 819-0395, JAPAN,

⁴Stony Brook University, Stony Brook, NY 11794-2275, U.S.A.

takahara@cstf.kyushu-u.ac.jp

Since surfaces and interfaces of soft materials play an important role in various technological applications, precise control of soft interfaces would greatly promote the innovation of materials science and technology. In this study, precise structure and physical property control of soft interfaces by immobilization of polymer brushes onto Si-wafer and polymer films are presented.

Various polymer brushes were prepared on the silicon wafer by surface-initiated atom transfer radical polymerization. Surface initiator, (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane, was synthesized, and immobilized on a cleaned silicon wafer by the chemical vapor adsorption method. Chemical structures of polymer brushes were shown in Figure 1.

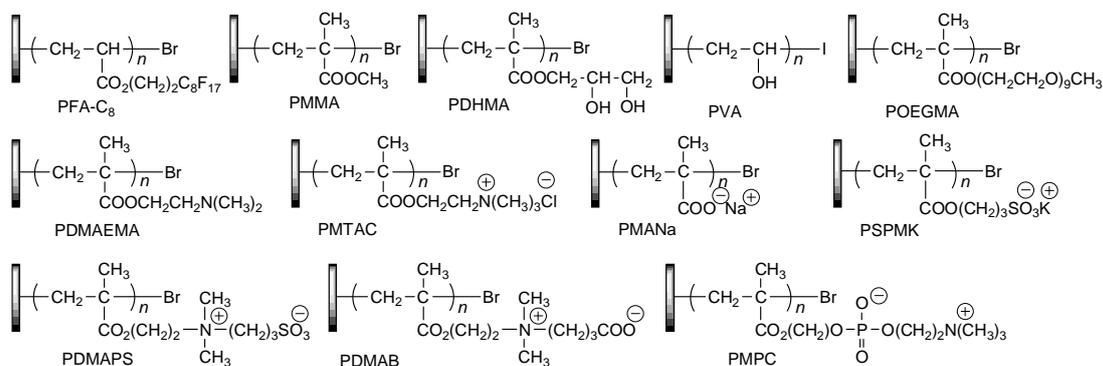


Figure 1. Chemical structures of polymer brushes

Surface free energies of the polymer brushes were estimated from contact angle measurement. The polyelectrolyte brushes showed significantly low water contact angles below 3~7 deg. In particular, a water droplet was quickly spread on the poly(MPC) brush surface. The surface free energy of the poly(SPMK) and poly(MPC) brush surfaces were estimated to be 72.9 mJ m⁻², which is quite similar to that of water. Particularly, PMPC brush showed excellent antifouling properties. On the other hand, PFA-C₈ brush showed very low surface free energy but hexadecane was spread at the water interface.

The effects of ionic strength on brush structure and surface properties of densely grafted polyelectrolyte brushes were analyzed by neutron reflectivity (NR) measurement and AFM thickness measurement. NR at PMTAC/D₂O and PMPC/D₂O interface revealed that the grafted polymer chains were fairly extended from the substrate surface¹⁾, while the thickness reduction of PMTAC brush was observed in 5.6 M NaCl/D₂O solution due to the screening of the repulsive interaction between polycations by hydrated salt ions. This swelling behavior in salt solution was also confirmed by AFM observation in salt solution. Interestingly, thickness change was not observed for zwitter ionic PMPC brush even in a high concentration salt solution. This can be attributed to the neutral nature of phosphorylcholine units. On the other hand, swelling behavior of PFA-C₈ brush in super critical carbon dioxide was evaluated by in situ NR.

Evanescent wave dynamic light scattering (EWDLS) method was proposed for evaluation of dynamics in the concentration fluctuations for the polymer brush in good, theta, and poor solvents. In EWDLS-experiments, an evanescent wave is created upon total reflection of a laser beam from the flat interface between a prism

immobilized polymer brush and the solution. This evanescent wave is used as the incident radiation for a dynamic light scattering experiment. The near-wall dynamics of polymer brush can be studied by EWDLS, if the intensity which is scattered off the evanescent wave by molecular motion of polymer brush is correlated. Through measurement of light at different scattering vectors and penetration depths, the relaxation modes for the polymer brush at various measuring depth was investigated.

Macroscopic friction tests on polymer brushes were carried out on a conventional ball-on-plate type reciprocating tribotester by sliding a glass ball on the substrates along a distance of 20 mm at a rate of $1.5 \times 10^{-3} \text{ m s}^{-1}$ in air and in water under a normal load of 0.49 N at room temperature. In the case of a non-modified silicon wafer under a normal load of 50 g (0.49 N), the theoretical contact area between the glass probe and substrate can be calculated as $3.51 \times 10^{-9} \text{ m}^2$ by Hertz's contact mechanics theory and the average pressure on the contact area was estimated to be 139 MPa.

Figure 2. shows the friction coefficients of poly(MTAC), poly(SPMK), and poly(MPC) brushes in water at a sliding velocity of $10^{-5} \sim 10^{-1} \text{ m s}^{-1}$. The polymer brushes were immobilized on both surface of silicon wafer and sliding glass ball. The friction coefficients of these brushes were 0.1~0.2 at the slower friction rate of $10^{-5} \sim 10^{-3} \text{ m s}^{-1}$, whereas the friction coefficient was dropped to be 0.01~0.03 at the higher sliding velocity over $10^{-2} \sim 10^{-1} \text{ m s}^{-1}$. The drastic reduction in the friction coefficients at a certain velocity could be caused by the transition of friction mode. With the low sliding rate, the interaction between the opposite brushes and the interpenetration of brushes dominated the friction to give a large friction coefficient (boundary or interfacial friction). With an increase in the sliding velocity, a thicker liquid layer would be formed between the sliding surfaces by the hydrodynamic lubrication effect to reduce the actual contact area and the friction force (mixed lubrication region). At higher sliding rates, we supposed that hydrodynamic lubrication partially took place between opposing swollen polyelectrolyte brushes to reduce the friction. Poly(SPMK) showed significantly low friction coefficients at the sliding rate of $10^{-3} \sim 10^{-1} \text{ m s}^{-1}$ probably because of water lubrication and the electrostatic repulsive interactions among the anionic groups.

The friction coefficients of polyelectrolyte brushes in aqueous solution are affected by a salt concentration. The poly(MTAC) brush in 10 mM of NaCl_{aq} solution showed same friction coefficient as in pure water, while the transition velocity of the reduction in the friction coefficient was shifted from 10^{-2} to 10^{-3} m s^{-1} . The friction coefficient in 1000 ~5000 mM of NaCl_{aq} solution at the higher sliding rate increased from 0.02 to 0.1. The low friction coefficient below 0.02 was observed in poly(SPMK) brush in 0 ~ 100 mM of NaCl_{aq} solution at the sliding velocity of $10^{-3} \sim 10^{-1} \text{ m s}^{-1}$, however, the friction coefficient increased to be 0.1 in a higher NaCl concentration above 1000 mM. In general, polyanion or polycation chains in aqueous solution with low ionic strength form a relatively expanded chain structures due to the intermolecular repulsive interaction. In contrast, the polyelectrolyte dissolved in higher ionic strength in solution behaves like an electrically neutral polymer to give smaller dimension because the electric interactions are screened by salt ions. Therefore, an increase in salt concentration would lead to the reduction of the electrostatic repulsion interaction among the brushes to result in a higher friction coefficient.

In the case of poly(MPC) in NaCl and CaCl_2 aqueous solutions, significant difference in friction coefficients between salt solution and water was not observed at the sliding velocity of 10^{-3} and 10^{-1} m s^{-1} . It can be related to the fact that the poly(MPC) is a quite unique polyelectrolyte of which chain structure in a aqueous solution hardly changed by salt effect due to a weak intermolecular interaction among phosphorylcholine units.

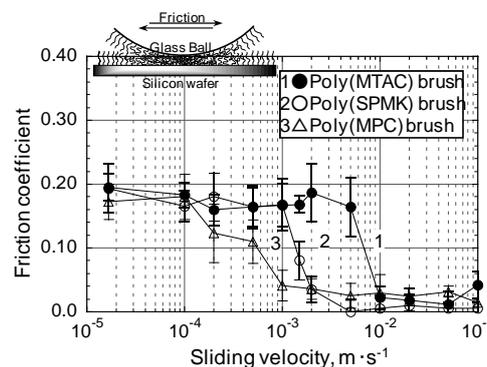


Figure 2. Sliding velocity dependence of the friction coefficient of (a) poly(MTAC), (b) poly(SPMK), and (c) poly(MPC) brushes in water by sliding a glass ball ($\Phi = 10\text{mm}$) immobilized with the corresponding polyelectrolyte brushes over a distance of 20 mm under a normal load of 0.49 N at 298 K.

References

- 1) M. Kobayashi, Y. Terayama, N. Hosaka, M. Kaido, A. Suzuki, N. Yamada, N. Torikai, K. Ishihara, A. Takahara, *Soft Matter* 3, 740 (2007).

L6

Designer Surfaces by Stimulus Responsive Polymer Brushes

G. Julius Vancso

*University of Twente, MESA⁺ Institute for Nanotechnology
7500 AE Enschede, The Netherlands
g.j.vancso@utwente.nl*

Polymers have been used with great success in coating films with various thickness values, from the few tens of nm to the hundreds of microns, applied to various surfaces. Examples for the applications include corrosion protection, decorative coatings, barrier films, as functional layers to alter surface properties such as wetting or friction, preventing blood clotting caused by biomedical implants, etc. Regarding ultrathin polymer films, the use of polymer based lithography resists has been enabling for optical projection lithography, employed in semiconductor chip fabrication. Macromolecules can also be attached to surfaces by one of their termini either using physical interactions or by chemical grafting [1]. Grafting of (reactive) chains to surfaces usually results in tethered macromolecules, which exhibit a random coil-like conformation in a good solvent and exhibit grafting densities on the order of 0.05 chains per nm² or lower. In such cases the average distance between grafting points is on the order of a few nm (4-5 nm) and higher. Such tethered macromolecules are called “polymer mushrooms”. If the grafting density increases, the chains become stretched, chain dynamics become weak, and the layer exhibits a “brush-like” behavior. Such grafted chain layers can be described by simple mean field theories [2]. “Grafting to” approaches usually do not yield high grafting densities, i.e. tethered brush chains; however by using surface-attached initiators the attachment density can be enhanced and brushes can be prepared. With the advent of controlled free radical polymerizations, brushes with controlled chain composition, chain attachment density, gradients, multicomponent structures, etc. can be obtained with relative ease [3]. Combinations of surface topological patterning of initiators (e.g. by various forms of hard and soft lithography and other surface micro/nanofabrication approaches) and surface initiated polymerizations (SIP) can provide complex engineered “designer” brush platforms that exhibit chemical and topological patterns with different functionalities. When polymers are used in the grafts that respond to changes of external stimuli, surface active materials can be fabricated which have intriguing

applications in sensing, release systems, as “smart” surfaces (wettability and adhesion switching), nanoactuators, self cleaning, etc.

In this presentation first a short general overview will be offered about polymer brushes, their synthesis (via SIP) and characterization. Regarding characterization, applications of Atomic Force Microscopy will be emphasized, in addition to other thin film characterization techniques [4].

Three case studies will follow. First the preparation of thermosensitive surfaces by controlled “grafting from” of poly(N-isopropylacrylamide) (PNIPAM) brushes, using a newly developed disulfide-containing photoinitiator-transfer-terminator agent immobilized on gold, will be presented [5]. PNIPAM brushes were grafted in a controlled manner from mixed self-assembled monolayers (SAMs) on Au substrates. The synthetic strategy used, in combination with soft lithography for patterning the initiators, allowed us to obtain tunable temperature-responsive PNIPAM brushes that exhibit also various topological patterns. The length of tethered chains was controlled by the irradiation time, whereas the grafting density was adjusted with SAM mixing ratios. The synthesis is biocompatible as no organic solvents should be used and no toxic compounds are involved in the polymerization. This technique is a promising tool for producing smart temperature-responsive platforms, with the potential for chemical control of the chain-terminating group.

A discussion on the growth of pH-responsive poly(hydroxyethyl methacrylate) (PHEMA) based polymeric nanostructures will follow [6]. These brushes were grown in a controlled manner by Atom Transfer Radical Polymerization (ATRP) based surface-initiated polymerization. Initiator nanopatterns were obtained on silicon wafers covered with silane resists which were patterned by AFM scanning probe oxidation lithography. AFM images confirmed isolated grafting of stimuli-responsive hedge and dot brush structures exhibiting dimensions corresponding to a few tens of chains.

As last example, preparation, characterization, properties and applications of a new functional polymer brush gel will be discussed. PHEMA linear and cross-linked brush chains were obtained by ATRP wherein cross linking was achieved with poly(ethylene glycol) dimethacrylate added to the reaction mixture. The brush structures were subsequently functionalized with carboxylic groups [7] which made the layers responsive to variations in the external pH. This functional brush gel was used for the controlled formation and in-situ

immobilization of silver and palladium nanoparticles, as catalytic coatings on the inner walls of glass microreactors. The brush film was grown directly on the microchannel interior via ATRP, which allows control over the polymer film thickness and thus the number of nanoparticles formed on the channel walls could be adjusted. By this process nanoparticle coverage values well beyond the coverage of monolayers could be achieved, thus loading of the catalytic particles was substantially enhanced. The metal nanoparticles were then employed in various catalytic reactions. The wide applicability of this microreactor device is demonstrated for the reduction of 4-nitrophenol and for the Heck reaction [8].

References

- [1] Polymer Brushes: Synthesis, Characterization, Applications, by Advincula, R.C., Brittain, W.J., Caster, K.C., and R  he, J., Editors, Wiley-VCH, Weinheim, 2004.
- [2] de Gennes, P.G.; Polymers at an interface: A simplified view, (1987) *Advances in Colloid and Interface Science*, 27 (3-4), pp. 189-209.
- [3] Edmondson, S., Osborne, V.L., Huck, W.T.S., Polymer brushes via surface-initiated polymerizations, (2004) *Chemical Society Reviews*, 33 (1), pp. 14-22.
- [4] Sui, X., Zapotoczny, S., Benetti, E.M., Sch  n, P.M., Vancso, G.J., Characterization and molecular engineering of surface-grafted polymer brushes across the length scales by atomic force microscopy, (2010) *Journal of Materials Chemistry*, in press.
- [5] Benetti, E.M., Zapotoczny, S., Vancso, G.J., Tunable thermoresponsive polymeric platforms on gold by "photoiniferter"-based surface grafting, (2007) *Advanced Materials*, 19 (2), pp. 268-271.
- [6] Benetti, E.M., Hong, J.C., Vancso, G.J., pH responsive polymeric brush nanostructures: Preparation and characterization by scanning probe oxidation and surface initiated polymerization, (2009) *Macromolecular Rapid Communications*, 30 (6), pp. 411-417.
- [7] Benetti, E.M., Sui, X., Zapotoczny, S., Vancso, G.J., Surface-grafted gel-brush/metal nanoparticle hybrids, (2010) *Advanced Functional Materials*, 20 (6), pp. 939-944.
- [8] Costantini, F., Benetti, E.M., Tiggelaar, R.M., Gardeniers, H.J.G.E., Reinhoudt, D.N., Huskens, J., Vancso, G.J., Verboom, W., A Brush-Gel Metal Nanoparticle Hybrid Film as an Efficient Supported Catalyst in Glass Microreactors, (2010) *Chemistry European Journal*, in press.

L7

Nanomechanical Thermal Analysis of Polymers Using Microcantilevers

Sangmin Jeon

*Department of Chemical Engineering,
Pohang University of Science and Technology (POSTECH), Pohang, Korea
E-mail: jeons@postech.ac.kr*

A nanomechanical thermal analysis method that uses cantilever sensors has been developed for investigating the glass transition phenomena of amorphous polymers.^{1,2} When a silicon cantilever coated with a polymer is heated or cooled, the difference between the volume expansion coefficients of the silicon and the polymer induces the cantilever to bend, which can be used to investigate not only T_g but also the *in-situ* changes in the volume of the polymer induced by physical aging or stress relaxation. The variations in the resonance frequency and Q factor with temperature can be related to the elastic modulus and loss tangent of the coated polymer. Compared to conventional methods for investigating the thermal properties of materials such as differential scanning calorimetry (DSC), dilatometry, thermogravimetric analyzer (TGA), and dynamic mechanical spectroscopy (DMS), cantilever sensors are more versatile than the conventional methods and need samples of only a few nanograms for measurements. In addition, the miniaturized array structure of the cantilever sensors makes it possible to achieve high sensitivity, fast thermal equilibrium and multiple sample measurements. In this presentation, thermomechanical properties of glass polymers, photoresponsive polymers, and paraffins will be discussed.

References

- [1] Namchul Jung, Sangmin Jeon, *Macromolecules*, 41, 6873, (2008).
- [2] Namchul Jung, Sangmin Jeon, *Macromolecules*, 41, 9819, (2008).

Quantitative Mechanical Property Measurement on Polymeric Materials from a Single Polymer Chain to Nano-Alloys, Nano-Composites

Ken NAKAJIMA*, So FUJINAMI, Dong WANG, Hao LIU, Makiko ITO and Toshio NISHI

*WPI Advanced Institute for Materials Research, Tohoku University,
2-1-1 Katahira, Aoba, Sendai, 980-8577, Japan
E-mail: knakaji@wpi-aimr.tohoku.ac.jp

Atomic force microscopy (AFM) was employed to perform quantitative mechanical property measurement on polymeric materials. We have not given much attention to AFM's high-resolution feature, while its nanometer-scale palpatibility has been our great concern. Nano-palpatation can be classified in two categories. One is the technique that can be called nanofishing, which reveals the entropic elasticity of a single polymer chain¹⁻³). A single polymer chain is picked up and pulled at its chemically modified terminals, resulting in the acquisition of structural information such as persistence length. The recent result showed that no energy dissipation during successive extension and contraction processes for a single polystyrene (PS) chain as shown in Fig. 1. Dynamic nanofishing, where a cantilever is imposed on the forced oscillation at its resonant frequency, enables us to investigate more fruitful information^{4,5}). Double Voigt model, as phenomenological model, was employed to analyze the result. The method gave extension-dependent changes of entropic elasticity and frictional coefficient with solvent molecules.

Another nano-palpatation is the technique to map elastic or viscoelastic properties of rubbery specimens in nano-scale. The technique also gives true topographic picture free from sample deformation rather than apparent topography that is commonly obtained by conventional AFM⁶). The technique has been applied to different types

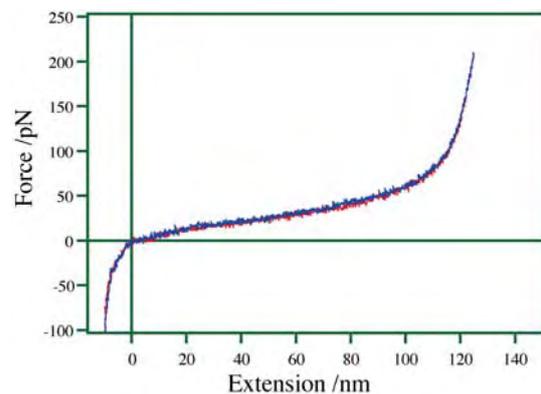


Fig.1 Static nanofishing of a single PS chain

of rubbery materials including stretched natural rubber (NR)⁷), carbon-reinforced NR⁸), CNT-reinforced NR, triblock copolymer-based thermoplastic elastomer⁹), dynamically-vulcanized polymer nanoalloy. In the case of pure NR, we examined the effect of elongational ratio to its Young's modulus in nano-scale and found the distribution of the

modulus is highly heterogeneous. We found the mechanical interface in filled NR specimens. This time, we will also discuss the inhomogeneous nature of viscoelastic butyl rubber as shown in Fig. 2. Although the specimen shows fully viscoelastic property at macroscopic scale, it showed elastic region as well as viscoelastic region in nano-scale. This finding was analyzed in more detail by force-distance curve measurement at each region. We will discuss the origin of this inhomogeneity by preparing different crosslinking conditions.

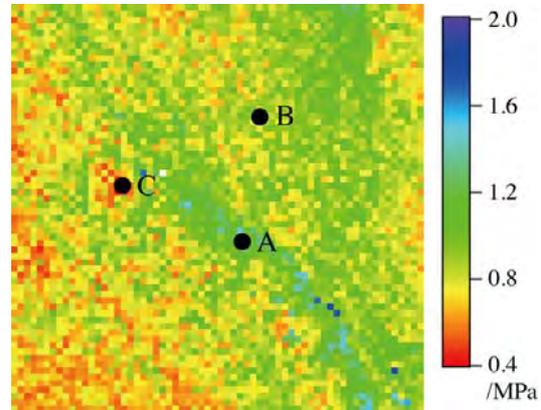


Fig.2 Nanomechanical mapping of butyl rubber (1.0 μm). Point A: fully elastic, Point B: partical viscoelastic, Point C: viscoelastic

References

- [1] K. Nakajima, H. Watabe and T. Nishi, Single polymer chain rubber elasticity investigated by atomic force microscopy, *Polymer*, 2006, 47, 2505.
- [2] K. Nakajima, H. Watabe and T. Nishi, Solvent effects on single polymer chain physics investigated by atomic force microscopy, *Kautsch. Gummi Kunststoffe*, 2006, 5-06, 256.
- [3] K. Nakajima and T. Nishi, Nanoscience of single polymer chains revealed by nanofishing, *Chem. Rec.*, 2006, 6, 249.
- [4] H. Watabe, K. Nakajima, Y. Sakai and T. Nishi, Dynamic force spectroscopy on a single polymer chain, *Macromolecules*, 2006, 39, 5921.
- [5] K. Nakajima and T. Nishi, Dynamic nanofishing of single polymer chains, *Rubber Chem. Technol.*, 2009, 82, 271.
- [6] H. Nukaga, S. Fujinami, H. Watabe, K. Nakajima, T. Nishi, Nanorheological analysis of polymer surfaces by atomic force microscopy, *Jpn. J. Appl. Phys.*, 2005, 44, 5425.
- [7] H. Watabe, M. Komura, K. Nakajima, T. Nishi, Atomic force microscopy of mechanical property of natural rubber, *Jpn. J. Appl. Phys.*, 2005, 44, 5393.
- [8] T. Nishi, H. Nukaga, S. Fujinami and K. Nakajima, Nanomechanical mapping of carbon black reinforced natural rubber by atomic force microscopy, *Chinese J. Polym. Sci.*, 2007, 25, 35.
- [9] D. Wang, S. Fujinami, K. Nakajima, T. Nishi, True surface topography and nanomechanical mapping measurements on block copolymers with atomic force microscopy, *Macromolecules*, 2010, 43, 3169.

Electrical Modes in Scanning Probe Microscopy used for Investigation of Polymers

Stefan A.L. Weber¹, M. Retschke¹, Niko Haberkorn², Patrick Theato^{2,3}, Hans-Jürgen Butt¹, and Rüdiger Berger¹

¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

²Institute of Organic Chemistry, University of Mainz, Duesbergweg 10-14, 55099 Mainz, Germany

³School of Chemical and Biological Engineering, WCU Program of Chemical Convergence for Energy & Environment (C2E2), College of Engineering, Seoul National University, 151-744 Seoul, Korea

With the development of miniaturized electronic structures variations in electrical properties need to be studied on a nanometer scale. In contrast to scanning tunneling microscopy, conductive scanning force microscopy (C-SFM) allows studying composite materials with both conducting and insulating domains [1]. For hard surfaces such as silicon based electronics the C-SFM method is now used routinely to map local conductivity. However the applications of flexible and soft polymeric electronic components demand new methods for local electrical characterization. In particular, a limitation in the characterization of soft, fragile structures is given by the operation of C-SFM in contact mode. Hereby high lateral forces can be exerted on the sample by the scanning tip leading sometimes to severe modifications in the sample surface [1]. In order to avoid modifications of polymer surfaces we developed a new, gentle method that combines torsion mode topography imaging with conductive scanning force microscopy. Other than in intermittent contact or tapping mode, in torsion mode the tip vibrates laterally with respect to the sample surface. Thus the tip sample distance is kept constant. Now, by applying an electrical potential between an electrical conductive tip and sample, a current can be measured. By scanning the tip, local variations in the conductivity of the sample can be recorded.

As example, the topography and local conductivity variations on fragile free-standing nanopillar arrays were investigated. These samples were fabricated by an anodized aluminium oxide template process using a thermally cross-linked triphenylamine-derivate semiconductor. The nanoscale characterization method is shown to be non-destructive. Individual nanopillars were clearly resolved in topography and current images that were recorded simultaneously. The non-destructive nature of the mode enables studies on soft and fragile surface structures in the field of optoelectronics, data and energy storage, sensing and actuating.

References

- [1] Stefan A.L. Weber, Niko Haberkorn, Patrick Theato, and Rüdiger Berger, *Nano Letters*, 10, 1194–1197 (2010).
- [2] R. Berger, H.-J. Butt, M. Retschke, S. Weber, *Macromolecular Rapid Communications*, 30, 1167-1178, (2009).

Interchain Hydrogen-Bonding And Co-nonsolvency Effect of Polymers in Aqueous or Mixed Aqueous Solvents

Charles C. Han, Jinkun Hao, Guangcui Yuan, He Cheng

Joint Laboratory of Polymer Science and Materials, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, CAS, Beijing 100190, P. R. China

The inter molecular complexation of poly(acrylic acid)-*graft*-poly(ethylene oxide) PAA-g-PEO) in water has been studied by the Dynamic light scattering and viscometry. The results have been compared with PAA/PEO mixtures at the same conditions. The inter-polymer hydrogen bonding and the entropy loss was the main physical effects which causes the formation of stable complexation.

On the other hand, when we used mixed solvent of water and THF for poly(*N*-isopropylacrylamide) (PNIPAM), it can be shown that both water and THF are solvents for PNIPAM, but PNIPAM can be precipitate in a mixed solvent. In this study, a PNIPAM-*co*-PEG micro-gel was used to prevent the precipitation, so the influence of the solvent compositional fluctuations (due to the phase behavior of H₂O/THF) on the solvency and/or non-solvency of the PNIPAM-*co*-PEG can be studied and interpreted through the H-bonding with water and Van der Waals interaction with THF.

Recent Development of Neutron Scattering Methods for Structural Characterization of Polymeric Systems

SHIBAYAMA Mitsuhiro

*Neutron Science Laboratory, Institute for Solid State Physics, University of Tokyo,
Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
E-mail: sibayama@issp.u-tokyo.ac.jp*

Neutron scattering methods have several advantages in structure characterization of polymeric systems. In this presentation, we demonstrate (1) contrast-variation method useful for investigations of multi-component systems, (2) visualization-by-swelling method capable of structural analysis in hidden inhomogeneities of rubbers, and (3) evaluation of incoherent scattering intensity by transmission measurement.

Polymer chain conformation analyses in bulk and in solutions, miscibility of polymer blends, microphase separation and/or order-disorder transitions in block copolymers, etc., have been extensively investigated during the past 40 years.[1] Polymer gels are suitable systems for neutron scattering studies since one can introduce necessary scattering contrast by simply using deuterated solvents. Recently, nanocomposite hydrogels have been gathering much attention because of their potential applications in various fields.[2] Nanocomposite (NC) gels, consisting of poly(*N*-isopropylacrylamide) (PNIPA) and synthetic clay, laponite, and water, are classified to super-tough gels and exhibit significant physical properties, such as high elongations, high ultimate strengths, high transparency, large swelling/deswelling ratios, and high deswelling speed, etc.[3] Mixtures of clay and polymer in solution exhibit unique rheological properties, such as viscosity thickening or thinning depending on the concentrations. In order to describe these three-component systems, it is necessary, in principle, to evaluate three self-term partial scattering functions, $S_{ii}(q)$, and three cross-term partial scattering functions, $S_{ij}(q)$. By applying incompressibility assumption, the number of terms can be reduced to three, i.e., $S_{CS}(q)$, $S_{PS}(q)$, and $S_{CP}(q)$, as written by $I(q) = (\Delta\rho_{CS})^2 S_{CC}(q) + (\Delta\rho_{PS})^2 S_{PP}(q) + 2\Delta\rho_{CS}\Delta\rho_{PS}S_{CP}(q)$, where C, P, and S denote the clay, polymer, and solvent, respectively, and Dr_{ij} is the scattering length density difference. Neutron scattering allows one to vary the scattering contrasts by changing the D/H composition in the solvent. By setting $Dr_{CS} = 0$ (or $Dr_{PS} = 0$), $S_{PP}(q)$ (or $S_{CC}(q)$) is selectively obtained (the contrast matching method). Furthermore, a systematic variation of the solvent scattering length, simultaneous equations of $S_{CS}(q)$, $S_{PS}(q)$, and $S_{CP}(q)$ are obtained. By using the singular value decomposition method, these unknown partial scattering functions are

quantitatively evaluated (the contrast variation method). The contrast-variation method was applied to investigate anisotropic systems, e.g., the deformation mechanism of NC gels[4] and shear-induced viscosity thickening/thinning of clay-polymer aqueous systems, where pixel-by-pixel decomposition was carried out.

Second example is the “visualization-by-swelling method”. SANS technique can be highly useful even for structural characterization of natural rubber because it makes invisible network structure “visible” by immersing the polymer in deuterated solvent and succeeding swell of polymer chains. We carried out SANS study for NR in deuterated toluene (D-toluene) as a solvent and showed that there exist large inhomogeneities originating from protein aggregates, in addition to the blob scattering visualized by this method.[5,6]

We proposed a method to evaluate the incoherent scattering intensity, $(dS/dW)_{\text{inc}}$, for H-containing systems. This method, which hereafter we call ‘the transmission method’ (‘T method’), simply uses the transmission T and the thickness t of the sample and is given by $\left(\frac{d\Sigma}{d\Omega}\right)_{\text{inc}} = \frac{1}{4\pi} \frac{1-T}{t}$. Since both T and t are values routinely obtained in a SANS measurement for data reduction, the T method is quite useful. The validity and applicability of the T method are examined from theoretical and experimental viewpoints.[7]

References

- [1] See for example, J. Higgins and H. Benoit, *Polymers and Neutron Scattering*, Clarendon Press, Oxford 1994.
- [2] P. Schexnailder and G. Schmidt, Nanocomposiet polymer hydrogels, *Colloid Polym. Sci.*, 2009, 287, 1.
- [3] K. Haraguchi and T. Takehisa, Nanocomposite Hydrogels: A Unique Organic-Inorganic Network Structure with Extraordinary Mechanical, Optical, and Swelling/De-swelling Properties, *Adv. Mater.*, 2002 14 1120.
- [4] T. Nishida, H. Endo, N. Osaka, H-J. Li, K. Haraguchi, and M. Shibayama, Studies on Deformation Mechanism of Nanocomposite Gels by Contrast Variation Small-Angle Neutron Scattering, *Phys. Rev. E*, 2009 80, 030801.
- [5] T. Karino, Y. Ikeda, S. Kohjiya, and M. Shibayama, M., Nonuniformity in Natural Rubber As Revealed by Small-Angle Neutron Scattering, Small-Angle X-ray Scattering, and Atomic Force Microscopy, *Biomacromolecules*, 2007, 8, 693.
- [6] T. Suzuki, N. Osaka, H. Endo, M. Shibayama, Y. Ikeda, H. Asai, N. Higashitani, Y. Kokubo, S. Kohjiya, Non-uniformity in Cross-linked Natural Rubber as Revealed by Contrast-variation Small-angle Neutron Scattering, *Macromolecules*, 2010, 43, 1556.
- [7] M. Shibayama, T. Matsunaga, M. Nagao, Evaluation of Incoherent Scattering Intensity by Transmission and Sample Thickness, *J. Appl. Cryst.*, 2009, 42, 621.

L12

Fluorescence Correlation Spectroscopy for the Physics of Polyelectrolyte Single Chains*

Zhao, Jiang; Wang, Shengqin; Jia, Pengxiang

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Up to now, there still exist a lot of questions not well-understood regarding the physical and chemical properties of polyelectrolytes in a number of aspects of the structures, dynamics, etc.¹ The unsolved mysteries and complications come from the long-ranged electrostatic interactions and the existence of multiple ions (counterions and co-ions). These factors have made the characterization of polyelectrolyte rather difficult, both in solution and in aggregation state. For example, scattering methods such as static and dynamic light scattering, which have been very successful in studying neutral polymers, has found their limitation in studying charged polymers as polyelectrolytes. In dynamic light scattering experiments, two types of diffusive motion have been discovered for decades - the so-called “slow mode” and “fast mode”. Although being noticed for years, the physical origins of these modes are still unclear. One of the most popular explanations attributes the slow mode to the transient clusters formed by multiple polymer chains and the fast mode to the motion of the counterions. This fact has made it difficult to determine the structures of the polyelectrolyte single chains, such as the chain dimension (radius of gyration, hydrodynamic radius), the persistence length, the exclusive volume, etc. This is so because these methods have relatively low signal-to-noise ratio and consequently they have to work at relative high polymer concentration, under which condition the inter-chain interactions and further multi-chain aggregation appear. The solution to overcome such a difficulty is to increase the detection sensitivity so that the detection limit can be improved to much lower and therefore detection can be conducted at very low concentration.

Single molecule fluorescence microscopy and spectroscopy is one of the most sensitive optical methods and is capable of detecting individual molecules, to track its motion, to analysis the emission spectra, etc.

Fluorescence Correlation Spectroscopy (FCS) analyzes the fluctuation of fluorescence photon counts inside the confocal excitation volume (300-500 nm in diameter and 1-2 μm in length). By analyzing autocorrelation functions of fluorescence fluctuation, the diffusion coefficient of the fluorescent species under study is determined. FCS has been widely used in the field of biology to study the diffusion in cellular environment.² However, it is only recently that this technique has

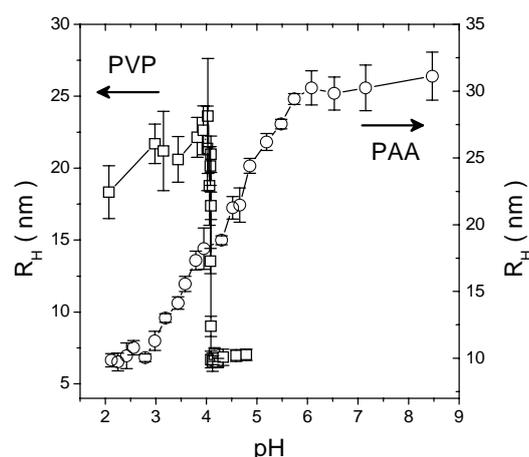


Figure 1 Hydrodynamic radius of single chain of PVP and PAA as a function of pH value.

* Project supported by the National Natural Science Foundation of China (NSFC).

been introduced to the field of polymer physics.³ FCS is very sensitive to monitor the fluctuation of fluorescence intensity and therefore is very capable of measuring diffusion rate of single fluorescent molecules, at a concentration of 10^{-9} - 10^{-12} M. This concentration range is at least 2-3 orders of magnitude lower than any other conventional techniques, and therefore provides a promising advantage when being applied to the problem of polyelectrolytes.

The conformation of polyelectrolyte single chain is highly dependent on the charge density of the backbone and the screening strength by external salt in the solution. FCS was applied to study conformation transition of polyelectrolytes, both strong (quenched) polyelectrolyte, such as polystyrene sulfonate (PSS^-) and weak (annealed) such as polyvinylpyridine (PVP) and polyacrylic acid (PAA). By tuning the pH value of the solution, the charge density of weak polyelectrolyte and the balance between the electrostatic repulsion of the charges on the chain and the hydrophobic attraction of the backbone.

Figure 1 shows the hydrodynamic radius of PVP and PAA as a function of pH value in the solution. The data clearly show the distinct difference of conformation transition - the discontinuous first-order transition of PVP and the continuous transition of PAA.⁴

For strong polyelectrolyte, its charge density is fixed as determined by the original chemistry. The factor governing the chain conformation is the polymer-counterion interaction, in which the electrostatic screening and counterion condensation involve. Figure 2 demonstrates the single chain contraction and re-expansion of PSS^- , in which the hydrodynamic radius of PSS^- was found to decrease at relatively low salt concentration, due to electrostatic screening of monovalent salt, and due to neutralization by multiple counterions. The chain is also found to re-expand for specific ions at higher concentration.⁴

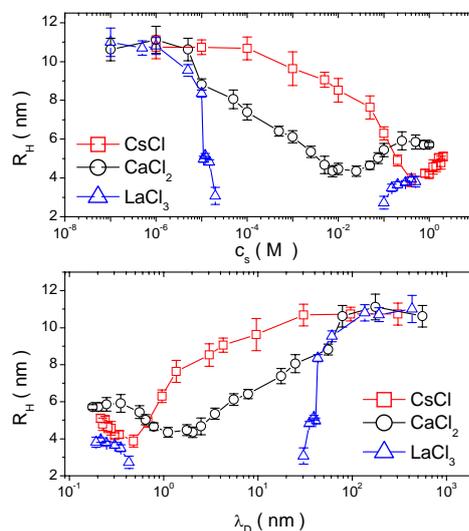


Figure 2 Value of hydrodynamic radius of PSS^- single chain as a function of salt concentration (top panel) and corresponding Debye length (bottom panel). The type of the salts is indicated in figures.

References:

- (1) F. Oosawa, Polyelectrolytes (Marcel Dekker, 1971); A. V. Dobrynin, M. Rubinstein, S. P. Obukhov, *Macromolecules* 29, 2974 (1996); *Macromolecules*, 32, 915 (1999).
- (2) D. Magde, E. Elson, W. W. Webb, *Phys. Rev. Lett.* 29, 705 (1972); R. Rigler, Widengren, *J. Bioscience*, 3, 180 (1990).
- (3) S. A. Sukhishvili, Y. Chen, J. D. Muller, E. Gratton, K. S. Schweizer, S. Granick, *Nature*, 406, 146 (2000).
- (4) P. X. Jia, J. Zhao *J. Chem. Phys.*, (2009) 131, 231103; S. Q. Wang, S. Granick, J. Zhao *J. Chem. Phys.* (2008) 129, 241102; S. Q. Wang, J. Zhao *J. Chem. Phys.* (2007) 126, 091104.

L13

Orientation Control of Microphase-Separated Domains of Block Copolymer Thin Films Placed on Surfaces with Tunable Interfacial Interactions and Roughness

CHAR, Kookheon*

*Intelligent Hybrids Research Center
School of Chemical & Biological Engineering
Seoul National University
Seoul 151-744, KOREA
E-mail: khchar@plaza.snu.ac.kr*

Polymer thin films with nanostructure and functions have recently received much attention due to many important potential applications such as nanolithography and nanopatterning for nanodevices, biologically relevant surfaces for sensors and drug delivery, photonic or electronic devices, and many others.

As the first part of the presentation, I will discuss the recent progress in our laboratory in block copolymer thin films: perpendicular orientation and defect minimization of block domains. Orientation of block copolymers (BCPs) in thin films is crucial to fully exploit the potential of these materials for applications in nanotechnology. A new approach will be introduced to induce the perpendicular orientation from the top of a BCP film toward a bottom substrate. Functional nano-objects such as quantum dots can also be arranged in block copolymer nanotemplates by selective solvent annealing. This new approach allows us to realize dual nano-object patterns in two different block regions.

The second part of the presentation consists of the orientation of microphase-separated domains of diblock copolymer thin films deposited on ordered nanoparticle (NP) monolayers. Ordered NP monolayers were prepared on silicon substrates with the Langmuir-Blodgett deposition technique. Parallel orientation of anisotropic microdomains (cylinders and lamellae) of BCP thin films with respect to the substrate is preferred on bare silicon substrates due to the preferential enthalpic interaction with one of BCP blocks, while the perpendicular orientation is preferred on the lattice-like ordered NP monolayers due to the roughness induced from the NP monolayers which can exert elastic deformation on the parallel-oriented microdomains, suppressing the substrate-induced parallel orientation. The effects of NP size as well as BCP film thickness on the orientation of BCP domains were systematically studied with AFM and Grazing Incidence Small-Angle X-ray Scattering (GISAXS).

Recent development of electron tomography for polymeric nano- and meso-structures

Hiroshi JINNAI^{a,b,*}

^a*Department of Macromolecular Science and Engineering, Graduate School of Science and Engineering, Kyoto Institute of Technology, Kyoto 606-8585, JAPAN*

^b*WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, JAPAN*

**E-mail: hjinnai@kit.ac.jp*

It has been shown that scanning transmission electron microtomography (STEMT) is quite effective for observing specimens with thicknesses on the order of micrometers in three dimensions (3D) [1-3]. In STEMT, the specimen is scanned using a focused electron beam, and the electrons from the convergence point are detected at the detector placed at a certain detection angle. Until recently, a wide detection angle corresponding to the mode often called the dark-field (DF-) mode was mainly used. Although the detection angle can vary and is one of the crucial experimental factors in STEMT, its effect on 3D reconstruction has never been discussed from either an experimental or a theoretical viewpoint. Moreover, the effectiveness of another mode of electron tomography, transmission electron microtomography (TEMT) [4,5], is not clear. In the present study, a polymeric specimen, an ABS resin, with a thickness of 1- μm and a fixed volume was observed using three different modes, namely, TEMT, small detection angle STEMT, referred to as bright-field (BF-) STEMT, and DF-STEMT, in order to examine their advantages and disadvantages by observing multiple scattering of electrons inside the specimen. We may also review some of our recent studies using TEMT [6] (if time allows).

Acknowledgements

The authors are grateful to Dr. S. Motoki, Dr. T. Kaneko, and Dr. T. Aoyama and Messrs. H. Nishioka, Y. Ohkura, and Y. Kondo (JEOL Ltd.) for their assistance in conducting the STEMT experiments. We gratefully acknowledge the financial support received through Grants-in-Aid No. 21241030 from the Ministry of Education, Science, Sports and Culture.

References

- [1] S. Motoki, T. Kaneko, Y. Aoyama, H. Nishioka, Y. Okura, Y. Kondo and H. Jinnai, Dependence of beam broadening on detection angle in scanning transmission electron microtomography, *J. Electron Microsc.*, in press.

- [2] K. Aoyama, T. Takagi, A. Hirase and A. Miyazawa, Stem tomography for thick biological specimens, *Ultramicroscopy*, 2008, 109, 70.
- [3] J. Loos, E. Sourty, K. Lu, B. Freitag, D. Tang and D. Wall, Electron tomography on micrometer-thick specimens with nanometer resolution, *Nano Lett.*, 2009, 9, 1704.
- [4] N. Kawase, M. Kato, H. Nishioka and H. Jinnai, Transmission electron microtomography without the “missing wedge” for quantitative structural analysis, *Ultramicroscopy*, 2007, 107, 8.
- [5] H. Jinnai, R. J. Spontak and T. Nishi, Transmission Electron Microtomography and Polymer Nanostructures, *Macromolecules*, 2010, 43, 1675.
- [6] H. Jinnai, T. Kaneko, K. Matsunaga, C. Abetz and V. Abetz, A double helical structure formed from an amorphous, achiral ABC triblock terpolymer, *Soft Matter*, 2009, 5, 2042.

Grazing Incidence X-Ray Scattering and Its Applications in Detailed Structure Analysis of Nanostructures

Moonhor Ree,* S. Jin, K. S. Jin, J. Yoon, Yecheol Rho, Byungcheol Ahn, Jungwoon Jung, Samdae Park, Jin Chul Kim, Mihee Kim, Sungmin Jung

Department of Chemistry, Pohang Accelerator Laboratory, Division of Advanced Materials Science, Center for Electro-Photo Behaviors in Advanced Molecular Systems, and Polymer Research Institute, POSTECH, Pohang 790-784, Korea

Phone: +82-54-279-2120 Fax: +82-54-279-3399 E-mail: ree@postech.edu

Homepage : <http://www.postech.ac.kr/chem/mree>

The Pohang Light Source (PLS) project was started in 1988 and its construction was completed in December, 1994. The PLS was designed to provide synchrotron radiation with continuous wavelengths down to 0.1 nm. The PLS was operated with 2.0 GeV until 1999 and upgraded to 2.5 GeV in 2000. The PLS has been serving domestic and international users since September, 1995. Currently 30 beamlines are in operation and 2 beamlines are under construction. Eight more beamlines are planned to be constructed within next five years. The user community in Korea has rapidly grown in number for the last 15 years and their research outputs also steeply increased in number (about 3,000 users visit the PLS facility every year) and significantly promoted in quality. Now the PLS has two main missions: one is to again upgrade the PLS to have 3.0 GeV power, 5 nm.rad emittance, 20 insertion device beamlines, and top-up mode operation system (so-called PLS-II project, which was started in January, 2009); the other is to construct an X-ray Free Electron Laser (XFEL) facility with 10 GeV power which aims to provide an X-ray laser with 0.05-0.1 nm wavelength and in femtosecond pulse (which is the PAL-XFEL project under an official review of Korean Government).

The PLS synchrotron radiation sources were used to characterize in detail nanostructures made of brush, star, and block copolymers. A variety of novel brush, star and block copolymers were designed and synthesized with optimizing functionality and self-assembly capability. In particular, brush polymers were extended to use as block components, providing brush polymer based block copolymers. Their self-assembly ability was practiced in various aspects of fabrication process in order to well control nanostructure, surface and functionality.

A series of functional brush copolymers based on polyether, polypeptide, polyvinyl, and polyimide backbones were synthesized with varying functionality at the bristle ends. In addition, several diblock copolymers, including linear and brush block copolymers, were prepared. Some star polymers were also synthesized. From these polymers, nanostructures were attempted to form in nanoscale thin films by conventional spin-coating and thermal or/and solvent annealing processes. The nanoscale thin films were quantitatively analyzed by using synchrotron grazing incidence X-ray scattering and reflectivity as well as atomic force microscopy. The surface and functionality of the nanostructures were studied in detail. Further, thermal, electrical and optical properties were investigated.

These studies demonstrated that brush copolymers can deliver well-defined nanostructures as well as well-controlled surfaces and functionalities, which are highly demanded in nanoscience, biomedical science, and information technology. Further, this study found that brush block containing

diblock copolymer can also provide very interesting self-assembly structure; moreover the self-assembly structures can go thermally induced phase transitions, creating attractive new nanostructures. Star polymers also provided very interesting nanostructures.

These studies were supported by the Korea Research Foundation (National Research Lab Program and Center for Electro-Photo Behaviors in Advanced Molecular Systems) and by the Ministry of Education, Science and Technology (Brain Korea 21 Program and World Class University Program). Synchrotron X-ray scattering and reflectivity measurements were supported by the Ministry of Education, Science and Technology, POSCO, and Pohang University of Science & Technology.

References

- [1] S. Jin, M. Ree et al., Synchrotron X-Ray Scattering Studies on Molecular Structures of Star-Shape Polystyrene with Various Arms, *J. Phys. Chem. B* (on Website; in press).
- [2] S. Jin, M. Ree et al., Synchrotron Grazing Incidence X-Ray Scattering Study of the Morphological Structures in Thin Films of a Polymethacrylate Diblock Copolymer Bearing POSS Moieties, *J. Phys. Chem. B* (in press).
- [3] K. S. Jin, M. Ree et al., Effect of C60 Fullerene on the Duplex Formation of i-Motif with Complementary DNA in Solution, *J. Phys. Chem. B* 2010, *114*, 4783.
- [4] G. Kim, Y. Rho, S. Park, H. Kim, S. Son, H. Kim, I. J. Kim, J. R. Kim, W. J. Kim, and M. Ree, The Biocompatibility of Self-Assembled Brush Polymers Bearing Glycine Derivatives, *Biomaterials* 2010, *31*, 3816.
- [5] M. Seo, M. Ree, S. Y. Kim et al., Surface-independent Vertical Orientation of Block Copolymer Films Directed by Comb-coil Architecture, *J. Mater. Chem.* 2010, *20*, 94..
- [6] G. Kim, M. Ree et al., Novel Brush Polymers with Phosphorylcholine Bristle Ends: Synthesis, Structure, Properties, and Biocompatibility, *Adv. Funct. Mater.* 2009, *19*, 1631.
- [7] S. R. Shin, K. S. Jin, M. Ree, S. J. Kim et al., Fullerene Attachment Enhances Performance of a DNA Nanomachine, *Adv. Mater.* 2009, *21*, 1907.
- [8] J. Yoon, M. Ree et al., Phase Transitions in Thin Films of a Diblock Copolymer Composed of a Linear Polymer Block and a Brush Polymer Block with Mesogenic Oligothiophenyl Bristles, *Macromolecules* 2008, *41*, 8778.
- [9] J. Yoon, M. Ree et al., Two-dimensionally Well-ordered Multilayer Structures in Thin Films of a Brush Polypeptide, *J. Phys. Chem. B* 2008, *112*, 5338.
- [10] K. Heo, T. Chang, M. Ree et al., Polystyrene-b-polyisoprene Thin Films with Hexagonally Perforated Layer Structure: Quantitative Grazing Incidence X-ray Scattering Analysis, *J. Appl. Crystallogr.* 2008, *41*, 281.
- [11] S. Jin, T. Chang, M. Ree et al., Detailed Analysis of Gyroid Structures in Diblock Copolymer Thin Films by Synchrotron Grazing Incidence X-ray Scattering, *J. Appl. Crystallogr.* 2007, *40*, 950.
- [12] B. Lee, M. Ree et al., Imprinting Well-controlled Nanopores in Organosilicate Dielectric Films: Triethoxysilyl-modified Six-armed Poly(ϵ -caprolactone) and Its Chemical Hybridization with Organosilicate Precursor, *Adv. Mater.* 2005, *17*, 696.
- [13] B. Lee, M. Ree et al., Ultralow-k Nanoporous Organosilicate Dielectric Films Imprinted with Dendritic Spheres, *Nat. Mater.* 2005, *4*, 147.
- [14] M. Ree, et al., Synchrotron Radiation Facilities in Korea: Pohang Light Source and Future XFEL Project, *Synchrotron Radiation News* 2009, *22*, 4.

Posters

1. Structural Analysis of Amphiphilic Liquid Crystalline Diblock Copolymer thin films and its Phase Transitions
Byungcheol Ahn, Jinhwan Yoon, Sangwoo Jin, Yecheol Rho, Sungmin Jung, Dongmin Kim, Jungwoon Jung, Kyungtae Kim, Samdae Park, Jinchul Kim, Wonsang Kwon, Junman Choi, Yonggi Ko, Mihee Kim, Tomokazu Iyoda, Hirohisa Yoshida, Moonhor Ree
2. Structure and Property Analysis of Nanoporous Low-k material using GISAXS and X-ray Reflectivity
Junman Choi, Kyuyoung Heo, Sung-Gyu Park, Jinhwan Yoon, Kyeong Sik Jin, Sangwoo Jin, Samdae Park, Jin Chul Kim, Dong Min Kim, Jungwoon Jung, Yecheol Rho, Byungcheol Ahn, Wonsang Kwon, Kyungtae Kim, Mihee Kim, Yong-Gi Ko, Sungmin Jung, Moonhor Ree
3. Honeycomb-Like Helical Fiber Structure by Self-Assembled Polypeptide
Jungwoon Jung, Gahee Kim, Jinhwan Yoon, Jong-Seong Kim, Taek Joon Lee, Samdae Park, Sangwoo Jin, Jinchul Kim, Dongmin Kim, Yecheol Rho, Byungcheol Ahn, Wonsang Kwon, Kyungtae Kim, Mihee Kim, Yong-Gi Ko, Sungmin Jung, Junman Choi, Heesoo Kim, Moonho Ree
4. Synchrotron X-Ray Scattering Studies on Characteristic Structure of Star and Dendritic Polymers
Sungmin Jung, Sangwoo Jin, Samdae Park, Jinchul Kim, Dongmin Kim, Jungwoon Jung, Yecheol Rho, Byungcheol Ahn, Wonsang Kwon, Kyungtae Kim, Mihee Kim, Yong-Gi Ko, Junman Choi, Moonhor Ree, Tomoya Higashihara, Takumi Watanabe, and Akira Hiaro
5. Three dimensional structural analysis of Fddd in diblock copolymer thin film
Jueun Jung, Hae-Woong Park, Junyoung Lee, Taihyun Chang, Hiroshi Jinnai
6. A Study on Dispersion of Inorganic Nanoparticles in the Polymer Nanocomposites
Jung-Hsuan Chen, Ya-Chun Sun, Shen-Chuan Lo, Li-Jiaun Lin, Chi-Yun Kang, Li-Duan Tsai
7. Characterization of polymer media for high density scanning probe based data storage
Tassilo Kaule, Sascha Pihan, Sebastian G.J. Emmerling, Yi Zhang Renate Förch, Jochen Gutmann, Hans-Jürgen Butt, Rüdiger Berger, , David Pires, Armin Knoll, Bernd Gotsmann, Urs Dürig

8. Determination of pH dependent structures of i-motif DNA using small angle X-ray scattering
Mihee Kim, Kyeong Sik Jin, Su Ryon Shin, Yecheol Rho, Byungcheol Ahn, Jungwoon Jung, Samdae Park, Dong Min Kim, Jin Chul Kim, Wonsang Kwon, Kyungtae Kim, Yong-Gi Ko, Junman Choi, Sungmin Jung, Moonhor Ree
9. Investigation of the Relationship between Structure and LC aligning ability of Polymer side chain
Yong-Gi Ko, Suk Gyu Hahm, Taek Joon Lee, Samdae Park, Jin Chul Kim, Dong Min Kim, Jungwoon Jung, Yecheol Rho, Byungcheol Ahn, Wonsang Kwon, Kyungtae Kim, Mihee Kim, Sungmin Jung, Junman Choi, Moonhor Ree
10. A study of structure and thermal degradation of flame retardant polycarbonate
Yoshiyuki Itoh , Hiroaki Sato, Masaaki Ubukata, Kanae Teramoto , Jun Tamura
11. Characterization of Organic/Inorganic Hydrogel using Irradiated Silica Particles by Gamma-Ray
Hoik Lee, Donghyun Kim, Daewon Sohn
12. Synthesis and Characterization of Model Star-Branched Polyelectrolytes
Holley, D. Wade, Baskaran, Durairaj, Mays, Jimmy W.
13. Quantitative Structure Analysis of Novel-conjugated Brush Copolymer Thin Film
Yecheol Rho, Jinhwan Yoon, Sangwoo Jin, Byungcheol Ahn, Tomoyasu Hirai, Rina Maeda, Taek Joon Lee, Samdae Park, Jin Chul Kim, KIM, Dong Mina, Jungwoon Jung, Wonsang Kwon, Kyungtae Kim, Mihee Kim, Yong-Gi Ko, Sungmin Jung, Junman Choi, Teruaki Hayakawa, Moonhor Ree
14. Finite element modeling and Crashworthiness of Expanded Polypropylene (EPP) for automotive seat
Srivastava Vivek, Sharma Ajay
15. Nanomechanical Thermal Analysis of Glass Transition of Poly(styrene-b-methyl methacrylate) using Silicon Cantilevers
Namchul Jung, Sangmin Jeon
16. Microthermogravimetry of a Single Microcapsule using Silicon Microresonators
Dongkyu Lee, Yongbeom Park, Soohyun Cho, Myungsun Yoo, Namchul Jung, Minhyuk Yun, Wooree Ko, Sangmin Jeon
17. The Effect of Screw Speed on Impact Strength of Polymer Blends through Twin Screw Extruder

M.R.Saeb, M.Omrani, M.Farahani, M.Razban

18. Nanomechanical Thermal Analysis of Photosensitive Polymers during Photodegradation Using Microcantilever Platform

Minhyuk Yun, Changyong Im, Namchul Jung, Sangmin Jeon

19. BioLCCC Model and Predictive Chromatography of Biopolymers

GORSHKOV Alexander V., EVREINOV Viktor V., GORHSKOV Mikhail

20. On the Movement of Spherical and Non-Spherical Particles Suspended in a Liquid and Exposed to Temperature Gradient Microthermal Field-Flow Fractionation

Josef Janča

21. Characterization of PS-g-PI Graft Copolymer with LCCC X SEC

Hyojoon Lee, Taihyun Chang

22. The Critical Molecular Size Parameter in Size Exclusion Chromatography: Theory and Experimental Evidence

Yanwei Wang, Iwao Teraoka, Flemming Y. Hansen, Günther H. Peters, O. Hassager

23. Rigorous 2D-LC analysis of comb shaped polymers using isotope effect

Seonyoung Ahn, Taihyun Chang

24. Compositional Characterization of PI-*b*-P2VP by Temperature-Gradient Interaction Chromatography

Junyoung Lee, Haiyung Hwang, Taihyun Chang

25. Photodegradation Behavior of High-Impact Polystyrene Studied by Pyrolysis-Gas chromatography

Hajime Ohtani, Takaaki Matsuda, Yasutaka Matsuda, Wataru Ito

26. Characterization of Cross-Linking Structure in Cured Thermosetting Resins by MALDI-Mass Spectrometry combined with Specific Sample Decomposition

Hajime Ohtani, Mami Kamiyama

27. Polymer Analysis using Offline SEC-FTIR, MALDI-MS, and DART-MS

Hiroshi Takayama, Koutatsu Matsubara, Tomoyuki Ozawa, Hisae Miyamoto, Tatsuya Seki

28. End-Functionality Study of PS-Br synthesized by ATRP using MALDI-ToF MS

Kihyun Kim, Taihyun, Chang, Aleya Hasneen, Hyun-Jong Paik

29. Synthesis of Polymer containing Platinum/Gold Nanoparticles and Physical Characterization
A-Young Sung, Ki-Hun Ye
30. Silver/Platinum Nanoparticles added Polymerization and Application for Contact Lens
A-Young Sung, Tae-Hun Kim
31. Assignment of NMR spectra of Poly(1-vinylpyrrolidone) by Multivariate Analysis
Tomohiro Hirano, Takuya Anmoto, Hikaru Momose, Koichi Ute
32. Determination of Comonomer Sequence Distributions of MMA-TBMA Copolymers by means of Multivariate Analysis of ^{13}C NMR Spectra
Hikaru Momose, Tomoya Maeda, Tomohiro Hirano, Koichia Ute
33. Characterization of Methacrylate Terpolymers by Multivariate Analysis of ^{13}C NMR Spectra
Tatsuya Naono, Hikaru Momose, Tomohiro Hirano, Koichi Ute
34. Thermo-sensitive Pluronic F127-bPEI-NONOate as a new nitric oxide donor
Jihoon Kim, Kaushik Singha, Won Jong Kim
35. Preparation of lanthanide alginate from algae and its characterization
Jin-San Kim, Tara Sankar Pathak, Sanghyuk Kang, Ki-Jung Paeng
36. Magnet-Assisted Gene Delivery with Hybrid Superparamagnetic Iron Oxide Nanoparticle-Branched Polyethylenimine Magnetoplexes on Vascular Endothelial Cells
Ran Namgung, Kaushik Singha, Mi kyung Yu, Sangyong Jon, Yong Sook Kim, Youngkeun Ahn, In-kyu Park, Won Jong Kim
37. Synthesis and Characterization of Bio-reducible BPEI-SS-PEG-cNGR as a Tumor Targeted Nonviral Gene Carrier
Sejin Son, Won Jong Kim
38. Programmable Permanent Data Storage Devices based on Nanoscale Thin Films of a Thermally Stable Aromatic Polyimide
Dong min Kim, Samdae Park, Kyungtae Kim, Yong-gi Ko, Jin chul Kim, Wonsang Kwon, Junman Choi, Moonhor Ree
39. High-Performance Unipolar and Bipolar Electronic Memory Polyimide Bearing Triphenylamine-Related Moieties
Kyungtae Kim, Samdae Park, Dongmin Kim, Yong-gi Ko, Jinchul Kim, Jungwoon

Jung, Yecheol Rho, Byungcheol Ahn, Wonsang Kwon, Mihee Kim, Sungmin Jung, Junman Choi, Moonhor Ree

40. Electrically programmable memory characteristics on the film surfaces of novel polyimide

Wonsang Kwon, Taekjoon Lee, Cha-Wen Chang, Sukgyu Hahm, Kyungtae Kim, Samdae Park, Dongmin Kim, Jinchul Kim, Sangwoo Jin, Jungwoon Jung, Yecheol Rho, Byungcheol Ahn, Mihee Kim, Yong-Gi Ko, Sungmin Jung, Junman Choi Guey-Sheng Liou, Moonhor Ree

41. Programmable Digital Memory Characteristics of Nanoscale Thin Films of a Fully Conjugated Polymer

Samdae Park, Taekjoon Lee, Sukgyu Hahm, Dongmin Kim, Kyungtae Kim, Jinchul Kim, Won-Sang Kwon, Junman Choi, Moonhor Ree

42. Enhanced Device Performance of Organic Solar Cells via Reduction of the Crystallinity in the Donor Polymer_

Jong-hwan Park, J.-I. Park, D. H. Kim, J.-H. Kim, J. S. Kim, J. H. Lee, M. Sim, S. Y. Lee, K. Cho

43. Charge transport anisotropy in the transistor of 6,13-bis(triisopropylsilylethynyl) pentacene single crystal with cofacial molecular stacks

Hyunho Choi, Dohwan Kim, Wihyoung Lee, Jung-ah Lim, Donghoon Kwak and Kilwon Cho

44. Bulk heterojunction solar cells based on preformed polythiophene nanowires via solubility-induced crystallization

Joohyun Kim, J. H. Park, J. H. Lee, J. S. Kim, M. Sim, C. Shim, K. Cho

45. High-Performance Organic Transistors from Soluble Acene-Polymer Blend Semiconductors

Wi Hyoung Lee, Donghoon Kwak, and Kilwon Cho

Structural Analysis of Amphiphilic Liquid Crystalline Diblock Copolymer thin films and its Phase Transitions

Byungcheol Ahn^a, Jinhwan Yoon^a, Sangwoo Jin^a, Yecheol Rho^a, Sungmin Jung^a, Dongmin Kim^a,
Jungwoon Jung^a, Kyungtae Kim^a, Samdae Park^a, Jinchul Kim^a, Wonsang Kwon^a, Junman Choi^a,
Yonggi Ko^a, Mihee Kim^a, Tomokazu Iyoda^b, Hirohisa Yoshida^c, Moonhor Ree^{*a}

^a Pohang University of Science and Technology, Pohang, Republic of Korea,

^b Tokyo Institute of Technology, Yokohama, Japan

^c Tokyo Metropolitan University, Tokyo, Japan,

* E-mail: ree@postech.edu, Tel: +82-54-279-2120

In this study, we investigated the temperature-dependent phase transition behaviors of thin films of an amphiphilic diblock copolymer, poly(ethylene oxide)-b-poly(11-[4-(4-butylphenyl-azo)phenoxy] undecyl methacrylate) (p(EO)-b-p(MAAZ)) and resulting morphological structures by using synchrotron grazing incidence X-ray scattering (GIXS) and differential scanning calorimetry. The quantitative GIXS analysis showed that the diblock copolymer in the homogeneous, isotropic melt state undergoes phase separation near 190 °C and then forms a body-centered cubic of p(EO) domain. In further cooling, p(EO) domain converted to a stable hexagonal cylinder structure near 120 °C. Also, liquid phase of the p(EO) cylinders undergoes crystallization near -15 °C. Complicated temperature-dependent disorder-order and order-order phase transitions in the films were found to take place reversibly during the heating run. We use these structural analysis results to propose molecular structure models at various temperatures for thin films of the diblock polymer.

Structure and Property Analysis of Nanoporous Low- k material using GISAXS and X-ray Reflectivity

Junman Choi, Kyuyoung Heo, Sung-Gyu Park, Jinhwan Yoon, Kyeong Sik Jin, Sangwoo Jin, Samdae Park, Jin Chul Kim, Dong Min Kim, Jungwoon Jung, Yecheol Rho, Byungcheol Ahn, Wonsang Kwon, Kyungtae Kim, Mihee Kim, Yong-Gi Ko, Sungmin Jung, Moonhor Ree*

Department of Chemistry and Center for Electro-Photo Behaviours in Advanced Molecular Systems, POSTECH, Pohang, Republic of Korea, 790-784

**E-mail: ree@postech.edu*

We have carried out grazing incidence X-ray scattering measurements and specular X-ray reflectivity analysis of the nanoporous structures of low dielectric constant (low k) carbon-doped silicon oxide (SiCOH) films, which were prepared with plasma-enhanced chemical vapor deposition (PECVD) from vinyltrimethylsilane, divinyltrimethylsilane, and tetraethylsilane as silane precursors and oxygen gas as an oxidant and then thermally annealed under various conditions. In addition, we measured the refractive indices and dielectric constants of the dielectric films. The nanoporous SiCOH thin films produced in the present study were homogeneous and had well-defined structures, smooth surfaces, and excellent properties and, thus, are suitable for use as low k interdielectric layer materials in the fabrication of advanced integrated circuits. In particular, the vinyltrimethylsilane precursor, which contains only one vinyl group, was found to produce SiCOH films after PECVD and annealing at 450 °C for 4 h with the highest population of nanopores and the lowest electron density, refractive index, and dielectric constant.

Honeycomb-Like α -Helical Fiber Structure by Self-Assembled Polypeptide

Jungwoon Jung^a, Gahee Kim^a, Jinhwan Yoon^a, Jong-Seong Kim^a, Taek Joon Lee^a, Samdae Park^a, Sangwoo Jin^a, Jinchul Kim^a, Dongmin Kim^a, Yecheol Rho^a, Byungcheol Ahn^a, Wonsang Kwon^a, Kyungtae Kim^a, Mihee Kim^a, Yong-Gi Ko^a, Sungmin Jung^a, Junman Choi^a, Heesoo Kim^{b,*}, and Moonho Ree^{a,*} E-mail: ree@postech.edu

^aDepartment of Chemistry, National Research Laboratory for Polymer Synthesis and Physics, Pohang Accelerator Laboratory, Center for Electro-Photo Behaviors in Advanced Molecular Systems, BK School of Molecular Science, Division of Advanced Materials Science, and Polymer Research Institute, Pohang University of Science & Technology, Pohang 790-784, Republic of Korea

^bDepartment of Microbiology, Dongguk University College of Medicine, Gyeongju 780-714, Republic of Korea

We have succeeded in fabricating well-grown molecular fibers of a poly(benzyloxycarbonyl-lysine), on substrates by using a conventional solution spin-coating and drying process. The polypeptide was synthesized by carrying out the ring-opening polymerization of benzyloxycarbonyl-lysine. The resulting films were quantitatively analyzed by AFM, FTIR and GIXS. These molecular fibers were found to consist of a honeycomb-like molecular assembly formed via the hexagonal close packing of the polypeptide chains in the α -helix conformation. The molecular dimensions of single chains were estimated to be 1.53 nm diameter and 3.04 nm length. From the molecular parameters of α -helical polypeptide chain, GIXS pattern was regenerated successfully. In addition, developed fibers were shown different fibril length and domain size in the films fabricated from different solution, THF and DMF. These differences might be due to the differences between the characteristics of THF and DMF. Therefore molecular mobility was affected by the solution during the film formation process.

Synchrotron X-Ray Scattering Studies on Characteristic Structure of Star and Dendritic Polymers

Sungmin Jung^a, Sangwoo Jin^a, Samdae Park^a, Jinchul Kim^a, Dongmin Kim^a, Jungwoon Jung^a, Yecheol Rho^a, Byungcheol Ahn^a, Wonsang Kwon^a, Kyungtae Kim^a, Mihee Kim^a, Yong-Gi Ko^a, Junman Choi^a, and Moonhor Ree^{*a}, E-mail: ree@postech.edu
Tomoya Higashihara^b, Takumi Watanabe^b, and Akira Hiaro^{*b}

^a*Department of Chemistry, National Research Laboratory for Polymer Synthesis and Physics, Pohang Accelerator Laboratory, Center for Electro-Photo Behaviors in Advanced Molecular Systems, BK School of Molecular Science, Division of Advanced Materials Science, and Polymer Research Institute, Pohang University of Science & Technology, Pohang 790-784, Republic of Korea*

^b*Polymeric and Organic Materials Department, Graduate School of Science and Engineering, Tokyo Institute of Technology, H-127, 2-12-1, Ohokayama, Meguro-ku Tokyo 152-8552, Japan*

We studied the molecular shapes and structural characteristics of a 33-armed, star polystyrene (PS-33A) and two 3rd-generation, dendrimer-like, star-branched poly(methyl methacrylate)s with different architectures (PMMA-G3a and PMMA-3Gb) and 32 end-branches under good solvent and theta (Θ) solvent conditions by using synchrotron small angle X-ray scattering (SAXS). The SAXS analyses were used to determine the structural details of the star PS and dendrimer-like, star-branched PMMA polymers. PS-33A had a fuzzy-spherical shape, where PMMA-G3a and PMMA-G3b has fuzzy-ellipsoidal shapes of similar size, despite their different chemical architectures. The star PS polymer's arms were more extended than those of linear polystyrene. Furthermore, the branches of the dendrimer-like, star-branched polymer were more extended than those of the star PS polymer despite having almost the same number of branches as PS-33A. The differences between the internal chain structures of these materials was attributed to their different chemical architectures.

Three dimensional structural analysis of *Fddd* in diblock copolymer thin film

Jueun Jung^a, Hae-Woong Park^a, Junyoung Lee^a, Taihyun Chang^{a,*}, Hiroshi Jinnai^b

^a*Department of Chemical, Pohang University of Science and Technology, Pohang, 790-784, Kyungbuk, Korea, Email: tc@postech.ac.kr*

^b*Materials and Life Science, Molecular Science and Engineering, Kyoto Institute of Technology, Kyoto, 606-8585, Japan*

Block copolymer adopts various nanoscale morphologies via microphase separation. The phase is governed by total number of segment (N), composition (f) and interaction parameter (χ) of each blocks. In diblock copolymer, which is the simplest one composed of two chemically different polymers, several structures such as lamellar, hexagonally packed cylinder, spheres arranged in body centered cubic lattice, double gyroid and hexagonally perforated lamellar are well established and recently *Fddd* phase was experimentally found in bulk state. *Fddd* phase is a three dimensional network morphology, of which the skeleton of the minor block consists of 3-fold connectors in orthorhombic unit cell with *Fddd* space group.

In this study, we identified *Fddd* phase in diblock copolymer thin film using transmission electron microtomography. When ordered morphology is fabricated onto a Si wafer, their orientation is influenced by the thin film confinement. The specific plane which makes the densest packing at out of direction is located to parallel to the film plane. *Fddd* phase is well aligned at the out-of-plane direction by interfaces without mechanical shear force. And interfacial layer deviated from internal structure, *Fddd*.

Reference

- [1] Kim, MI; Wakada, T; Akasaka, S; Nishitsuji, S; Saijo, K; Hasegawa, H; Ito, K; Takenaka, M; Determination of the *Fddd* Phase Boundary in Polystyrene-block-polyisoprene Diblock Copolymer Melts, *Macromolecules*, 2009, 42, 5266
- [2] Ahn, H; Shin, C; Lee, B; Ryu, DY; Phase Transitions of Block Copolymer Film on Homopolymer-Grafted Substrate, *Macromolecules*, 2010, 43, 1958

A Study on Dispersion of Inorganic Nanoparticles in the Polymer Nanocomposites

Jung-Hsuan Chen^{a,*}, Ya-Chun Sun^a, Shen-Chuan Lo^{a,b}, Li-Jiaun Lin^a, Chi-Yun Kang^a, Li-Duan Tsai^a

^a*Material and Chemical Research Laboratories, Industrial Technology Research Institute,
Hsinchu, 31050 Taiwan, Republic of China, E-mail: jhc@itri.org.tw*

^b*Nanotechnology Research Center, Industrial Technology Research Institute,
Hsinchu, 31050 Taiwan, Republic of China*

In the past decade, inorganic nano-filler have been attracting increasing attention in the scientific and industrial community as they are capable of improving the mechanical and physical properties of the polymer. [1-3]. Lots of research literatures have been reported that the addition of inorganic nanofiller; such as clay, silica, carbon nanofiber and carbon nanoparticles; in the polymer can improve its mechanical, thermal and electrical properties. Their nanometer size, shape and distribution leading to high specific surface areas and extraordinary mechanical, electrical, and thermal properties make them become unique nano-fillers for structural and multifunctional composites. However, to date, few work has been devoted to the quantitatively characterization method both in nano and micro scale for the structure and dispersion of the nano-filler in the polymer based on scanning probe microscopy (SPM) techniques.

In the present study, the polymer nanocomposites apply to hybrid conductive electrode films were fabricated with carbon nanoparticles and home-made specified polymer. Since the dispersion and distribution of carbon nanoparticles would affect the electrical properties of the nanocomposites film, therefore, it was an important issue to resolve the dispersion of carbon particles in the polymer. The quantitative measurement of carbon particles dispersion in the polymer was developed in this study. Including: 1. flat specimen preparation procedure for SPM with surface roughness below 1 um, 2. production of high resolution morphological images, phase images and current images of SPM, and 3. quantitatively calculation method of the dispersion of carbon nanoparticles in the polymer. The detail of the quantitatively method for dispersion of nano-fillers proposed will be presented in this conference.

Reference

- [1] H. C. Leventis, S. P. King, A. Sudlow, M. S. Hill, K. C. Molloy, S. A. Haque, Nanostructured Hybrid Polymer-Inorganic Solar Cell Active Layers Formed by Controllable in Situ Growth of Semiconducting Sulfide Networks, *Nano Letters*, 2010, *10*, 1253.
- [2] S. Lewis, V. Haynes, R. Wheeler-Jones, J. Sly, R. M. Perks, L. Piccirillo, Surface characterization of poly(methylmethacrylate) based nanocomposite thin films containing Al₂O₃ and TiO₂ nanoparticles, *Thin Solid Film*, 2010, *518*, 2683.
- [3] A. Montazeri, R. Naghdabadi, Study the Effect of Viscoelastic Matrix Model on the Stability of CNT/Polymer Composites by Multiscale Modeling, *Polymer Composites*, 2009, *30*, 1545.

Characterization of polymer media for high density scanning probe based data storage

Tassilo Kaule ^{*,a}, Sascha Pihan ^a, Sebastian G.J. Emmerling ^a, Yi Zhang ^a, Renate Förch ^a, Jochen Gutmann ^a, Hans-Jürgen Butt ^a, Rüdiger Berger ^a, David Pires ^b, Armin Knoll ^b, Bernd Gotsmann ^b, Urs Dürig ^b

^aMax Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany,

^bZurich Research Laboratory, IBM Research, 8803 Rüschlikon, Switzerland

*Email: kaule@mpip-mainz.mpg.de

Polymers are very interesting materials for ultra high-data-density storage media. Hereby writing and reading can be realized by scanning probe microscopy methods and data densities beyond 1 Tbit/inch² were reported, recently [1]. Here we present our investigations on plasma polymerized thin films which can be specifically tailored to the requirements of ultra high-data-density storage media. In particular, stacks of polymer films were characterized by means of scanning probe microscopy methods and X-ray reflectivity (XRR) measurements. Stacks of polymers were deposited via plasma-polymerization [2-3] on top of spin coated polystyrene (PS) films or on Si wafer substrates. Two different precursor monomers were investigated which vary in their oxygen content: Hexamethyldisiloxane (HMDSO) (C₆H₁₈OSi₂) and norbornene (C₇H₁₀). The plasma dissociates precursor monomers, generates radicals which may react with each other and thus lead to a film formation on top of all surfaces in the reactor chamber. Furthermore surfaces in the plasma reactor are exposed to the bombardment of ionized species which may influence substrate properties. By increasing the plasma power more radicals can be formed which often result in a higher crosslinked polymer film. Thus, the mechanical properties of the polymer film can be adjusted for a specific application. In order to further control the film properties the plasma deposition process can be performed in the presence of additional gases in the plasma reactor, e.g. oxygen.

We investigated stacks of films made by plasma polymerization of HMDSO deposited under alternating plasma conditions leading to an alternation of mechanical properties [4]. Scanning force microscopy on the face-side of fractured pieces of the multilayer structures revealed a significant phase contrast between the layers. The direct visualization of the interface using the mechanical contrast between layers allowed the estimation of the interfacial roughness. We found that the interfaces between hard, oxygen rich HMDSO films deposited on top of softer, oxygen-poor HDMSO films resulted in an interface roughness of 10 nm. In the reverse case, a significantly lower interface roughness of 3 nm was determined.

We attribute the increase of the interfacial roughness compared to the surface roughness being < 1 nm to partial etching of the films by the subsequent deposition process.

The knowledge that was obtained with the stack of plasma deposited layers was extended to the investigation of hyper thin plasma polymer layers that were deposited on spin coated polystyrene substrates. Such hyper thin films with thicknesses < 10 nm can be used as suitable wear resistant cover layers for high density data recording. A hyper thin polymer cover layer is required to enable thermomechanical writing in the layered medium using scanning probe methods. Thus the exact thickness, the surface and the interface roughness plays a crucial role in the performance of the high density data storage medium. Results from XRR measurements showed that the plasma polymerized norbornene films had thickness below 10 nm with an measurement accuracy better than 1 nm. Furthermore, XRR showed that the interface between the plasma deposited cover and the spin coated PS layer has a roughness of about 10 Å. This interface roughness is significantly higher compared to the surface roughness of spin coated PS only (5 Å). This effect can be explained by etching of the PS layer during the plasma process. Although the interface roughness is increased, wear resistivity depends on the binding strength between the PS and the cover layer. This binding strength is increased by creating more reactive binding sites on the PS surface during etching of the surface. Thus, the stack investigated here showed an excellent wear resistivity in comparison to the uncovered PS media.

Our characterization of stacked polymeric systems leads to insights of the interface roughness between thin polymer layers. We demonstrated that hyper thin plasma deposited polymer layers can significantly enhance the wear properties of soft polymer storage media. Writing and reading of plasma polymer covered PS films were demonstrated at an area density > 1 Tbit/inch².

References

- [1] D. Wiesmann, C. Rawlings, F. Porro, B. Gotsmann, A. Knoll, D. Pires, U. Duerig, Multi Tbit/in² Storage Densities with Thermomechanical Probes, Nano Letters, 2009, Vol.9, No.9, 3171 – 3176
- [2] L. Chu, W. Knoll, R. Förch, Pulsed Plasma Polymerized Di(ethylene glycol) Monovinyl Ether Coatings for Nonfouling Surfaces, Chem. Mater., 2006, 18, 4849-4844
- [3] R. Forch, Z. H. Zhang, W. Knoll, Soft Plasma Treated Surfaces: Tailoring of Structure and Properties for Biomaterial Applications Plasma Processes and Polymers, 2005, 2, 351-372.
- [4] Y. Zhang, J. Arfsten, S. A. Pihan, T. Kaule, R. Förch, R. Berger, Interface roughness of plasma deposited polymer layers, Journal of Colloid and Interface Science, submitted April 2010.

Determination of pH dependent structures of i-motif DNA using small angle X-ray scattering

Mihee Kim^a, Kyeongsik Jin^a, Suryon Shin^b, Yecheol Rho^a, Byungcheol Ahn^a, Jungwoon Jung^a, Samdae Park^a, Dongmin Kim^a, Jinchul Kim^a, Wonsang Kwon^a, Kyungtae Kim^a, Yong-Gi Ko^a, Junman Choi^a, Sungmin Jung^a, Moonhor Ree^{a*}

*^aDepartment of Chemistry, National Research Laboratory for Polymer Synthesis and Physics, Pohang Accelerator Laboratory, Center for Electro-Photo Behaviors in Advanced Molecular Systems, BK School of Molecular Science, Division of Advanced Materials Science, and Polymer Research Institute, Pohang University of Science & Technology, Pohang 790-784, Republic of Korea *E-mail: ree@postech.edu*
^bCenter for Bio-Artificial Muscle and Department of Biomedical Engineering, Hanyang University, Seoul 133-791, Republic of Korea

DNA has been shown to be an extremely versatile building material that is suitable for artificial nanomotor and nanomachines owing to self-assembly ability. i-motif is a four-stranded DNA structure that forms intramolecular noncanonical base pair interactions between a protonated and an unprotonated cytosine residue under slightly acidic conditions. Understanding of the detailed three-dimensional (3D) structure of i-motif DNA at various pH values is becoming an important challenge in the design of DNA-nanoactuator devices and biological cycle operating systems. We have investigated for the first time the structure of i-motif DNA in solution at various pH conditions by using synchrotron small-angle X-ray scattering technique. To facilitate direct structural comparison between solution structures of i-motif DNA at various pH values, we created atomic coordinates of i-motif DNA from a fully folded to unfolded atomic model. Under mild acidic conditions, the conformations for i-motif DNA appeared to be similar to that of the partially unfolded i-motif atomic model in overall shape, rather than the fully folded i-motif atomic model. On the other hand, i-motif DNA adopted fully folded random coil conformation bearing some resemblance to the simulated right handed helical conformation under alkali condition. Collectively, our observations indicate that i-motif DNA molecule is structurally dynamic over a wide pH range, adopting multiple conformations ranging from the folded i-motif structure to a random coil conformation. As the i-motif structure has been used as an important component in nanomachines, we can therefore believe that the structural evidence presented herein will promote the development of future DNA-based molecular-actuator devices.

Investigation of the Relationship between Structure and LC aligning ability of Polymer side chain

Ko Yong-Gi, Hahm Suk Gyu, Lee Taek Joon, Park Samdae, Kim Jin Chul, Kim Dong Min, Jung Jungwoon, Rho Yecheol, Ahn Byungcheol, Kwon Wonsang, Kim Kyungtae, Kim Mihee, Jung Sungmin, Choi Junman and Ree Moonhor *

*Department of Chemistry, National Research Laboratory for Polymer Synthesis and Physics, Center for Electro-Photo Behaviors in Advanced Molecular Systems, BK School of Molecular Science, Division of Advanced Materials Science, and Polymer Research Institute, Pohang University of Science & Technology, Pohang, Republic of Korea, 790-784 *E-mail: ree@postech.edu*

Most of the applications of Polyimides (PIs) are their use in liquid crystal (LC) alignment layers in flat-panel LC display (LCD) devices.¹⁻³ In the present study we synthesized three new soluble and photoreactive polyimides (PSPIs) bearing cinnamoyl, 3-(2-furyl)acryloyl, and methacryloyl chromophores, and characterized their thin films with and without linearly polarized UV light (LPUVL) exposure or rubbing treatment, in particular investigating their thermal properties, photoreactivity, photoalignability, rubbing-alignability, molecular orientation, and surface topography, as well as their alignability, pretilting and anchoring of LC molecules. These PSPIs were found to have excellent properties and processabilities that make them suitable as LC alignment layer materials for the rubbing-free production of LCD devices, particularly LCD devices with large display areas such as LCD televisions.

A study of structure and thermal degradation of flame retardant polycarbonate

Yoshiyuki Itoh, Hiroaki Sato, Masaaki Ubukata, Kanae Teramoto, Jun Tamura

^a Mass Spectrometry Business Unit, JEOL Ltd., 1-2 Musashino 3-Chome, Akishima, Tokyo 196-8558, Japan ^b Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16-1, Onogawa, Tsukuba, Ibaraki 305-8569, Japan Email: tamura@jeol.co.jp

Many kinds of brominated flame retardants (BFRs) are used as additives for plastic materials. The impact of BFRs on the environment and their potential risks for animals and humans is big concern for the scientific community. Recently, the analysis methods of low-molecular-weight BFRs were developed and the information about their risks began to be accumulated. On the other hands, the investigation about analysis methods or risk assessment of high-molecular-weight BFRs has not progressed enough.

In this study, the structural analysis of the high-molecular-weight BFRs were investigated by using a pyrolyser (Py) combined with gas chromatograph – time-of-flight mass spectrometer (GC-TOFMS) system and matrix-assisted laser desorption/ionization (MALDI) – Spiral TOFMS system¹⁾, a very high resolving power MALDI-TOFMS system. In addition, the thermal degradation of such BFRs was also evaluated by using a direct analysis in real time (DART)²⁾ – TOFMS system.

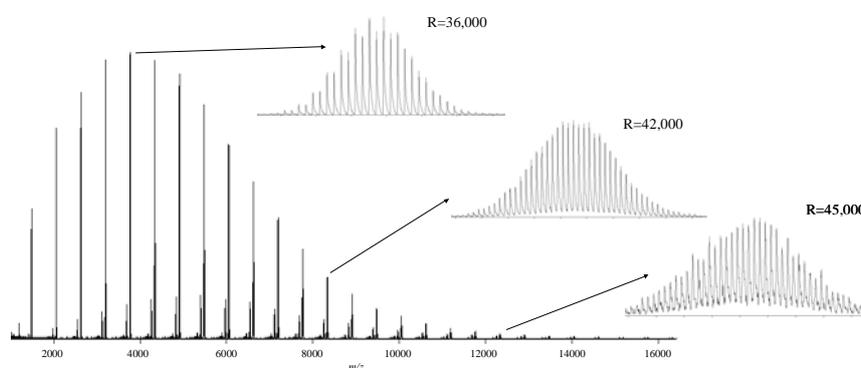
Brominated flame retardant polycarbonate (FRPC), a high-molecular-weight BFR, was purchased from NIHON-KAGAKUJYOHO Ltd. FRPC sample dissolved in tetrahydrofuran (THF) was directly applied for Py-GC-TOFMS analysis without further sample preparation. The same sample solution was analyzed by DART-TOFMS. Volatile compounds generated from FRPC at 300°C DART gas stream condition were detected. The FRPC sample solutions were also analyzed by the MALDI-SpiralTOFMS. Both of fresh sample and the sample that had been analyzed by DART-TOFMS were analyzed to investigate the thermal degradation of FRPC under the 300°C DART gas stream condition.

Mass spectrum signals of the fresh FRPC sample measured by MALDI-SpiralTOFMS using trans-2-(3-(4-t-Butyl-phenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) as a matrix distributed in the range of m/z 900 – 20,000. Mass spectral peaks around m/z 920 showed a typical isotopic pattern of brominated compounds. This pattern suggested that the signals were of the FRPC monomer that contains four bromine atoms. Other peaks were attributed to dimer, trimer, etc., up to (and beyond) triacontamer.

The measured accurate m/z value of the monoisotopic ion of the sodiated FRPC monomer was 914.9136. The elemental composition of the ion was deduced as $C_{37}H_{36}O_6Br_4Na$, suggesting that the end group on either end is *tert*-butylphenyl group. The result of Py-GC-TOFMS analysis also suggested the presence of *tert*-butylphenyl group in the FRPC sample.

With the DART-TOFMS analysis, no apparent MS signals were observed under 200 °C DART gas stream condition, but the MS signal from FRPC monomer was detected at 300 °C. The FRPC sample that had been exposed to the 300 °C DART gas stream was re-analyzed by MALDI-SpiralTOFMS and the mass spectral peaks attributed to the thermal degradation products of FRPC were clearly observed.

In this study, we achieved to collect the overall information of a high-molecular-weight BFR, FRPC, by using the combination analysis of DART-TOFMS, Py-GC-TOFMS and MALDI-SpiralTOFMS. Especially, it is suggested that the high mass-resolving power of SpiralTOFMS has an advantage for the analysis of brominated compounds such as BFRs that gives a complicated mass spectrum due to their isotopic distribution. The combination of DART-TOFMS and MALDI-SpiralTOFMS allowed for the easy detection of the volatile compounds and the thermal degradation products from FRPC.



Wide Mass Range Spectrum of FRPC obtained by MALDI-SpiralTOF

References

- [1] Satoh, T., Sato, T., Tamura, J., Development of a High-Performance MALDI-TOF Mass Spectrometer Utilizing a Spiral Ion Trajectory, *J. Am. Soc. Mass Spectrom.*, 2007, 18, 1318
- [2] Cody, R.B.; Laramée, J.A.; Durst, H.D., Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions, *Anal. Chem.*, 2005, 77, 2297

Characterization of Organic/Inorganic Hydrogel using Irradiated Silica Particles by Gamma-Ray

Hoik Lee, Donghyun Kim, and Daewon Sohn*

** Department of Chemistry, Hanyang University, 17 Seongdong-Gu, Seoul 133-791, Korea
E-mail: dsohn@hanyang.ac.kr*

A hydrogel is a material that has a 3D network structure consisting of long chain molecules cross-linked to each other. Hydrogels are greatly interesting due to their promising applications in diverse fields such as sensors, adsorbents, and drug delivery system in pharmacy. We presented a novel method of synthesis of hydrogels having pure network structure. The hydrogels were directly prepared by polymerization on peroxide surface generated by irradiating ^{60}Co gamma-ray on the surface of silica particle. The peroxidized nano-particles acted as both an initiator and a cross-linker in a mixture of peroxideized nano-particles and acrylic acid.

To verify the mechanism of the formation of hybrid systems with silica particles and poly(acrylic acid) (pAA), we tried to change the size and concentration of silica particles and monomers, and to characterize the hydrogels by Raman, ATR-IR, and solid ^{13}C NMR. The chemical bondings of hydrogel are checked by wide area illumination (WAI) scheme, called wide Raman spectroscopy. Raman spectra of hydrogels show the Si-O-C bonding between silica particle and acrylic acid (Figure 1). At 1620cm^{-1} peak is corresponding to the C=C bonding from acrylic acid monomer that remained in hydrogels. Characterization peak at 820cm^{-1} is the combination of Si-O-C and pAA chain. We analyze the peak of 820cm^{-1} with Gaussian distribution fitting to explain the bonding between the particles and pAA.

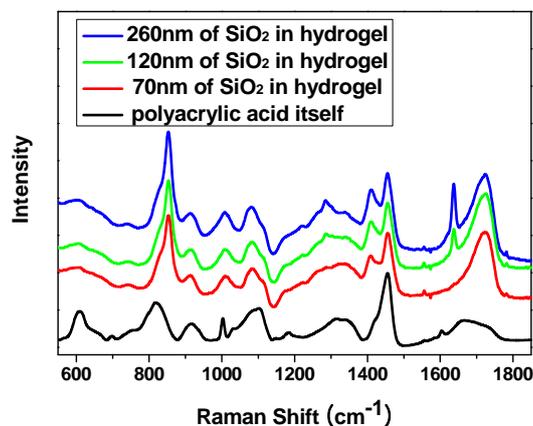


Figure 1. Raman spectra of hydrogel having different size of silica particle.

References

- [1] J. Kim, J. Koo, T. Shirahase, A. Takahara, D. Sohn, Preparation of organic/inorganic hybrid gel after r-ray radiation, *Chem. Lett.*, 2009, 38, 1112.
- [2] M. Kim, H. Chung, Y. A. Woo, M. S. Kemper, New reliable Raman collection system using the wide area illumination (WAI) scheme combined with the synchronous intensity correction standard for the analysis of pharmaceutical tablets, *Anal. Chim. Acta*, 2006, 579, 209.
- [3] K. Haraguchi, R. Farnworth, A. Ohbayashi, T. Takehisa, Compositional Effects on Mechanical Properties of Nanocomposite Hydrogels Composed of Poly(N,N-dimethylacrylamide) and Clay, *Macromolecules*, 2003, 36, 5732.
- [4] W. StÖber, A. Fink, Controlled growth of monodisperse silica spheres in the micron size range, *J. Colloid Interface Sci.*, 1968, 26, 62.
- [5] Y. Lee, J. Choi, Y. Choi, D. Sohn, Temperature Dependence of Hydrophobically End-Capped Poly(ethylene oxide): End Chain Effect Using ¹³C MAS NMR, *J. Phy. Chem. B*, 2003, 107, 12377.

Synthesis and Characterization of Model Star-Branched Polyelectrolytes

HOLLEY^{1,2}, D. Wade, BASKARAN¹, Durairaj, MAYS^{*1,2,3}, Jimmy W.

¹*Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA*

²*Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA*

³*Center for Nanophase Materials Sciences, ORNL, Oak Ridge, TN 37831 USA*

** E-mail: jimnymays@utk.edu*

A series of star-branched sodium poly(styrene sulfonate) (NaPSS) polymers with low polydispersity and near quantitative sulfonation was synthesized by using anionic polymerization and post-polymerization sulfonation. Thermogravimetric analysis was demonstrated to be a useful tool for analysis of NaPSS. The resulting polyelectrolyte stars were characterized in aqueous solution by a combination of size exclusion chromatography, static and dynamic light scattering, and viscometry. The radius of gyration based shrinkage factors, g , for the NaPSS stars were consistently slightly larger than those measured for their uncharged precursors in a thermodynamically good solvent but were in good accord with theoretically predicted values (Zimm-Stockmayer). In contrast to the well-known behavior of linear polyelectrolytes, the reduced viscosities of star-branched NaPSS in the no salt limit were found to fit a simple Huggins relation at low concentrations of polymer. Star NaPSS was adsorbed onto cleaved mica from pure water and aqueous salt solution, followed by imaging with atomic force microscopy (AFM). Radii estimated from AFM were found to correlate with radii measured in solution.

Quantitative Structure Analysis of Novel-conjugated Brush Copolymer Thin Film

RHO, Yecheol^a, YOON, Jinhwan^a, JIN, Sangwoo^a, AHN, Byungcheol^a, HIRAI, Tomoyasu^b,
MAEDA, Rina^b, LEE, Taek Joon^a, PARK, Samdae^a, KIM, Jin Chul^a, KIM, Dong Min^a, JUNG,
Jungwoon^a, KWON, Wonsang^a, KIM, Kyungtae^a, KIM, Mihee^a, KO, Yong-Gi^a, JUNG, Sungmin^a,
CHOI, Junman^a, HAYAKAWA, Teruaki^{*b}, REE, Moonhor^{*a}

^a*Department of Chemistry, National Research Laboratory for Polymer Synthesis & Physics, Pohang Accelerator Laboratory, Center for electro-photo behaviors in advanced molecular systems, and BK School of Molecular Science, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea,*

^b*Department of Organic & Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-S8-26, O-okayama, Meguro-ku, Tokyo 152-8552, Japan
E-mail: ree@postech.edu (M.R.); hayakawa@op.titech.ac.jp (T.H.)*

We quantitatively investigated the temperature-dependent phase transition behaviors in thin films of an interesting semirod-coil diblock copolymer, poly(styrene)-*b*-poly(oligothiophene side chain modified isoprene) (PS-*b*-POTI), and the resulting morphological structures using synchrotron grazing incidence X-ray scattering combined with DSC. These analyses provided detailed information about the morphologies of the phase-separated domains and the molecular structures formed in each domain. At room temperature, the diblock copolymer molecules in thin films were found to form an alternately stacked structure comprised of amorphous PS and smectic-A POTI microdomains whose stacking direction is parallel to the film plane. On heating, the films underwent a phase transformation to a hexagonal cylinder structure with cylindrical POTI domains in the PS matrix oriented normal to the film plane. This phase conversion is induced by the transformation of the POTI domains from a smectic-A phase to an isotropic phase, where the smectic-A phase is composed of a laterally ordered structure of interdigitated bristles in the POTI blocks. On the basis of these structural analysis results, we propose models for the molecular structures of the diblock polymer thin films at various temperatures.

Finite element modeling and Crashworthiness of Expanded Polypropylene (EPP) for automotive seat

Srivastava Vivek^{*a} and Sharma Ajay^b

^a *Karyon Consultancy and Solutions^a, Lucknow, U.P. India.*

Email: reachtovivek@gmail.com

^b *JSP International^b, Madison Heights, MI, USA*

The seating system occupies the major portion of the total automotive coach space and plays a critical role in occupant safety during crash. The robust design and desired performance of the seat under dynamic impact loading is indispensable. This study evaluates the efficacy of the use of polymer material (EPP) as a replacement of understructure of the automotive seats. The performance of EPP has been evaluated by numerical simulations. In this simulation, the multi-body models of 50 percentile RH III dummy and seating systems are used. The results show that the performance of the seat has improved. It has been observed that occupant safety parameters have significantly improved. The simulations also show that the EPP structure absorbs more energy as compared to the traditional understructure of steel.

Nanomechanical Thermal Analysis of Glass Transition of Poly(styrene-b-methyl methacrylate) using Silicon Cantilevers

Namchul Jung, Sangmin Jeon*

Email: jeons@postech.ac.kr

Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, 790-784, Korea

Nanomechanical thermal analysis (NTA) was used to study the glass transition behaviors of Poly(styrene-b-methyl methacrylate). A few nanogram samples of Poly(styrene-b-methyl methacrylate) with different molecular weight ratio were coated onto the one side of silicon microcantilevers, and the variations with temperature in the deflection, Q factor and resonant frequency of the cantilevers were measured simultaneously. The changes in the resonance frequency and the inverse of the Q factor of the cantilever are related to the variations in the elastic modulus and the loss tangent of Poly(styrene-b-methyl methacrylate), respectively. The difference between the volume expansion coefficients of Poly(styrene-b-methyl methacrylate) and silicon induced the cantilever to bend, and this variation was used to determine the glass transition temperature as well as the physical properties of the Poly(styrene-b-methyl methacrylate) sample.

References

- [1] N. Jung, H. Seo, D. Lee, C. Y. Ryu and S. Jeon, Nanomechanical Thermal Analysis of the Glass Transition of Polystyrene Using Silicon Cantilevers, *Macromolecules*, 2008, 41, 6873
- [2] N. Jung and S. Jeon, Nanomechanical Thermal Analysis with Silicon Cantilevers of the Mechanical Properties of Poly(vinyl acetate) near the Glass Transition Temperature, *Macromolecules*, 2008, 41, 9819

Microthermogravimetry of a Single Microcapsule using Silicon Microresonators

LEE, DONGKYU^a; PARK, YONGBEOM^a; CHO, SOOHYUN^b; YOO, MYUNGSUN^a; JUNG,
NAMCHUL^a; YUN, MINHYUK^a; KO, WOOREE^a; JEON, SANGMIN^{a*}

^a Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, Korea
^b POSCO, Technical Research Laboratory, 699, Gumho-Dong, Gwangyang, Jeonnam, 549-090, Korea
(south)

* Email: jeons@postech.ac.kr

We synthesized polyurethane microcapsules containing chlorobenzene using interfacial polymerization and measured thermomechanical properties of a single microcapsule using silicon microcantilevers. A chlorobenzene-containing polyurethane microcapsule was placed on the free end of a silicon cantilever, and the temperature dependence of the resonance frequency was measured. As the cantilever was heated, the resonance frequency showed step-like increases at 109 and 270 °C due to the rupture of the capsule and the thermal degradation of the polyurethane shell, respectively. The frequency changes due to the rupture of a single capsule measured by the cantilever were much sharper than the transitions measured by conventional thermogravimetric analysis (TGA), which measures the average mass change of a collection of capsules characterized by a large size distribution. When two capsules were placed on the cantilever, their individual rupture temperatures could be clearly identified. In addition, the permeability of the polyurethane shell with respect to chlorobenzene was measured, and rupture temperature was found to decrease with increasing permeability.

References

- [1] Cho, S. H.; White, S. R.; Braun, P. V., self healing polymer coatings, *Adv. Mater.*, 2009, 21, 645.
- [2] Berger, R.; Lang, H. P.; Gerver, C.; Gimzewski, J.K.; Fabian, J.H.; Scandella, L.; Meyer, E.; Gntherodt, H.-J., micromechanical thermogravimetry, *Chem. Phys. Lett.*, 1998, 294, 363
- [3] Lee, J.; King, W. P., Microthermogravimetry using a microcantilever hot plate with integrated temperature compensated piezoresistive strain sensors, *Rev. Sci. Instrum.*, 2008, 79, 054901.

The Effect of Screw Speed on Impact Strength of Polymer Blends through Twin Screw Extruder

M.R.Saeb^{*a}, M.Omrani^b, M.Farahani^a, M.Razban^a

^aIslamic Azad University of Mahshahr, Postal code: 63519, Khoozestan, Iran.

^bUniversity of Tehran, Technical faculty, Polymer Group, Tehran, Iran.

*E-mail: mrsaeb2008@gmail.com

Blending two or more immiscible polymers is a well known technique to improve some crucial characteristics such as mechanical, morphological and thermal properties in multi-component systems. It is understood earlier that the final properties of a polymer blend is strongly affected by several factors; e.g. composition, viscosity ratio, interfacial tension, shear rate, elasticity, and processing conditions [1]. Furthermore, employing a suitable coupling agent causes increasing the interfacial adhesion between minor(s) and major phases through blending immiscible polymers [2, 3]. It is shown that the final properties of extruded compounds are directly functions of processing conditions [4, 5]. Among these parameters, screw speed can be highlighted as an indication of shear effect on flow field inside the channel of a twin-screw extruder. In this work, we are interested to study the mentioned parameter in PP/PC/SEBS ternary blend. The SEBS-g-MAH is employed as a coupling agent to improve the interfacial bonding in as well. Three screw speeds of 70,100 and 130 rpm are those selected as processing variables based on blend characteristics [2, 3]. The composition of ingredients is kept constant for all three blends herein: 70%wt PP, 15%wt PC, 7.5%wt SEBS, and 7.5%wt SEBS-g-MAH. Testing samples are produced by using Brabender twin-screw extruder and the Izod impact strength of notched specimens is according to the ASTM D-256 using Zwick pendulum-type tester. It is observed that the impact strength of the PP/SEBS/PC ternary blend is extensively influenced by the screw speed and a linear trend can be recognized in the range of screw speed alterations.

Keywords: Impact Strength, Screw Speed, Polymer blends, Twin Screw Extruder

References

- [1] B.D. Favis, *J App Polym Sci*, 1990, 39,285-300.
- [2] L. A. Utracki, *Polymer Alloys and Blends*, Oxford Univ. Press New York,1989 .
- [3] M. Xanthos, "Reactive Extrusion, Principles and practice", *Hanser: Munich*, 1992, 55-199.
- [4] L. Levitt, and C. Macosko. *Polym Eng Sci*, 1996, 36, 1647-1655,.
- [5] A.N.Wilkinson, M.L. Clemens, V.M. Harding, *Polymer*, 2004, 45, 5239.

Nanomechanical Thermal Analysis of Photosensitive Polymers during Photodegradation Using Microcantilever Platform

YUN, MINHYUK, IM, CHANGYONG , JUNG, NAMCHUL , JEON, SANGMIN*

*Department of Chemical Engineering, Pohang University of Science and Technology, Pohang,
790-784, Korea*

**E-mail: jeons@postech.ac.kr*

Poly(methyl methacrylate) (PMMA) and Poly(vinyl cinnamate) (PVCN) are one of photosensitive polymer. When irradiated by 254nm UV light, PMMA undergoes cleavage of ester side group to lead main chain scission, and the cinnamate side group of PVCN goes through [2+2] cycloaddition reaction to form crosslink network. In comparison to the not-irradiated PMMA and PVCN, the crosslinked PMMA and PVCN have different mechanical and thermal properties, such as surface stress, modulus and T_g (Glass transition temperature). Using Nanomechanical thermal analysis (NTA) based on microcantilever platform, here we measured resonant frequency and deflection of PMMA- and PVCN-coated microcantilever and observed mechanical and thermal properties with increasing crosslinking density. The surface stress, modulus and T_g of PMMA were observed to decrease under UV irradiation, and those of PVCN increased.

Reference

- [1] N. Jung, H. Seo, D. Lee, C. Y. Ryu and S. Jeon, Nanomechanical Thermal Analysis of the Glass Transition of Polystyrene Using Silicon Cantilevers, *Macromolecules*, 2008, 41, 6873
- [2] N. Jung and S. Jeon, Nanomechanical Thermal Analysis with Silicon Cantilevers of the Mechanical Properties of Poly(vinyl acetate) near the Glass Transition Temperature, *Macromolecules*, 2008, 41, 9819
- [3] T. Haramina, R. Kirchheim, Mechanical Spectroscopy of PVCN with Increasing Cross-Linking Degree, *Macromolecules*, 2007, 40, 4211

BioLCCC Model and Predictive Chromatography of Biopolymers

GORSHKOV Alexander V.*^a, EVREINOV Viktor V.^a, GORHSKOV Mikhail V.^b

^a*N.N. Semenov Institute of Chemical Physics, Russian Academy of Science, Kosygina 4, 119991, Moscow, Russian Federation*

^b*Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences, 38 Leninsky Pr., Bld. 2, 119334, Moscow, Russian Federation*

**E-mail: alex.gorshkov@gmail.com*

Macromolecules of biopolymers have the most difficult structure among other types of polymers. The structure and, hence, the way the biopolymer are functioning, is determined by their amino acid (AA) sequence. Reading the sequence, determination of variations of sequence as a result of mutations, rearrangements of AA residues, or post-translation modifications are important tasks of analytical chemistry related to wide scope of problems in the Life Science.

Liquid chromatography (LC) is a widely accepted step in sequencing based on the mass spectrometry (MS) and used to simplify the mixtures of peptides in the digests before the MS based identifications. Until recently, that was the only role for LC, although it is quite obvious that the mechanisms behind the separation are determined by the physical properties of biopolymers, and, therefore, the retention volume should correlate with their structures. Similar to polymers, the adsorption of biopolymers reflects a balance between the interaction energy and the entropy losses near the surface, and further depends on the spatial correlation between AA residues bonded into a chain. Therefore, an order of AA in a sequence and their modifications affect the macromolecule's retention volume. Can LC be used for the identification of protein sequences, their modifications and mutations?

In the polymer LC an adsorption critical point plays a key role. This point divides adsorption and exclusion separation modes, and separation near that point is highly sensitive to the particular chain structure. Separation mechanism in this critical region is described in terms of ideal chain adsorption model. Application of this model to biopolymers (called Liquid Chromatography of Biopolymers at Critical Conditions, BioLCCC) provides with universal viewpoint on the basic features of their separation [1]. This model establishes the quantitative relation between the retention volume and AA order in a chain. Thus, the separation of biopolymers depends on both the AA composition and the AA sequence. Biopolymers having the same AA compositions but different AA order, as well as different locations and numbers of modified AA in a chain, may have quite different retention volumes.

In this presentation we describe the proposed approach to extract information regarding the biopolymers' sequence from the chromatographic data. Specifically, we will focus the attention on the following problems: (1) the mechanism of biopolymers separation under gradient LC that results in sequence dependent retention volume; (2) prediction of the biopolymers' retention volumes based on their sequence; and (3) the utility of prediction algorithms for filtering and/or validation of MS-based identifications.

References

- [1] V. Gorshkov, V. V. Evreinov, I. A. Tarasova, and M. V. Gorshkov. Applicability of the Critical Chromatography Concept to Proteomics Problems: Dependence of Retention Time on the Sequence of Amino Acids. *Polymer Science, series B*, 2007, Vol. 49, Nos. 3–4, p. 93

On the Movement of Spherical and Non-Spherical Particles Suspended in a Liquid and Exposed to Temperature Gradient Microthermal Field-Flow Fractionation

Josef Janča

*Department of Physics and Materials Engineering,
Tomas Bata University in Zlin, Czech Republic Email: jjanca@ft.utb.cz*

The increasing importance of the fractionation and characterization of various nanoparticles and micron-sized particles of the synthetic, polymer, and natural origin requires a deeper understanding of the mechanisms of transport phenomena leading to the separation, or accompanying it. Several separation techniques are suitable for the determination of particle size distribution (PSD) or just for the fractionation of polydisperse samples in order to obtain the fractions of narrower PSD. Field-Flow Fractionation (FFF) belongs to the methods which can conveniently be applied to separate and characterize the mentioned species. The new Microthermal FFF has already been used to fractionate the synthetic polymers, various nanoparticles, and micron-sized particles on the basis of differences in molar mass of the polymers or of differences in size of the particulate species ^[1]. The theoretical analysis presented in this study indicates that Microthermal FFF is a good candidate to separate the particles also according to differences in their shape.

The differences in the ratios of the rotational as well as the translational diffusion coefficients of the non-spherical to spherical particles, the heterogeneity of thermal conductivity of the particle body, and the heterogeneity in surface chemical nature make possible to separate the particles according to differences in shape.

Since the local entropy production related to the particle body must be positive, the rotational Brownian movement of a particle in temperature gradient is restricted ^[2-4]. In the steady state, both spherical and non-spherical particles can be oriented with regard to the unidirectional temperature gradient. Such an orientation can occur if the particle exhibits the heterogeneity either of the chemical nature of its surface or of thermal conductivity of its body. The orientation of spherical and non-spherical particles whose different parts exhibit different thermal diffusion coefficients D_T is schematically demonstrated in Figure 1. Entropy driven orientation causes a change in the velocity of the rotational motion and translational

thermophoretic displacement of a particle in comparison with a spherical particle of the same volume, suspended in the same liquid. Since the ratio of thermal diffusion coefficient D_T to translational diffusion coefficient D determines the retention in Microthermal FFF and the orientation of the non-spherical particles has an impact on D , it should allow the separation of spherical and non-spherical particles of the same volume.

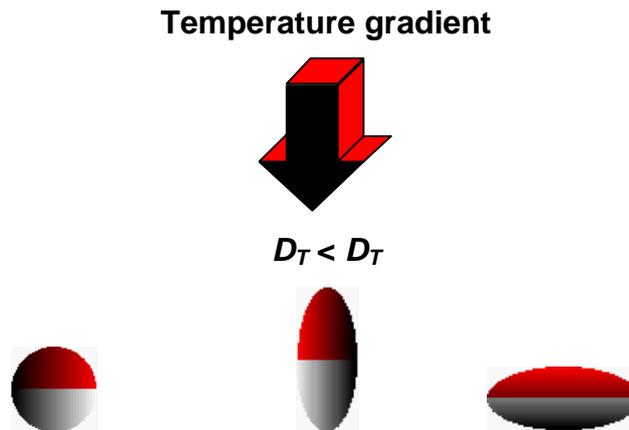


Figure 1. Schematic representation of the orientation of the spherical and non-spherical particles exposed to temperature gradient and exhibiting heterogeneous nature of their surfaces and thus the differences in thermal diffusion coefficients of different parts of particle surfaces.

References

- [1] J. Janča, *Microthermal Field-Flow Fractionation: Analysis of Synthetic, Natural, and Biological Macromolecules and Particles*, HNB Publishing, New York, 2008.
- [2] L. D. Landau, E. M. Lifschitz, *Statistical Physics*, 3rd Edition, Butterworth-Elsevier, New York, 1980.
- [3] D. Kondepudi, I. Prigogine, *Modern Thermodynamics: From Heat Engines to Dissipative Structures*, John Wiley & Sons, Chichester, 1998.
- [4] D. Jou, J. Casas-Vázquez, G. Lebon, *Extended Irreversible Thermodynamics*, Springer-Verlag, Berlin, Heidelberg, New York, 2001.

Characterization of PS-g-PI Graft Copolymer with LCCC X SEC

LEE, Hyojoon; CHANG, Taihyun*

Department of Chemistry, POSTECH, Pohang, 790-784, Korea

**E-mail: tc@postech.ac.kr*

Graft copolymer is a polymer having side chains composed of different monomers to that of the main chain. Since the backbone and graft chains are generally incompatible, most graft copolymers are multiphase materials exhibiting unique and interesting morphologies.¹⁾ Usually graft copolymers are characterized by size exclusion chromatography. But it is not enough to characterize synthetic graft copolymers because they often include side products. Two-dimensional liquid chromatography (2D-LC) is a combination of adequately selected two different LC separation methods and it has been used to effectively characterize bivariate distributions existing in synthetic polymers.

In this study, we analyzed PS-g-PI graft copolymers with 2D-LC by combining liquid chromatography at the critical condition (LCCC) and size exclusion chromatography (SEC). The polystyrene-graft-polyisoprene (PS-g-PI) was prepared by tailored anionic polymerization to yield precisely spaced graft chains. LCCC permits the characterization of individual blocks of copolymer by making one block chromatographically "invisible".²⁾ PS-g-PI was separated with respect to its PI block length by LCCC, which is at the critical condition of PS. Fractionated polymers were characterized by SEC.

References

- [1] Wonmok Lee, Donghyun Cho, and Taihyun Chang*, Characterization of Polystyrene-b-polyisoprene Diblock Copolymers by Liquid Chromatography at the Chromatographic Critical Condition, *Macromolecules*, 2001, 34, 2353
- [2] Akira Hirao,* Takumi Watanabe, and Ryosuke Kurokawa, Precise Synthesis of Exact Graft Polystyrenes with Branches from Two to Five in Number by Iterative Methodology Based on Living Anionic Polymerization, *Macromolecules*, 2009, 42, 3973

The Critical Molecular Size Parameter in Size Exclusion Chromatography: Theory and Experimental Evidence

WANG, YANWEI^a; TERAOKA, IWAO^b; HANSEN, FLEMMING Y.^c; PETERS, GÜNTHER H.^c; HASSAGER, O.^{a,*}

^a*Danish Polymer Center, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby, DK-2800, Denmark*

^b*Department of Chemical and Biological Sciences, Polytechnic*

Institute of New York University, 333 Jay Street, Brooklyn, New York 11201

^c*Department of Chemistry, Technical University of Denmark, Kgs. Lyngby, DK-2800, Denmark*

* *Email: oh@kt.dtu.dk*

Size Exclusion Chromatography (SEC) separates polymer molecules by their size in dilute solutions, but it has been a matter of debate for decades what size parameter to use. It is widely believed that SEC separates polymer molecules by their equilibrium partition coefficients between a dilute bulk solution phase located at the interstitial space and confined solution phases within the pores of the column packing material.¹⁻⁴ The seminal work of Grubisic, Rempp and Benoit⁵ demonstrated that polymer molecules, regardless of details in chemical composition and chain architecture, follow a so-called universal calibration curve in a plot of the hydrodynamic volume of a given fraction of a polymer versus the SEC retention volume of that fraction. The presence of the universal calibration curve indicates that polymer molecules are partitioned between bulk and confined solutions according to their hydrodynamic volume. However, as the hydrodynamic volume is a dynamic quantity, it has been puzzling for decades that a process which is believed to be an equilibrium phenomenon is controlled by a dynamic property of polymers.

In an attempt to resolve this dilemma, Sun *et al.*⁶ carried out an extensive experimental study in 2004 with three groups of nearly monodisperse polymer samples including linear polystyrenes, linear polyethylenes and branched polyethylenes with several types of long chain branching. Measurements of radius of gyration, molecular weight, intrinsic viscosity and elution volume of these various samples revealed a rather puzzling conclusion that the radius of gyration correlates with the elution volume of linear chains more satisfactorily than does the hydrodynamic volume, while the reverse is the case for branched chains. As was also shown in the experiments by Farmer *et al.*⁷ with polystyrene samples of linear, comb and centipede architectures, the branched chains deviate from the radius of gyration versus retention volume curve determined by linear ones, with the most heavily branched samples deviating the most.

Complementary to SEC experiments, theoretical studies on the partitioning of polymer chains are also valuable in understanding the separation mechanism in SEC. Efforts have been directed to finding the most relevant molecular size parameter that characterizes the equilibrium partition coefficients for different polymer architectures.^{3,4,8-11} It is now known that the answer is

the mean span dimension.⁹⁻¹¹ In the range of the partition coefficient relevant to SEC separation, linear and various types of branched polymer chains follow a nearly universal curve in the plot of the partition coefficient as a function of the mean span dimension for a given pore geometry; however, this is not the case, if the partition coefficient is plotted against some other size parameters such as the radius of gyration and the hydrodynamic radius.^{10,11}

We have recently carried out detailed calculations of the partition coefficients and the mean span dimensions for various types of branched architectures including those studied by Sun *et al.* in Ref. 6.¹¹ A brief summary of our results will be reported in this poster presentation. In particular, we demonstrate the consistency between theoretical calculations and experimental data. An explanation is provided to the aforesaid rather puzzling experimental findings. Examples are shown to illustrate how the use of the mean span dimension could improve the interpretation of SEC data.

Acknowledgement

Wang, Y. acknowledges financial support by the Danish Research Council for Technology and Production Sciences under Grant 274-08-0051.

References

- [1] Giddings, J. C.; Kucera, E.; Russell, C. P.; Myers, M. N., Statistical theory for the equilibrium distribution of rigid molecules in inert porous networks. Exclusion Chromatography, *J. Phys. Chem.*, 1968, 72, 4397.
- [2] Casassa, E. F., Equilibrium distribution of flexible polymer chains between a macroscopic solution phase and small voids, *J. Polym. Sci., Polym. Lett.*, 1967, 5, 773.
- [3] Casassa, E. F.; Tagami, Y., An equilibrium theory for exclusion chromatography of branched and linear polymer chains, *Macromolecules*, 1969, 2, 14.
- [4] Casassa, E. F., Comments on Exclusion of Polymer Chains from small pores and its relation to gel permeation chromatography, *Macromolecules*, 1976, 9, 182.
- [5] Grubisic, Z.; Rempp, P.; Benoit, H., A universal calibration for gel permeation chromatography, *J. Polym. Sci., Polym. Lett.*, 1967, 5, 753.
- [6] Sun, T.; Chance, R. R.; Graessley, W. W.; Lohse, D. J., A study of the separation principle in size exclusion chromatography, *Macromolecules*, 2004, 37, 4304.
- [7] Farmer, B.; Terao, K.; Mays, J., Characterization of model branched polymers by multi-detector SEC in good and theta solvents, *Int. J. Polym. Anal. Charact.*, 2006, 11, 3.
- [8] Teraoka, I., Calibration of retention volume in Size Exclusion Chromatography by hydrodynamic radius, *Macromolecules*, 2004, 37, 6632.
- [9] Gorbunov, A. A.; Vakhrushev, A. V., Theory of chromatography of complex cyclic polymers: eight-shaped and daisy-like macromolecules, *Polymer*, 2004, 45, 6761.
- [10] Wang, Y.; Peters, G. H.; Hansen, F. Y.; Hassager, O., Equilibrium partitioning of macromolecules in confining geometries: Improved universality with a new molecular size parameter, *J. Chem. Phys.* 2008, 128, 124904.
- [11] Wang, Y.; Teraoka, I.; Hansen, F. Y.; Peters, G. H.; Hassager, O., A theoretical study of the separation principle in size exclusion chromatography, *Macromolecules*, 2010, 43, 1651.

Rigorous 2D-LC analysis of comb shaped polymers using isotope effect

Seonyoung Ahn, Taihyun Chang*

Department of Chemistry

Pohang University of Science and Technology, Pohang, 790-784, Korea

*sunyoung@postech.ac.kr * tc@postech.ac.kr*

For the characterization of branching, size exclusion chromatography (SEC) coupled with viscosity detector and light scattering detector has been employed on the basis of the Zimm-Stockmayer theory.¹ However, SEC separates the polymers according to the hydrodynamic volume only and is incapable of fractionating the polymers with complex chain architecture into homogeneous fractions. On the other hand, temperature gradient interaction chromatography (TGIC) is able to separate branched polymers with far better sensitivity to molecular weight than SEC.²

In this study, we demonstrate the use of the temperature gradient interaction chromatography (TGIC) to characterize the partially deuterated comb shaped polymers. Normal phase TGIC can separate the comb polymer according to the molecular weight quite well. We also found that a significant isotope effect exists in the reverse phase TGIC retention between deuterated and hydrogenous polymers. Taking advantage of the isotope sensitivity of RPLC, the comb polymers are cross fractionated by NPLC and RPLC, and the two dimensional mapping with respect to the backbone chain length and the number of side-chains is fully established.

Reference

- [1] B.H. Zimm, W.H. Stockmayer, The dimensions of chain molecules containing branches and rings, *J. Chem. Phys.* 1949, 17, 1301.
- [2] T. Chang, Polymer characterization by interaction chromatography, *J. Polym. Sci. Polym. Phys. Ed.* 2005, 43, 1591.

Compositional Characterization of PI-*b*-P2VP by Temperature-Gradient Interaction Chromatography

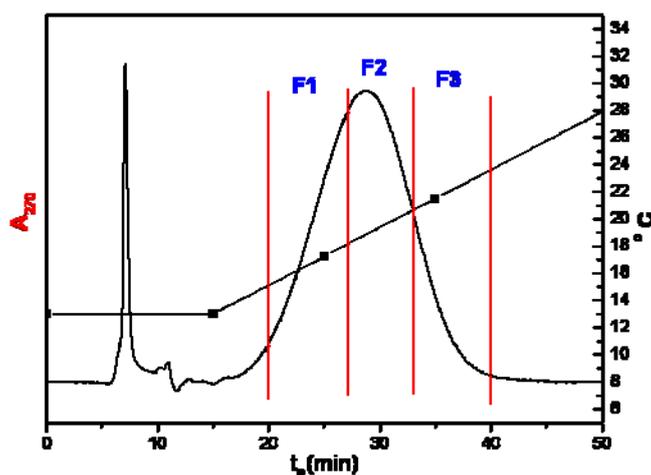
Junyoung Lee, Haiyung and Taihyun Chang*

Department of Chemistry, POSTECH, Pohang, Republic of Korea, 790-784
tc@postech.ac.kr

Block copolymers can spontaneously self-assemble in a selective solvent to form micelles of various morphologies, such as spherical micelle, cylindrical micelle, vesicle and so on.¹ Recently, Huang *et al.* reported the donut-shaped micelles of highly uniform shape and size using PI-*b*-P2VP (polyisoprene-*block*-poly(2-vinylpyridine)) in polar solvents.²

The composition of block copolymer affects the morphology of micelles formed in solution so that the shape and size of donut micelles could be modified if we control the composition. We tried to obtain PI-*b*-P2VP of different compositions by fractionating an anionic-polymerized PI-*b*-P2VP by temperature-gradient interaction chromatography (TGIC).

In this study, we fractionated PI-*b*-P2VP by RP-TGIC according to the PI block size since the nonpolar stationary phase in the column interacts with the PI block more strongly. The shape and size of PI-*b*-P2VP micelles were investigated by AFM.



References

- [1] (a) Zhang, L.; Eisenberg, A. *Science* **1995**, 268, 1728. (b) Discher, D.E.; Eisenberg, A. *Science* **2002**, 297, 967. (c) S.Jain, F.S. Bates, *Science* **2003**, 300, 460.
- [2] Huang, H.; Chung, B.; Jung, J.; Park, H. W.; Chang, T. *Angew. Chem. Int. Ed.* **2009**, 121, 4664.

Photodegradation Behavior of High-Impact Polystyrene Studied by Pyrolysis-Gas chromatography

Hajime OHTANI*, Takaaki MATSUDA, Yasutaka MATSUDA, Wataru ITO

*Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555,
JAPAN*

**E-mail: ohtani.hajime@nitech.ac.jp*

High-impact polystyrenes (HIPS) used for cover materials of office automation systems such as printers and photocopiers are often recovered for material recycling. In this process, it is important to know the degrees and mechanisms of deterioration of the materials for efficient recycling. In this work, photodegradation behavior of HIPS was investigated by pyrolysis-gas chromatography (Py-GC).

HIPS usually contains several percent of butadiene rubber (BR) component to improve its shock resistance. In the pyrogram of an ordinary HIPS, minor but distinct peaks of butadiene monomer and dimer were clearly observed along with major peaks of styrene monomer, dimer and trimer from polystyrene main chain. On the other hand, in the case of ultraviolet-irradiated HIPS, the peaks of butadiene monomer and dimer almost disappeared in the pyrogram while the styrene-related peaks were still observed similarly to those for the original HIPS. This fact suggests that the photodegradation of HIPS is mainly caused by the decomposition of BR components accompanied with the deterioration especially on the impact properties. Furthermore, as for the market-recovered HIPS for cover materials, the degrees of yellowing of the materials were well correlated with the decrease in the relative peak intensities of butadiene monomer and dimer observed in their pyrograms. This result demonstrated that degree of deterioration of HIPS is conveniently evaluated by Py-GC on the basis of the intensities of the BR related peaks observed in the programs.

Characterization of Cross-Linking Structure in Cured Thermosetting Resins by MALDI-Mass Spectrometry combined with Specific Sample Decomposition

Hajime OHTANI*, Mami KAMIYAMA

Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, JAPAN

**E-mail: ohtani.hajime@nitech.ac.jp*

Structural characterization of the cross-linking networks in cured resins has been not an easy task even using advanced spectroscopic methods mainly because of their insoluble nature. Recently, the authors reported a technique to analyze the chain length distribution of network junctions in photocured acrylic resins using matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) combined with supercritical methanolysis of the resin samples^{1,2}. Here the resin samples sealed with methanol were decomposed under supercritical conditions to form a series of the methyl acrylate (MA) oligomers reflecting the sequences of network junctions, followed by the MALDI-MS measurements of the methanolysis products. The observed MALDI mass spectra showed a series of peaks of MA oligomers, in the m/z range up to around 4,000. This fact demonstrated that relatively longer sequences of network junctions (at least 50 acrylate units) were formed during the photocuring in the given resin samples.

In this work, thermosetting allyl ester resins were characterized basically by the same approach. In this case, to suppress side reactions such as dehydrogenation, the decomposition of the cured allyl ester resin samples was performed in tetramethylammonium hydroxide (17%) solution in methanol at lower temperature around 100°C. Several series of poly(allyl methyl ether)s with various end groups were observed in MALDI mass spectra of the decomposition products reflecting the sequence of network junctions, which were then successfully interpreted in terms of the thermosetting conditions such as temperature and time.

References

- [1] H. Matsubara, S. Hata, Y. Kondo, Y. Ishida, H. Takigawa, H. Ohtani, Characterization of cross-linking structures in UV-cured acrylic ester resin by MALDI-MS combined with supercritical methanolysis, *Anal. Sci.*, 2006, 22, 1403.
- [2] H. Matsubara, H. Kataoka, H. Ohtani, Characterization of network structure in radiation-cured resins of polyfunctional acrylic ester and *N*-vinylpyrrolidone by MALDI-MS combined with supercritical methanolysis, *Polym.Chem.*, in press.

Polymer Analysis using Offline SEC-FTIR, MALDI-MS, and DART-MS

TAKAYAMA Hiroshi*, MATSUBARA Koutatsu, OZAWA Tomoyuki, MIYAMOTO Hisae, SEKI Tatsuya

Nissan Chemical Industries, LTD., Chemical Research Department

**E-mail: takayamah@nissanchem.co.jp*

A technique for analyzing polymers with FTIR or MS (MALDI, DART) after automatic fraction separation of SEC has been studied. IR spectroscopy gives useful information concerned with molecular functional groups. MALDI-MS is a powerful tool for not only determining a molecular weight distribution but also characterizing the repeat units and end groups of polymers [1]. DART-MS enables observation of the pyrolysis products in the condition of high temperature ion source (over 400 degrees centigrade). Our previous report showed that SEC-DART-MS could identify some kinds of polymers for each fraction [2]. In this work, we showed SEC-IR and SEC-MS could characterize the model polymer sample consisted of polycarbonate (PC; $M_w = 26,000$)/poly(methyl methacrylate) (PMMA; $M_w = 124,000$).

Samples were prepared for each measurement. The fractions separated with SEC were spotted on the plate automatically, followed by the measurements of FTIR, MALDI-MS, and DART-MS.

Using SEC-FTIR, the peak of C=O vibration mode (1731 cm^{-1}) of PMMA was observed in the high molecular weight fractions, while the peak of C=O vibration mode (1788 cm^{-1}) of PC was strongly observed in the low molecular weight fractions (Fig. 1). In Fig. 2 (SEC-MALDI-MS), the molecular weight distribution of PC was determined for each fraction. Moreover, the PC series which had different end groups were identified. In Fig. 3 (SEC-DART-MS), the pyrolysis ion of PMMA was detected in the high molecular weight fractions, while the PC pyrolysis ions were observed in the low molecular weight fractions. Therefore, we obtained the information that PMMA was the main component in the high molecular weight fractions and PC was detected mainly in the lower molecular weight fractions. Also, we found out the detail molecular structures.

As the results of the above, these methods were the powerful techniques for blend polymer analysis.

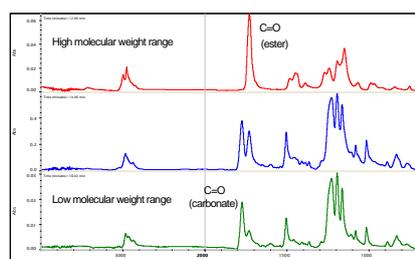


Figure 1. IR spectra

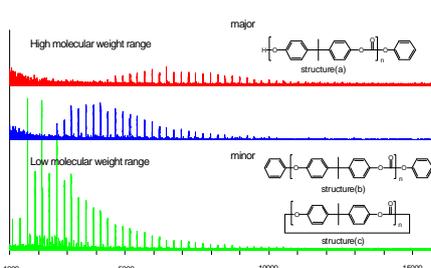


Figure 2. MALDI mass spectra

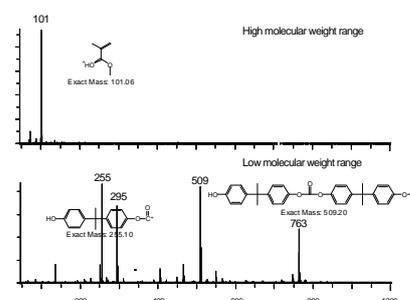


Figure 3. DART mass spectra

References

- [1] Scott D. Hanton, X. Michael Liu, GPC Separation of Polymer Samples for MALDI Analysis, *Anal. Chem.*, 2000, 72, pp 4550.
- [2] T. Ozawa, K. Matsubara, H. Takayama, H. Miyamoto, T. Seki, Abstract of 13th symposium on polymer analysis in Japan, 2008, pp85.

End-Functionality Study of PS-Br synthesized by ATRP using MALDI-ToF MS

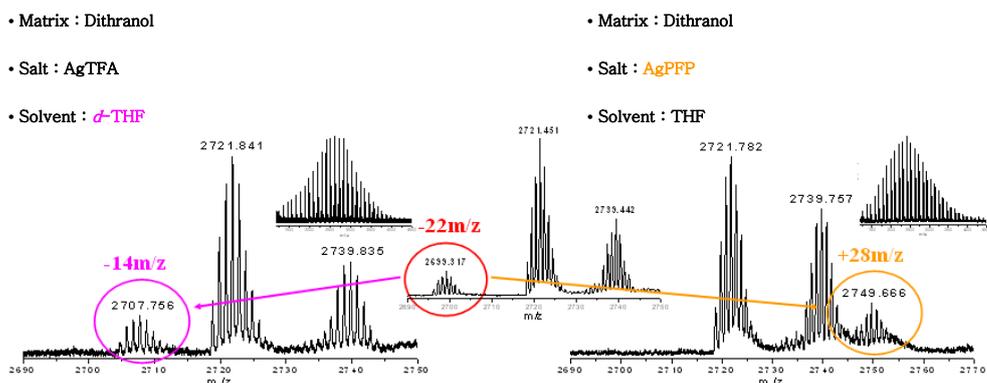
Kihyun Kim^a, Taihyun Chang^{a,*}, Aleya Hasneen^b, Hyun-Jong Paik^b

^a Department of Chemistry and Division of Advanced Materials Science, Pohang University of Science and Technology, Pohang, 790-784, Korea

^b Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

The polymer synthesized by conventional radical polymerization is difficult to control the molecular characteristics such as molecular weight distribution (MWD), chain end functionalities, chain architectures or compositions. In this regard, recently developed controlled radical polymerization (CRP) technique can do a far better job. For example, polymerization of styrene by atom transfer radical polymerization (ATRP), which is one of the CRP, yield PS-Br with a relatively narrow MWD, which in turn can be used as a macroinitiator to synthesize a block copolymer or be transformed to other end-group using some organic reactions. Despite the importance of the end-functionality of PS-Br synthesized by ATRP, its characterization cannot be said to be done rigorously.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) is a powerful tool to characterize the molecular characteristics of polymers. A few research groups have tried to analyze the PS-Br by MALDI-ToF MS, but the reactivity of the end group of PS-Br resulted complex spectra to make the interpretation difficult. In this work, we analyzed MALDI-ToF MS spectra to successfully elucidate the by-products from reaction of the end-group during the MALDI process.



Synthesis of Polymer containing Platinum/Gold Nanoparticles and Physical Characterization

A-Young Sung*, Ki-Hun Ye

Department of Ophthalmic Optics, Daebul University, Jeonnam, 526-702, Korea
E-mail: say@mail.daebul.ac.kr

Platinum/gold nano particles were added to mixture of MA(methacrylic acid), HEMA(ethylene glycol dimethacrylate) and NVP(N-vinyl pyrrolidone) in a mould at various concentration to manufacture high-performance ophthalmic lens materials containing platinum/gold nano particles which could protect eye from environmental factors. The resulting mixture was copolymerized in the presence of AIBN(azobisisobutyronitrile) initiator. Also, the cast mould method was used in order to produce the contact lens in this study. The size of platinum found to be 5~10 nm by FE-SEM. we analyzed the physical properties of the polymer by using average value of refractive index, contact angle, water content, oxygen transmittance and optical transmittance. The addition of platinum nano particles to the polymer allowed the lens to have various colors without coloring agents. The refractive index of 1.420~1.427, water content of 38~42%, visible transmittance of 89~92%, contact angle of 38~42° and oxygen transmissibility of $9\sim 13 \times 10^{-9}$ cm/s ml O₂/ml × mmHg were obtained. Also, tensile strength of the polymer was 0.13~0.20 kgf. The visible transmittance and probe current graph in order to calculate oxygen transmissibility of the polymer is shown in Fig. 1~2. Therefore, the ophthalmic lens material produced using platinum/gold nano particles satisfied the basic physical properties required for contact lens application.

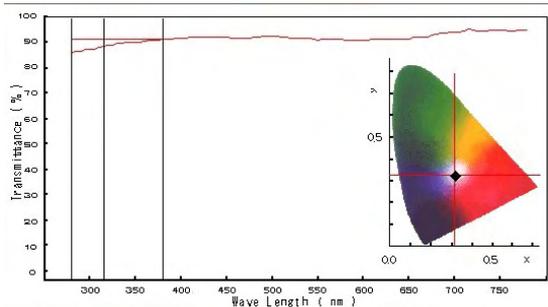


Fig. 1. Optical transmittance of contact lens

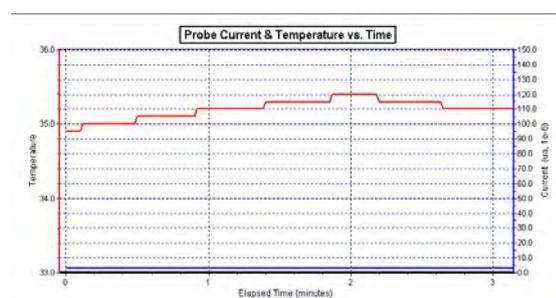


Fig. 2. Oxygen transmissibility of contact lens

References

- [1] Lim, S. K.; Lee, S. K.; Hwang, S. H.; Kim, H. Y. *Macromol. Mater. Eng.* 2006, 291, 1265.
- [2] Li, J. X.; Wang, L.; Shenm, R. L.; Xum, Z. J.; Li, P.; Wan, G. J. Huang, N. *Surf. Coat. Technol.* 2007, 201, 8155.

Silver/Platinum Nanoparticles added Polymerization and Application for Contact Lens

A-Young Sung*, Tae-Hun Kim

*Department of Ophthalmic Optics, Daebul University, Jeonnam, 526-702, Korea
Tel:82-19-9759-5020; E-mail: say@mail.daebul.ac.kr*

Silver nano particle has been applied to various fields due to antimicrobial property and high conductivity. In this study, silver/platinum nano particles were added to mixture of styrene, MA(methacrylic acid), HEMA(ethylene glycol dimethacrylate), NVP(N-vinyl pyrrolidone) in a mould at various concentration. The resulting mixture was copolymerized by heating at 70°C for 40 min, 80°C for 40 min, 100°C for 40min repectively with the cross-linker EGDMA(ethylene glycol dimethacrylate) in the presence of AIBN(azobisisobutyronitrile) initiator. Also, the cast mould method was used in order to fabricate the ophthalmic contact lens in this study. The size of silver nano particles found to be 2~5 nm by FE-SEM and the concentration of the used silver nano colloid was 25 ppm.

For analysis of the produced polymer, we measured the refractive index, contact angle, water content, oxygen transmittance and optical transmittance of the polymer. The refractive index of 1.427~1.435, water content of 32~38%, visible transmittance of 85~89%, tensile strength of 0.17~0.25 kgf and oxygen transmissibility of $7\sim 10\times 10^{-9}$ cm/s ml O₂/ml × mmHg were obtained. Also, the result of measurement showed that refractive index decreased while the water content increased as the silver colloid was added.

Keywords: silver, platinum, water content, refractive index, tensile strength

References

- [1] Li, J. X.; Wang, L.; Shenm, R. L.; Xum, Z. J.; Li, P.; Wan, G. J. Huang, N. *Surf. Coat. Technol.* 2007, 201, 8155.
- [2] Rai, M.; Yadav, A.; Gade, A. *Biotechnol. Adv.* 2009, 27, 76.

Assignment of NMR spectra of Poly(1-vinylpyrrolidone) by Multivariate Analysis

Tomohiro Hirano^a; Takuya Anmoto^a, Hikaru Momose^{a,b}; Koichi Ute^a

^a Department of Chemical Science and Technology, The University of Tokushima,
2-1 Minamijosanjima, Tokushima 770-8506, Japan

Email: hirano@chem.tokushima-u.ac.jp

^b Mitsubishi Rayon Co. Ltd., 2-1 Miyuki-cho, Otake, Hiroshima, 739-0693, Japan

We have reported stereospecific radical polymerizations of *N,N*-dimethylacrylamide¹ and *N*-vinylacetamide² utilizing hydrogen bonding interaction. In the course of the study, we found that tartrates accelerated radical polymerization of 1-vinylpyrrolidone (VP) in toluene at low temperatures by complexing with the monomers through hydrogen bonding. The ¹H NMR spectra of the main-chain methylene groups in chain of the polymers suggested the formation of isotactic-rich polymers whose isotacticity increased with decreasing polymerization temperature. The tacticity at triad levels, however, was unable to be determined from the ¹³C NMR spectra of the main-chain methine carbons because of the complicated splitting.

We also reported that multivariate analysis was useful to obtain qualitative and quantitative information about structural features of copolymers from their complicated ¹³C NMR spectra without assigning individual signals.³ In this study, we attempted to assign NMR spectra of PVP with the aid of principal component analysis (PCA).

The 24 samples were prepared by radical polymerization with varying the polymerization conditions such as solvent, temperature, and additive. Figure 1 shows NMR spectra of the main-chain methine carbons (–CH–) and the main-chain methylene protons (–CH₂–) of the polymer prepared in toluene at 0 °C in the presence of diethyl L-tartrate, as measured in D₂O at 60 °C or in CDCl₃ at 55 °C. The signals of the –CH₂– showed typical splitting due to dyad tacticity in CDCl₃ at 55 °C, whereas the signals assignable to *r* dyad overlapped with those assignable to *m* dyad in D₂O at 60 °C. On the other hand, the signals of the –CH– split into 3 peaks in D₂O at 60 °C, whereas those roughly split into 2 peaks in CDCl₃ at 55 °C.

Thus, bucket integrations of the spectral regions of the –CH– (48.0 – 44.3 ppm; measured in D₂O at

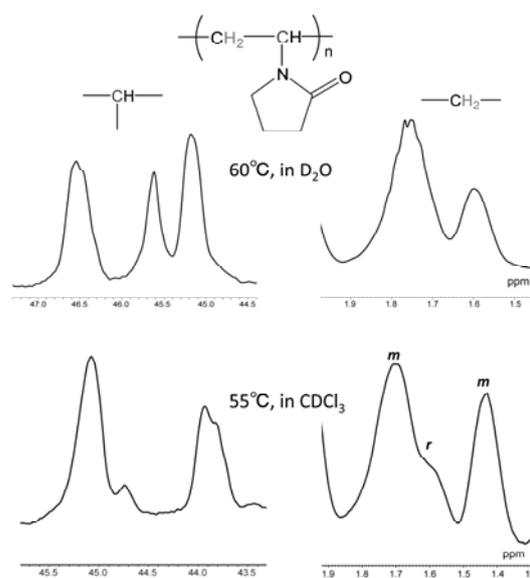


Figure 1. NMR spectra of the –CH– and the –CH₂– of PVP, as measured in D₂O at 60 °C or in CDCl₃ at 55 °C.

60 °C) and of the $-\text{CH}_2-$ (1.87 – 1.27 ppm; measured in CDCl_3 at 55 °C) were performed at an interval of 0.1 ppm and 0.02 ppm, respectively, with JEOL Alice2 ver.5 for metabolome ver.1.6 software. PCA was conducted with the data set thus obtained, using Pattern Recognition Systems Sirius ver.7.0 software. The variances for the first (PC1) and second principal components (PC2) were 83.0 % and 7.5 %, respectively, indicating that the two components explained 90.5 % of the spectral information.

Figure 2 shows the relationship between the PCA loadings and the chemical shift along with the corresponding NMR spectra of the $-\text{CH}-$ and the $-\text{CH}_2-$. In the $-\text{CH}_2-$ region, positive PC1 loadings were observed for the signals assignable to *m* dyad (1.72-1.66 and 1.44-1.36 ppm), whereas negative PC1 loadings were observed for the signals assignable to *r* dyad (1.64-1.54 ppm). In the $-\text{CH}-$ region, positive PC1 loadings were observed at 46.95-46.45 ppm, whereas negative PC1 loadings were observed at 45.95-45.45 ppm, suggesting that the signals at lower and middle magnetic fields were assignable to *mm* and *rr* triads, respectively.

The signals of the $-\text{CH}_2-$ with *m* configuration shifted gradually at higher magnetic field as the isotacticity of the polymers increased, suggesting the influence of the stereostructure at tetrad levels. In the $-\text{CH}_2-$ region, positive PC2 loadings were observed at 1.70-1.54 ppm and at 1.38-1.34 ppm, whereas negative PC2 loadings were observed at 1.50-1.42 ppm, suggesting that positive PC2 loadings correlated with *mm* and *rr* stereosequences and negative PC2 loadings correlated with *mr* stereosequence. In the $-\text{CH}-$ region, positive PC2 loadings were observed at 46.95-46.65 ppm and at 45.95-45.55 ppm, corresponding to the signals assigned as *mm* and *rr* triads with PC1 loadings. Negative PC2 loadings were observed at 45.35-44.65 ppm and at 46.45-46.15 ppm, giving the assignments as shown in Figure 2.

In conclusion, we successfully assigned the signals of the $-\text{CH}-$ of PVP at triad levels with the aid of PCA loadings. This method utilized the correlation between ^1H and ^{13}C NMR spectra measured in different solvents and at different temperatures. Thus, this method is expected to be a promising new way for characterization of synthetic polymers, because such correlation is unobtainable by usual two-dimensional NMR techniques.

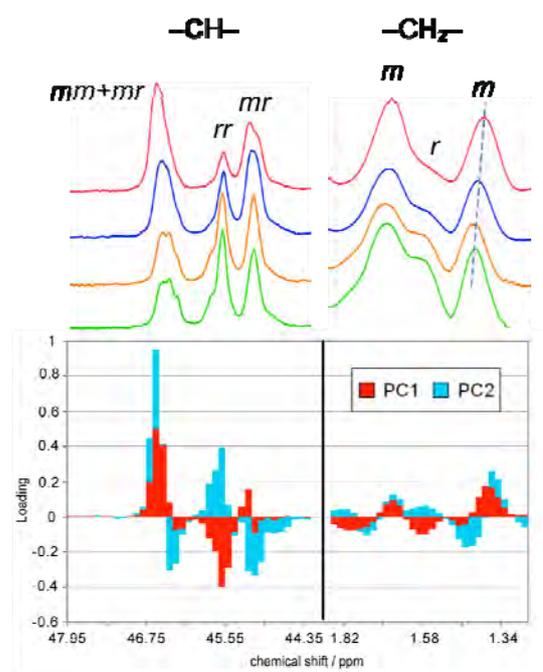


Figure 2. PCA loadings along with NMR spectra of the $-\text{CH}-$ and the $-\text{CH}_2-$ groups in chain of PVP.

Reference

- [1] Hirano, T.; Masuda, S.; Nasu, S.; Ute, K.; Sato, T. Syndiotactic-specific radical polymerization of *N,N*-dimethylacrylamide in the presence of tartrates: a proposed mechanism for the polymerization, *J. Polym. Sci., Part A, Polym. Chem.*, 2009, *47*, 1192.
- [2] Hirano, T.; Okumura, Y.; Seno, M.; Sato, T., Remarkable effect of hydrogen-bonding interaction on stereospecificity in the radical polymerization of *N*-vinylacetamide, *Eur. Polym. J.*, 2006, *42*, 2114.
- [3] Momose, H.; Hattori, K.; Hirano, T.; Ute, K., Multivariate analysis of ¹³C NMR spectra of methacrylate copolymers and homopolymer blends, *Polymer*, 2009, *50*, 3819.

Determination of Comonomer Sequence Distributions of MMA-TBMA Copolymers by means of Multivariate Analysis of ^{13}C NMR Spectra

MOMOSE, Hikaru^{a,b}; MAEDA, Tomoya^a; HIRANO, Tomohiro^a; UTE, Koichi^{a,*}

^a Department of Chemical Science and Technology, The University of Tokushima,
2-1 Minami-josanjima, Tokushima 770-8506, Japan

^b Mitsubishi Rayon Co. Ltd., 2-1 Miyuki-cho, Otake, Hiroshima, 739-0693, Japan

Many functional polymer materials are multi-component copolymers. Detailed analysis of their structural factors is necessary for improvement in material performances. NMR spectroscopy is one of the most powerful tools for analysis of primary structures of copolymers. However, resonances arising from each group in copolymers often exhibit superposed splitting due to comonomer sequences and configurational sequences, and thus assignment of the individual peaks is troublesome. Increasing the number of monomer components in copolymers makes the resonances broader and more complicated. Recently, we successfully determined the chemical compositions of copolymers of methyl methacrylate (MMA) and *tert*-butyl methacrylate (TBMA) by multivariate analysis of ^{13}C NMR spectra without assigning the individual resonance peaks.¹ In the present paper, we focus on the determination of comonomer sequence distributions in the poly(MMA-*co*-TBMA)s by principal component analysis (PCA) and partial least-squares regression (PLSR).

All homopolymers and copolymers were prepared by polymerization with 2,2'-azobisisobutyronitrile (AIBN) in ethyl lactate at 80 °C under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were measured for 8 wt/vol% solution in CDCl_3 at 55 °C using a JEOL ECX400 spectrometer equipped with a 10 mm ^{13}C - $^{15}\text{N}\{^1\text{H}\}$ tunable probe. Bucket integration of the spectral regions 15.1 – 23.1 ppm (the α -methyl carbons), 44.1 – 48.1 ppm (the backbone quaternary carbons) and 175.0 – 179.0 ppm (the carbonyl carbons) was performed at an interval of 0.25 ppm with JEOL Alice2 ver.5 for metabolome ver.1.6 software. PCA and PLSR were conducted using Pattern Recognition Systems Sirius ver.7.0 software.

Figure 1 shows PCA score plots for the data sets of PMMA, PTBMA, nine samples of their blends and 16 samples of poly(MMA-*co*-TBMA)s with various chemical compositions. Linear relationship between the first principal component (PC1) score and the chemical composition in mol% of TBMA units for all samples was obtained with a correlation coefficient (R^2) of 0.998, indicating that the PC1 scores reflected the chemical compositions in polymer samples. The plots for the copolymers (■, □) showed an inverted parabolic relationship. The minimum in the second principal component (PC2) scores was observed for the copolymer

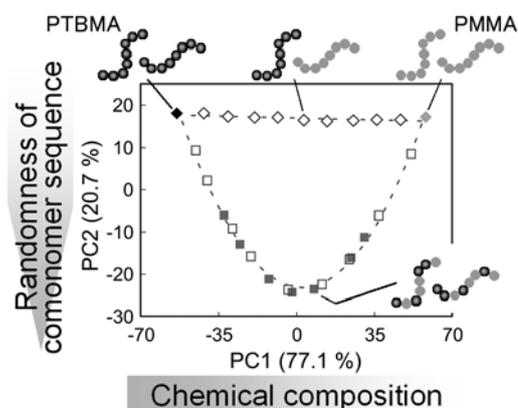


Figure 1. PCA score plots for ^{13}C NMR signals of the carbonyl, backbone quaternary and α -methyl carbons of PMMA (◇), PTBMA (◆), their blends (◇) and poly(MMA-*co*-TBMA)s obtained at early (□) and late (■) stages of copolymerization.

with a chemical composition approximately 50 mol%. These results suggest that the PC2 score should reflect randomness of comonomer sequences. As an index of the randomness, the fraction of hetero (MMA-TBMA) dyad sequence, f_{MT} , was employed (Equation (1)^{2,3}) where f_{MMA} and f_{TBMA} denote mole fractions of MMA and TBMA in a given copolymer, respectively.

$$f_{MT} = \frac{4 \cdot f_{MMA} \cdot f_{TBMA}}{1 + \sqrt{1 + 4(r_{MMA} \cdot r_{TBMA} - 1) \cdot f_{MMA} \cdot f_{TBMA}}} \quad (1)$$

The monomer reactivity ratios, r_{MMA} and r_{TBMA} , were determined to be 0.81 ± 0.06 and 1.26 ± 0.03 , respectively, by the Kelen-Tüdös method for the nine copolymers obtained at early stages of copolymerization. Linear relationship between the PC2 score and f_{MT} has been obtained with an R^2 of 0.996.

Because the NMR spectra also include the information about the fractions of the two homo dyads, f_{MM} (MMA-MMA) and f_{TT} (TBMA-TBMA), the dyad sequence distribution for a given copolymer can be predicted by PLSR using the calculated distributions of the copolymers obtained at early stages of copolymerization as a training set. Figure 2 shows the relationship between the calculated and predicted fractions of the three dyad sequences of the training set. They showed an excellent linear relationship in each series with low relative standard deviations (RSD), indicating that the dyad sequence distribution was predicted

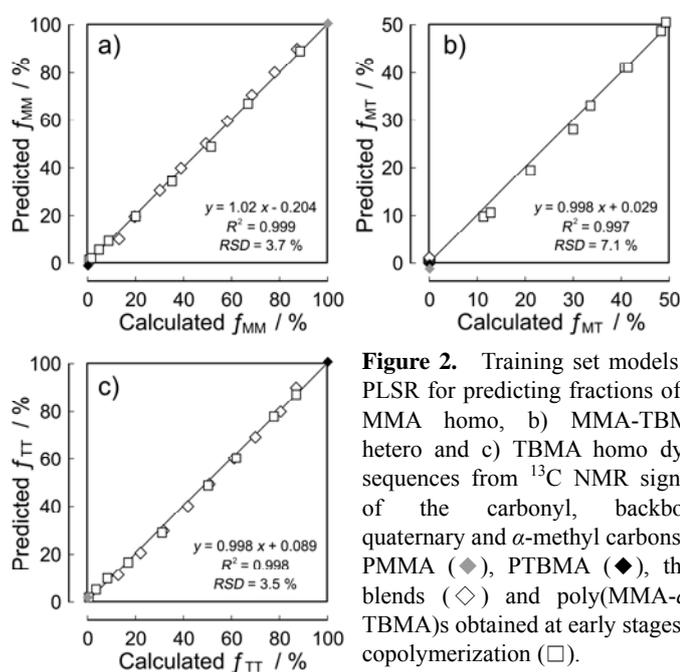


Figure 2. Training set models of PLSR for predicting fractions of a) MMA homo, b) MMA-TBMA hetero and c) TBMA homo dyad sequences from ^{13}C NMR signals of the carbonyl, backbone quaternary and α -methyl carbons of PMMA (\blacklozenge), PTBMA (\blacklozenge), their blends (\diamond) and poly(MMA-co-TBMA)s obtained at early stages of copolymerization (\square).

with highly accuracy and precision. Figure 3 shows the predicted distribution of seven copolymers obtained at higher yields, which deviated slightly from the simulation for the copolymers obtained at early stages of copolymerization.

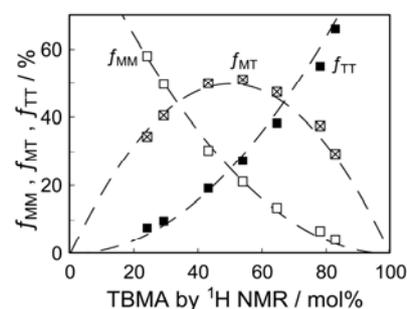


Figure 3. Dyad sequence distributions of poly(MMA-co-TBMA)s obtained at higher yields. Each broken line indicates the dyad sequence calculated from the monomer reactivity ratios and the chemical composition of copolymers.

¹ Momose, H.; Hattori, K.; Hirano, T.; Ute, K., **Multivariate analysis of ^{13}C NMR spectra of methacrylate copolymers and homopolymer blends**, *Polymer*, **2009**, *50*, 3819. ² Ito, K.; Yamashita, Y., **Copolymer composition and microstructure**, *J. Polym. Sci. Part A: General Papers*, **1965**, *3*, 2165. ³ Tosi, C., **Graphical representation of composition and sequence distribution in copolymers**, *Makromol. Chem.*, **1967**, *108*, 307.

Characterization of Methacrylate Terpolymers by Multivariate Analysis of ^{13}C NMR Spectra

NAONO, Tatsuya^a; MOMOSE, Hikaru^{a,b}; HIRANO, Tomohiro^a; UTE, Koichi^{a,*}

^a Department of Chemical Science and Technology, The University of Tokushima,
2-1 Minami-josanjima, Tokushima 770-8506, Japan

^b Mitsubishi Rayon Co. Ltd., 2-1 Miyuki-cho, Otake, Hiroshima, 739-0693, Japan

* E-mail: ute@chem.tokushima-u.ac.jp

NMR spectroscopy is widely used for molecular characterization of polymers. However, it is generally difficult to obtain quantitative information about comonomer sequence distribution and stereoregularity of multi-component copolymers directly from their NMR spectra. This is because the NMR resonances arising from each group in copolymers often exhibit complicated splitting due to comonomer sequences and configurational sequences and the assignment of the individual peaks is troublesome (Figure 1). Recently, we reported that the methods of multivariate analysis were successfully applied to determine the chemical composition¹⁾ and comonomer sequence distribution of the copolymers of methyl methacrylate (MMA) and *tert*-butyl methacrylate (TBMA) from their ^{13}C NMR spectra without making assignment of the individual resonance peaks. In the present paper, we have extended this approach to the characterization of terpolymers made up of MMA, TBMA, and 2-hydroxyethyl methacrylate (HEMA).

All homopolymers, copolymers, and terpolymers used in this study were prepared by polymerization with 2,2'-azobisisobutyronitrile in ethyl lactate at 80 °C under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were measured for 8 % (w/v) solution in CDCl_3 (homopolymers, copolymers, and homopolymer blends) or in a 4/6 mixture of CDCl_3 and $(\text{CD}_3)_2\text{SO}$ (terpolymers) at 55 °C using a JEOL ECX400 spectrometer equipped with a 10 mm ^{13}C - $^{15}\text{N}\{^1\text{H}\}$ tunable probe. An Alice2 ver.5 for metabolome ver.1.6 software (JEOL) and a

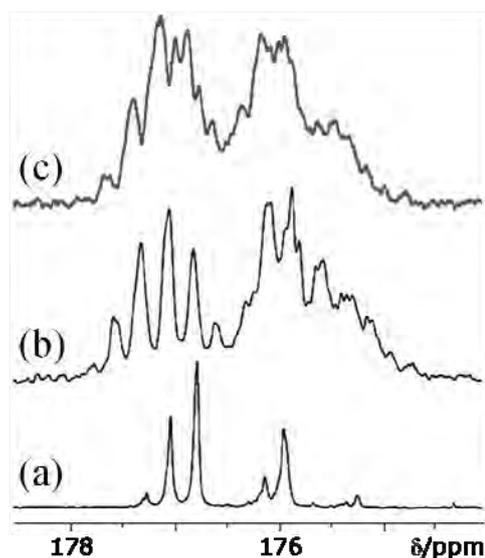


Figure 1. ^{13}C NMR spectra due to the carbonyl groups of PMMA (a), poly(MMA-*co*-TBMA) (b), and poly(MMA-*co*-TBMA-*co*-HEMA) (c) in CDCl_3 at 55°C (100 MHz).

60 °C) and of the $-\text{CH}_2-$ (1.87 – 1.27 ppm; measured in CDCl_3 at 55 °C) were performed at an interval of 0.1 ppm and 0.02 ppm, respectively, with JEOL Alice2 ver.5 for metabolome ver.1.6 software. PCA was conducted with the data set thus obtained, using Pattern Recognition Systems Sirius ver.7.0 software. The variances for the first (PC1) and second principal components (PC2) were 83.0 % and 7.5 %, respectively, indicating that the two components explained 90.5 % of the spectral information.

Figure 2 shows the relationship between the PCA loadings and the chemical shift along with the corresponding NMR spectra of the $-\text{CH}-$ and the $-\text{CH}_2-$. In the $-\text{CH}_2-$ region, positive PC1 loadings were observed for the signals assignable to *m* dyad (1.72-1.66 and 1.44-1.36 ppm), whereas negative PC1 loadings were observed for the signals assignable to *r* dyad (1.64-1.54 ppm). In the $-\text{CH}-$ region, positive PC1 loadings were observed at 46.95-46.45 ppm, whereas negative PC1 loadings were observed at 45.95-45.45 ppm, suggesting that the signals at lower and middle magnetic fields were assignable to *mm* and *rr* triads, respectively.

The signals of the $-\text{CH}_2-$ with *m* configuration shifted gradually at higher magnetic field as the isotacticity of the polymers increased, suggesting the influence of the stereostructure at tetrad levels. In the $-\text{CH}_2-$ region, positive PC2 loadings were observed at 1.70-1.54 ppm and at 1.38-1.34 ppm, whereas negative PC2 loadings were observed at 1.50-1.42 ppm, suggesting that positive PC2 loadings correlated with *mm* and *rr* stereosequences and negative PC2 loadings correlated with *mr* stereosequence. In the $-\text{CH}-$ region, positive PC2 loadings were observed at 46.95-46.65 ppm and at 45.95-45.55 ppm, corresponding to the signals assigned as *mm* and *rr* triads with PC1 loadings. Negative PC2 loadings were observed at 45.35-44.65 ppm and at 46.45-46.15 ppm, giving the assignments as shown in Figure 2.

In conclusion, we successfully assigned the signals of the $-\text{CH}-$ of PVP at triad levels with the aid of PCA loadings. This method utilized the correlation between ^1H and ^{13}C NMR spectra measured in different solvents and at different temperatures. Thus, this method is expected to be a promising new way for characterization of synthetic polymers, because such correlation is unobtainable by usual two-dimensional NMR techniques.

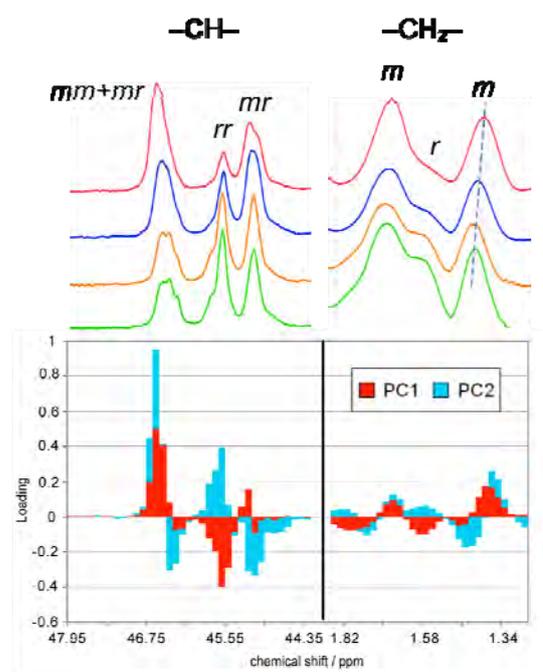


Figure 2. PCA loadings along with NMR spectra of the $-\text{CH}-$ and the $-\text{CH}_2-$ groups in chain of PVP.

with a chemical composition approximately 50 mol%. These results suggest that the PC2 score should reflect randomness of comonomer sequences. As an index of the randomness, the fraction of hetero (MMA-TBMA) dyad sequence, f_{MT} , was employed (Equation (1)^{2,3}) where f_{MMA} and f_{TBMA} denote mole fractions of MMA and TBMA in a given copolymer, respectively.

$$f_{MT} = \frac{4 \cdot f_{MMA} \cdot f_{TBMA}}{1 + \sqrt{1 + 4(r_{MMA} \cdot r_{TBMA} - 1) \cdot f_{MMA} \cdot f_{TBMA}}} \quad (1)$$

The monomer reactivity ratios, r_{MMA} and r_{TBMA} , were determined to be 0.81 ± 0.06 and 1.26 ± 0.03 , respectively, by the Kelen-Tüdös method for the nine copolymers obtained at early stages of copolymerization. Linear relationship between the PC2 score and f_{MT} has been obtained with an R^2 of 0.996.

Because the NMR spectra also include the information about the fractions of the two homo dyads, f_{MM} (MMA-MMA) and f_{TT} (TBMA-TBMA), the dyad sequence distribution for a given copolymer can be predicted by PLSR using the calculated distributions of the copolymers obtained at early stages of copolymerization as a training set. Figure 2 shows the relationship between the calculated and predicted fractions of the three dyad sequences of the training set. They showed an excellent linear relationship in each series with low relative standard deviations (RSD), indicating that the dyad sequence distribution was predicted with highly accuracy and precision. Figure 3 shows the predicted distribution of seven copolymers obtained at higher yields, which deviated slightly from the simulation for the copolymers obtained at early stages of copolymerization.

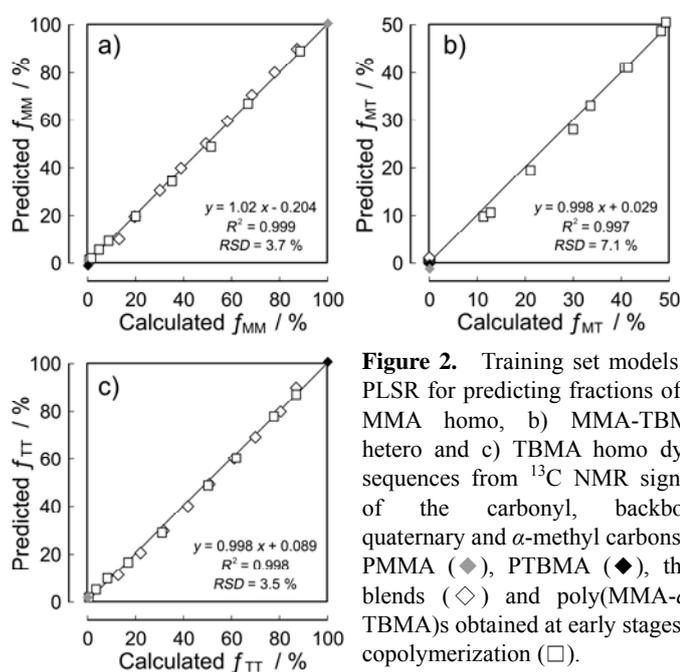


Figure 2. Training set models of PLSR for predicting fractions of a) MMA homo, b) MMA-TBMA hetero and c) TBMA homo dyad sequences from ^{13}C NMR signals of the carbonyl, backbone quaternary and α -methyl carbons of PMMA (\blacklozenge), PTBMA (\blacklozenge), their blends (\diamond) and poly(MMA-co-TBMA)s obtained at early stages of copolymerization (\square).

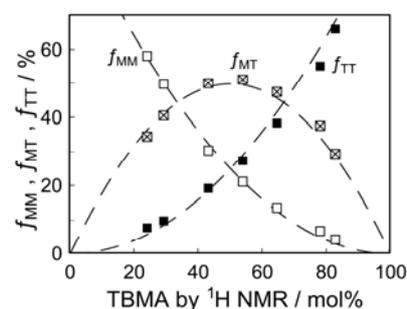


Figure 3. Dyad sequence distributions of poly(MMA-co-TBMA)s obtained at higher yields. Each broken line indicates the dyad sequence calculated from the monomer reactivity ratios and the chemical composition of copolymers.

¹ Momose, H.; Hattori, K.; Hirano, T.; Ute, K., **Multivariate analysis of ^{13}C NMR spectra of methacrylate copolymers and homopolymer blends**, *Polymer*, **2009**, *50*, 3819. ² Ito, K.; Yamashita, Y., **Copolymer composition and microstructure**, *J. Polym. Sci. Part A: General Papers*, **1965**, *3*, 2165. ³ Tosi, C., **Graphical representation of composition and sequence distribution in copolymers**, *Makromol. Chem.*, **1967**, *108*, 307.

Characterization of Methacrylate Terpolymers by Multivariate Analysis of ^{13}C NMR Spectra

NAONO, Tatsuya^a; MOMOSE, Hikaru^{a,b}; HIRANO, Tomohiro^a; UTE, Koichi^{a,*}

^a Department of Chemical Science and Technology, The University of Tokushima,
2-1 Minami-josanjima, Tokushima 770-8506, Japan

^b Mitsubishi Rayon Co. Ltd., 2-1 Miyuki-cho, Otake, Hiroshima, 739-0693, Japan

* E-mail: ute@chem.tokushima-u.ac.jp

NMR spectroscopy is widely used for molecular characterization of polymers. However, it is generally difficult to obtain quantitative information about comonomer sequence distribution and stereoregularity of multi-component copolymers directly from their NMR spectra. This is because the NMR resonances arising from each group in copolymers often exhibit complicated splitting due to comonomer sequences and configurational sequences and the assignment of the individual peaks is troublesome (Figure 1). Recently, we reported that the methods of multivariate analysis were successfully applied to determine the chemical composition¹⁾ and comonomer sequence distribution of the copolymers of methyl methacrylate (MMA) and *tert*-butyl methacrylate (TBMA) from their ^{13}C NMR spectra without making assignment of the individual resonance peaks. In the present paper, we have extended this approach to the characterization of terpolymers made up of MMA, TBMA, and 2-hydroxyethyl methacrylate (HEMA).

All homopolymers, copolymers, and terpolymers used in this study were prepared by polymerization with 2,2'-azobisisobutyronitrile in ethyl lactate at 80 °C under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were measured for 8 % (w/v) solution in CDCl_3 (homopolymers, copolymers, and homopolymer blends) or in a 4/6 mixture of CDCl_3 and $(\text{CD}_3)_2\text{SO}$ (terpolymers) at 55 °C using a JEOL ECX400 spectrometer equipped with a 10 mm ^{13}C - $^{15}\text{N}\{^1\text{H}\}$ tunable probe. An Alice2 ver.5 for metabolome ver.1.6 software (JEOL) and a

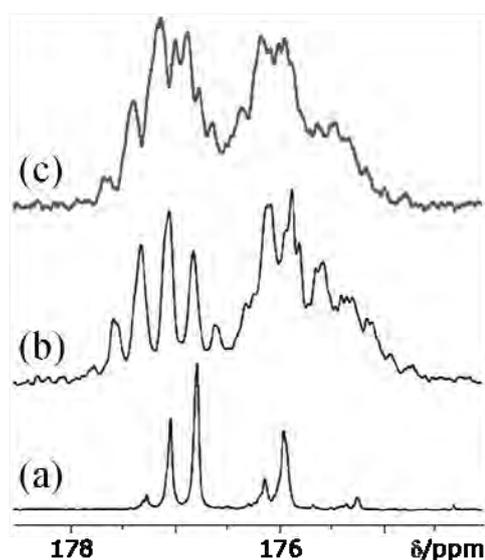


Figure 1. ^{13}C NMR spectra due to the carbonyl groups of PMMA (a), poly(MMA-*co*-TBMA) (b), and poly(MMA-*co*-TBMA-*co*-HEMA) (c) in CDCl_3 at 55°C (100 MHz).

Sirius ver.7.0 software (Pattern Recognition Systems) were used for the principal component analysis (PCA) and partial least-squares regression (PLSR) of the data sets.

Bucket integration of the spectral regions 15.0–20.0 ppm (the α -methyl carbons), 42.0–48.0 ppm (the backbone quaternary carbons) and 173.0–179.0 ppm (the carbonyl carbons) was performed at an interval of 0.10 ppm. Figure 2 shows the PCA score plots for the data set of the integral values of totally 78 samples (3 homopolymers, 33 blends of the homopolymers, 12 poly(MMA-*co*-TBMA)s, 14 poly(MMA-*co*-HEMA)s, 16 terpolymers). The variances for the first (PC1), second (PC2) and third principal components (PC3) were 51.0, 29.8, and 15.1%, respectively, and their total amounted to 95.9%, indicating that the spectral information of the data set was explained well with these three parameters. The PC1 and PC2 showed relationship to the chemical composition whereas the PC3 showed relationship to the randomness of comonomer sequence. PLSR using the spectra of the homopolymer blends as a training set has allowed us to propose a calibration model which predicts the fractions of MMA, TBMA and HEMA units for a given terpolymer with relative standard deviations of 8.1, 5.6 and 10.7 mol%, respectively.

Reference

- [1] Momose, H.; Hattori, K.; Hirano, T.; Ute, K., Multivariate analysis of ^{13}C NMR spectra of methacrylate copolymers and homopolymer blends, *Polymer*, 2009, 50, 3819.

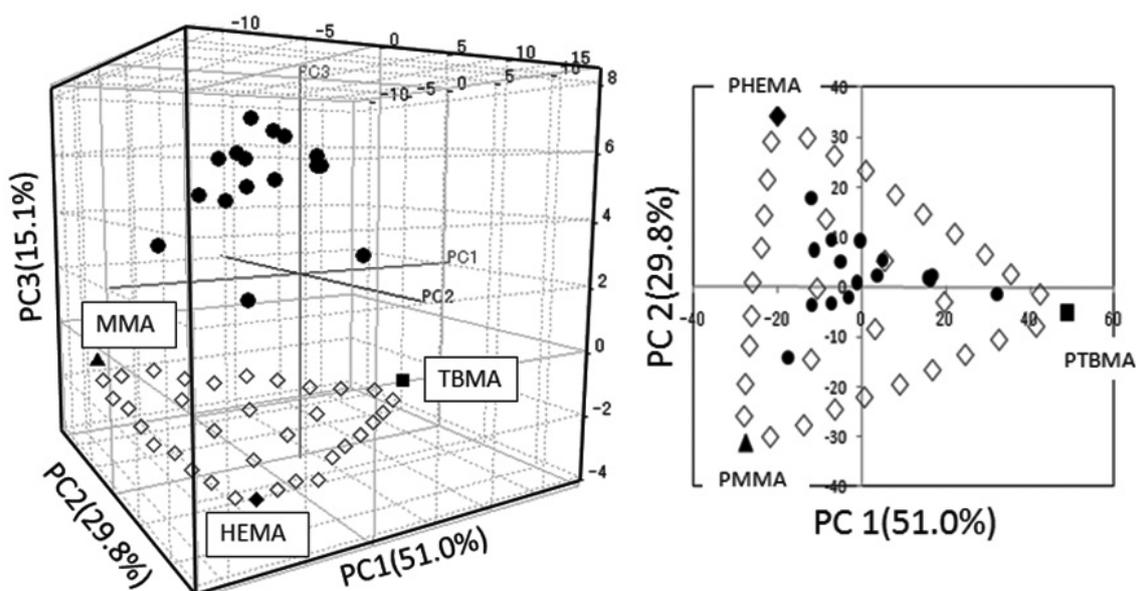


Figure 2. Principal component score plots for the ^{13}C NMR spectra of 78 samples.

PMMA (◆), PTBMA (▲), PHEMA (■), homopolymer blends (◇), poly(MMA-*co*-TBMA)s (△), poly(MMA-*co*-HEMA)s (□), poly(MMA-*co*-TBMA-*co*-HEMA)s (●).

Thermo-sensitive Pluronic F127-bPEI-NONOate as a new nitric oxide donor

Jihoon Kim ^a, Kaushik Singha ^a, Won Jong Kim^{a*}.

^a*Dept. of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Korea.*

**Email: wjkim@postech.ac.kr*

Although percutaneous transluminal coronary angioplasty (PTCA) has been used to patients with cardiovascular and coronary artery disease over 20 years and it improves the quality of the life, this technique causes patients' suffer and fear from reoccurrence of stenosis, restenosis, after implantation of stents. To prevent restenosis, drug-eluting stents are developed. Paclitaxel and doxorubicin loaded stents shows decreased restenosis, but it damaged vascular endothelial cells as well as vascular smooth muscle cells. Therefore, it is important to develop the method which reduces the proliferation of the smooth muscles cells and platelet adhesion and induces the proliferation of the endothelial cells. Nitric oxide (NO) is a highly reactive free radical molecule known for mammalian biological signaling pathway. This NO has been shown to reduce platelet adhesion and proliferation of smooth muscle cells, but in general method, fast NO release of NO donor is a disadvantage for further application.

NONOates is 1-substituted diazen-1-ium-1,2 diolates (diazoniumdiolates), one type of nitric oxide donor, which give nitric oxide in vivo conditions and the release pattern and total amount of nitric oxide can be controlled by its backbone. In the experiment, we select Pluronic[®] F127, triblock copolymer which has the thermosensitive characteristics to control the release of NO by gelation and bPEI (branched polyethyleneimine) which has secondary amine for conjugation of NONOates. We tested three types of bPEI-NONOates and then made the F127-bPEI. After the test of F127-bPEI, we could make the F127-bPEI-NONOates.

That is, in this experiment, we could make thermo-sensitive nitric oxide-releasing donor and test the possibility as a new stent material.

References

- [1] Friedman, A. J.; Han, G.; Navati, M. S.; Chacko, M.; Gunther, L.; Alfieri, A.; Friedman, J. M. Sustained release nitric oxide releasing nanoparticles: characterization of a novel delivery platform based on nitrite containing hydrogel/glass composites. *Nitric Oxide* 2008, 19, 12.
- [2] Zuckerbraun, B. S.; Stoyanovsky, D. A.; Sengupta R.; Shapiro, R. A.; Ozanich, B. A.; Rao, J.; Barbato J. E.; Tzeng, E. Nitric oxide-induced inhibition of smooth muscle cell proliferation involves S-nitrosation and inactivation of RhoA. *Am J Physiol Cell Physiol* 2007, C824.
- [3] Jo, Y. S.; van der Vlies, A. J.; Gantz, J.; Thacher, T. N.; Antonijevic, S.; Cavadini, S.; Demurtas D. Stergiopoulos, N.; Hubbell, J. A. Micelles for delivery of nitric oxide. *J. Am. Chem. Soc.*, 2009, 131 (40), 14413.
- [4] Keefer, L. K. Biomaterials: thwarting thrombus. *Nat. Mater.*, 2003, 2, 357
- [5] Dzau, V. J.; Braun-Dullaeus, R. C.; Sedding, D. G. Vascular proliferation and atherosclerosis: new perspectives and therapeutic strategies. *Nat. Med.* 2002, 8, 1249
- [6] Bohl K. S.; West, J. L. Nitric oxide-generating polymers reduce platelet adhesion and smooth muscle cell proliferation. *Biomaterials* 2000, 21 (22), 2273.
- [7] Shishido, S, M.; Seabra, A, B.; Loh, W.; Ganzarolli de Oliveira, M. Thermal and photochemical nitric oxide release from S-nitrosothiols incorporated in Pluronic F127 gel: potential uses for local and controlled nitric oxide release. *Biomaterials* 2003, 24 (20), 3543

Preparation of lanthanide alginate from algae and its characterization

Jin-San Kim, Tara Sankar Pathak, Sanghyuk Kang, Ki-Jung Paeng*

Chemistry, Yonsei University, Wonju, Kangwondo, Republic of Korea, 220-710

Alginic acid and metal alginates were prepared from fresh algae, edible seaweed (*Undaria pinnatifida*) which is a kind of brown seaweeds using tailored extraction method. We confirmed that metal alginates were made from an alginic acid comparing FT-IR spectra in the preliminary work. Asymmetric stretching of free carboxyl group of metal alginate was moved in calcium and cobalt alginates : regarding cobalt alginate, wavenumber at 1630 cm^{-1} was shifted to 1585 cm^{-1} . We think that the change of charge density around the carbonyl group was created. In this work, we used lanthanide alginate to search for next promising application research. Surface morphology with scanning electron microscopy (SEM), the decomposition of metal alginate and formation of respective carbonate at high temperature in TGA and DSC study and quantitative analysis result of metal treated in lanthanide alginate using ICP-OES will be presented.

Magnet-Assisted Gene Delivery with Hybrid Superparamagnetic Iron Oxide Nanoparticle-Branched Polyethylenimine Magnetoplexes on Vascular Endothelial Cells

NAMGUNG, Ran^a, SINGHA, Kaushik^a, YU, Mi Kyung^b, JON, Sangyong^b, KIM, Yong Sook^c, AHN, Youngkeun^c, PARK, In-Kyu^c, KIM, Won Jong^{a,*}

^a*Department of Chemistry, BK21 Program, Polymer Research Institute, Pohang University of Science and Technology, San 31, Hyoja-dong, Pohang 790-784, Korea*

^b*Department of Life Science, GIST, 1 Oryong-dong, Buk-gu, Gwangju 500-712, Republic of Korea*

^c*Department of Biomedical Sciences, Chonnam National University Medical School, Centre for Biomedical Human Resources at Chonnam National University, Gwangju 501-746, Korea*

* E-mail: wjkim@postech.ac.kr

Emergence of gene therapy provides a highly versatile and potent armor in combating various human diseases (1). Irrespective of the vector types, efficient gene transfection demands appreciable concentration of efficient cell-binding delivery vectors at the target site at the onset of gene delivery. Therefore it is necessary to develop simple, fast and efficient methods or strategies which can expedite the accumulation of the therapeutic cargo on the surface of the target cells and can be remotely controlled by physical means, particularly in in vivo systemic administrations. Among various physical methods, magnet-assisted transfection (2, 3) utilizing magnetic nanoparticles has gained considerable attention due to the promising efficiency, non-toxicity of these magnetic particles and simple experimental needs.

The work demonstrated the development of thermally cross-linked superparamagnetic nanomaterial which possessed polyethylene glycol moiety and covalently linked branched polyethylenimine (BPEI), and exhibited highly efficient magnetofection even under serum conditioned media. The study showed its high anti-biofouling, cell viability and serum stability and thus revealed a potential magnetic nanoparticle-mediated targeted gene delivery system. The sequential steps for the enhanced magnetofection had been studied by monitoring cellular uptake with the aid of confocal microscopy.

Inflammation and endothelial dysfunction are major threshold developments in the progression of atherosclerosis (4). The early stage of the disease involves the activation of the endothelium triggered by variety of stimuli including oxidized lipids and cytokines such as tumor necrosis factor (TNF- α). TNF- α is one of the major inflammatory cytokines that

mediates a wide range of biological responses including inflammation, infection, injury, and apoptosis (5). Activated endothelium then expresses specific adhesion receptors and cytokines that enhance the recruitment of leukocytes as well as factors which accelerate clot formation, into the vessel wall (6). Thus, the mitigation of the initial activation of endothelium triggered by TNF- α could be of great importance in preventing the severe progression of atherosclerosis. Therefore genetic modification of endothelial cells by transferring therapeutic gene in order to resist injury-mediated activation, has gained an increasing attention as an alternative to drug therapy.

The BPEI-SPION superparamagnetic particle mediated rapid and efficient transfection in primary vascular endothelial cells (HUVEC) successfully inhibits expression of PAI-1 which is responsible for various vascular dysfunctions such as vascular inflammation and atherosclerosis and thereby provides a potential strategy to transfect highly sensitive HUVEC.

This rapid targeted magnetofection should open up plethora of opportunities to combat several vascular diseases like atherosclerosis and other diseases which requires fast and target-specific delivery of concerned genes. In addition to these advantages this magnetic nanoparticles could be endowed with stimuli-responsiveness as well as other functional attributes to address various impediments associated with other target-specific gene delivery and to meet various therapeutic needs.

References

- [1] Pack, D. W.; Hoffman, A. S.; Pun, S.; Stayton, P. S. Design and development of polymers for gene delivery, *Nat. Rev. Drug. Discov.* 2005, 4, 581.
- [2] Dobson, J. Gene therapy progress and prospects: magnetic nanoparticle-based gene delivery, *Gene Ther.* 2006, 13, 283.
- [3] Scherer, F.; Anton, M.; Schillinger, U.; Henkel, J.; Bergemann, C.; Kruger, A. Gansbacher, B.; Plank, C. Magnetofection: enhancing and targeting gene delivery by magnetic force in vitro and in vivo, *Gene Ther.* 2002, 9, 102.
- [4] Kim, Y. S.; Ahn, Y.; Hong, M. H.; Joo, S. Y.; Kim, K. H.; Sohn, I. S. Park, H. W.; Hong, Y. J.; Kim, J. H.; Kim, W.; Jeong, M. H.; Cho, J. G.; Park, J. C.; Kang, J. C. Curcumin Attenuates Inflammatory Responses of TNF-[α]-Stimulated Human Endothelial Cells, *J. Cardiovasc. Pharmacol.* 2007, 50, 41.
- [5] Baud, V.; Karin, M. Signal transduction by tumor necrosis factor and its relatives, *Trends Cell Biol.* 2001, 11, 372.
- [6] Ross, R. Atherosclerosis - an inflammatory disease, *N. Engl. J. Med.* 1999, 340, 115.
- [7] Namgung, R.; Singha, K.; Yu, M. K.; Jon, S.; Kim, Y. S.; Ahn, Y.; Park, I. K.; Kim, W. J. Hybrid superparamagnetic iron oxide nanoparticle-branched polyethylenimine magnetoplexes for gene transfection of vascular endothelial cells, *Biomaterials*, 2010, 31, 4204.

Synthesis and Characterization of Bioreducible BPEI-SS-PEG-cNGR as a Tumor Targeted Nonviral Gene Carrier

SEJIN SON, WON JONG KIM*

Department of Chemistry, BK21 program, Polymer Research Institute, Pohang University of Science and Technology, San 31, Hyoja-dong, Pohang 790-784 (Korea)

**E-mail: wjkim@postech.ac.kr*

The rational design of integrated, multi-functional polymeric carriers is prerequisite for the successful nonviral cancer gene therapy [1]. We developed identical functionalization conditions which would allow simultaneous installation of various types of functionalities in one-pot reaction under mild conditions through pre-thiolation strategy incorporating thiol-containing components. The combining effect of targeting and intracellular reducible functions concerning gene transfection in various cancer cells was investigated in this work with the view point of physicochemical properties and cellular uptake mechanism.

We confirmed that the synthesis of cNGR conjugated reducible BPEI polymers (BPEI-SS-cNGR) by conjugating cNGR-PEG5K to BPEI1.2K-SH at a molar ratio of 1:6.62. To test the ability of cNGR-functionalized bio-reducible polymers for targeting and delivering pDNA to tumors, B16F1 cells which showed high level of expression of CD13, and MDA-MB-231 cells as a CD13 negative control were chosen as the model of tumor cells. As the result of preincubation with excess amount of free cNGR peptide, competitive inhibition of CD13 receptor by free cNGR significantly inhibited the gene expression of BPEI-SS-cNGR/pDNA polyplex in CD13 positive B16F1 cell (Figure 1, a), but did not show inhibitory effect in CD13 negative MDA-MB-231 cells. The presence of free cNGR in the medium resulted in a near 8 fold decrease of gene expression efficiency on B16F1 cells which demonstrated that free cNGR and the cNGR motif on the surface of BPEI-SS-cNGR /pDNA competed with the same CD13 receptor.

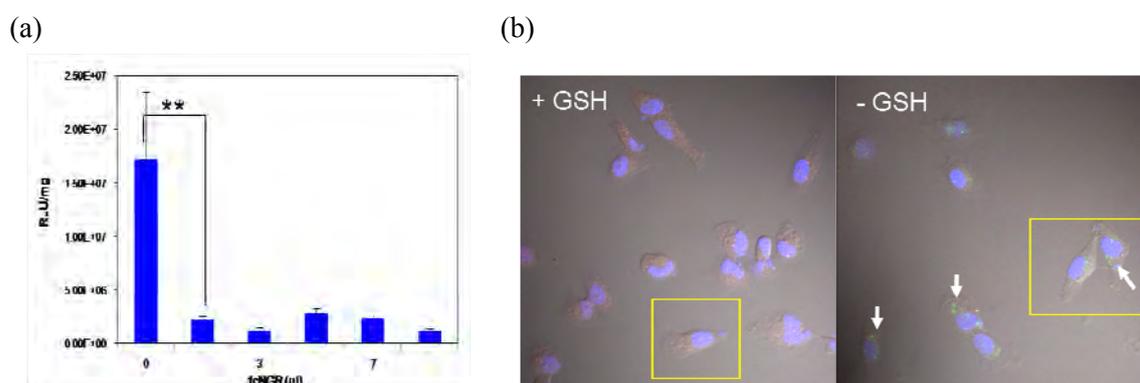


Figure 1. (a) Targeting efficiency of cNGR conjugated polymer to CD13-positive cells was evaluated by competitive inhibition assay using free cNGR (fcNGR). ** $p < 0.01$ compared with each group. (b) Intracellular trafficking of BPEI-SS-cNGR (green)/pDNA (red) complex by CLSM after pretreatment of HT1080 cells with GSH MEE. The nuclei were stained with DAPI (blue).

The disulfide cross-linked polymer was designed to exploit the reducibility providing a clear opportunity to design vectors that are stable in the plasma but dissociate within the cytoplasm. To address this aspect, in our initial experiments, we confirmed the destabilization of the BPEI-SS-cNGR/pDNA complex in the presence of disulfide reducing agents, DTT (5 mM or 5 μ M), indicating the degradability of the polymer via redox reactions. Hydrodynamic size of BPEI-SS-cNGR/pDNA complex in the PBS solution containing 5 mM DTT was increased steadily from 100 nm to 520 nm as incubation time goes by and this size was approximately similar with that of LMW BPEI1.2K/pDNA complex. Additionally, observing the intracellular trafficking by CLSM after pretreatment of HT1080 cells with GSH MEE to increase intracellular GSH pool revealed that the BPEI-SS-cNGR/pDNA complex could facilitate efficient intracellular dissociation compared with untreated cell. For CLSM images, pDNA was labeled with TOTO (red) and BPEI-SS-cNGR polymer was labeled with FITC (green). After 1 hr incubation for GSH MEE treated HT1080 cell, pDNA (red color) dispersed homogeneously through the cytoplasm region indicating pDNA dissociated from BPEI-SS-cNGR, while aggregated BPEI-SS-cNGR polymer (green) dots were observed in cytoplasm and even in nucleus (white arrows) and the red color did not bright (Figure 1, b). It implies that increase of intracellular GSH concentration enhances the dissociation of pDNA from BPEI-SS-cNGR polymer resulted in higher transfection efficiency.

Therefore, the influence of the disulfide reduction on the gene expression was further confirmed with BSO as an inhibitor of gamma-glutamylcysteine synthetase (gamma-GCS) lowering intracellular GSH concentration. Because of the effect of BSO on the inhibition of GSH production, the luciferase expression level was decreased by \sim 2.9 times in a BSO dose dependent manner. From these comprehensive evaluations, we conclude that the BPEI-SS-cNGR polymer may at least partially undergo an gamma-GCS dependent, and therefore GSH-dependent, reduction inside the cell.

References

- [1] Hubbell, J. A., Non-viral gene delivery: Multifunctional polyplexes as locally triggerable nonviral vectors, *Gene Ther.* 2006, 13, 1371–1372.
- [2] Wood, K. C., Azarin, S. M., Arap, W., Pasqualini R., Langer R. and Hammond P. T., Tumor-Targeted Gene Delivery Using Molecularly Engineered Hybrid Polymers Functionalized with a Tumor-Homing Peptide, *Bioconjugate Chem.* 2008, 19, 403–405
- [3] Peng, Q. Zhong, Z. and Zhuo, R. Disulfide Cross-Linked Polyethylenimines (PEI) Prepared via Thiolation of Low Molecular Weight PEI as Highly Efficient Gene Vectors. *Bioconjugate Chem.* 2008, 19, 499-506.

Programmable Permanent Data Storage Devices based on Nanoscale Thin Films of a Thermally Stable Aromatic Polyimide

Dongmin Kim, Samdae Park, Kyungtae Kim, Yong-gi Ko, Jin chul Kim, Wonsang Kwon, Junman Choi, Moonhor Ree *

Department of Chemistry, National Research Laboratory for Polymer Synthesis and Physics, Pohang Accelerator Laboratory, Center for Electro-Photo Behaviors in Advanced Molecular Systems, BK School of Molecular Science, Division of Advanced Materials Science, and Polymer Research Institute, Pohang University of Science & Technology, Pohang 790-784, Republic of Korea
**E-mail: ree@postech.edu*

In this study, we newly synthesized a thermally and dimensionally stable polyimide, poly(4,4'-amino(4-hydroxyphenyl)diphenylene hexafluoroisopropylidenediphthalimide) (6F-HTPA PI), which is an analogue of 6F-TPA PI. The glass transition and thermal stability of the 6F-HTPA PI product were measured in nitrogen atmosphere. The polymer product was found to have $T_d = 400$ °C and $T_g = 150$ °C. Thus this PI is thermally stable and has a high T_g , as observed for conventional PIs used widely in the electronic industry because of their advantageous properties, such as high thermal stability, excellent dimensional stability, excellent mechanical properties, good adhesion, and excellent optical transparency. Moreover, the PI synthesized in our study was found to exhibit excellent film formation capability, providing high quality nanoscale thin films with smooth surface via a simple and conventional spin-coating process. The 6F-HTPA PI is highly soluble in organic solvents such as dimethylacetamide, *N*-methyl-2-pyrrolidone and cyclopentanone, and thus easily processed as nanoscale thin films through conventional solution spin-, roll- or dip-coating and subsequent drying. Interestingly the 6F-HTPA PI was found to exhibit excellent write-once-read-many-times memory (WORM) behavior with a high ON/OFF ratio (up to 10^6) and a long retention time, which is quite different from the volatile DRAM behavior observed for the 6F-TPA PI. Moreover, the WORM behavior was found to be unipolar in positive voltage sweep as well as in negative voltage sweep. Such the WORM characteristics were nicely demonstrated even at high temperatures up to 150 °C. In addition, the switching mechanism of the WORM memory devices was investigated.

High-Performance Unipolar and Bipolar Electronic Memory Polyimide Bearing Triphenylamine-Related Moieties

Kyungtae Kim, Samdae Park, Dongmin Kim, Yong-gi Ko, Jinchul Kim, Jungwoon Jung, Yecheol Rho, Byungcheol Ahn, Wonsang Kwon, Mihee Kim, Sungmin Jung, Junman Choi, Moonhor Ree*

*Department of Chemistry, National Research Laboratory for Polymer Synthesis and Physics, Pohang Accelerator Laboratory, Center for Electro-Photo Behaviors in Advanced Molecular Systems, BK School of Molecular Science, Division of Advanced Materials Science, and Polymer Research Institute, Pohang University of Science & Technology, Pohang 790-784, Republic of Korea
E-mail: ree@postech.edu*

Synthesis and electrical switching characteristics of a new high-performance polyimide (PI), poly(3,3'-di(4-(diphenylamino)benzylidene)liminoethoxy)-4,4'-biphenylenehexafluoroisopropylidenedipthalimide) (6F-HAB-TPAIE PI) is reported. This PI bears triphenylamine-related moieties as side groups and is dimensionally stable up to 280 °C and thermally stable up to 440 °C. In devices fabricated with the PI as an active memory layer, the active PI was found to operate at less than ± 2 V in electrically bistable unipolar and bipolar switching modes by controlling the compliance current. The PI layer exhibits repeatable writing-reading-erasing capability with high reliability in ambient air conditions as well as at high temperatures up to 130 °C. This PI also exhibits a high ON/OFF current ratio up to 10^9 . The observed nonvolatile memory behaviors are described by Schottky emission and local filament formation. This study has demonstrated that this thermally, dimensionally stable PI polymer is a promising material for mass production at low cost for high-performance, programmable, nonvolatile memory devices that can be operated with low power consumption in unipolar and bipolar switching modes.

Electrically programmable memory characteristics on the film surfaces of novel polyimide

Wonsang Kwon¹, Taek Joon Lee¹, Cha-Wen Chang², Suk Gyu Hahm¹, Kyungtae Kim¹, Samdae Park¹, Dong Min Kim¹, Jin Chul Kim¹, Sangwoo Jin¹, Jungwoon Jung¹, Yecheol Rho¹, Byungcheol Ahn¹, Mihee Kim¹, Yong-Gi Ko¹, Sungmin Jung¹, Junman Choi¹ Guey-Sheng Liou³ and Moonhor Ree^{1*}

¹*Department of Chemistry, National Research Laboratory for Polymer Synthesis and Physics, Center for Electro-Photo Behaviors in Advanced Molecular Systems, Polymer Research Institute, and BK School of Molecular Science, Pohang University of Science & Technology, Pohang 790-784, Republic of Korea* *Email: ree@postech.edu ²*Department of Applied Chemistry, National Chi Nan University, 1 University Road, Puli, Nantou Hsien 54561, Taiwan, Republic of China* ³*Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan, Republic of China*

The electrically programmable memory devices based on nanoscale thin film of a thermally and dimensionally stable 6F-2TPA PI films were fabricated and investigated their switching characteristics and reliability. The 6F-2TPA PI films exhibit versatile memory characteristics that depend on the film thickness. All the PI films are initially present in the OFF state. The PI films with thicknesses in the range 34-74nm exhibit excellent WORM (i.e. fuse-type) memory characteristics with and without polarity depending on the thickness. The WORM memory devices are electrically stable, even in air ambient, for a very long time. The devices' ON/OFF current ratio is high, up to 1010. Therefore, these WORM memory devices can provide an efficient, low-cost means of permanent data storage. On the other hand, the 100nm thick PI films exhibit excellent DRAM memory characteristics with polarity. The ON/OFF current ratio of the DRAM devices is as high as 1011. These extreme thickness-dependent I-V results can be understood by considering the HOMO and LUMO levels and thicknesses of the 6F-2TPA PI film, the work functions of the top and bottom electrodes.

These properties open up the possibility of the low-cost mass production of high density and very stable digital nonvolatile WORM and volatile DRAM memory devices.

Programmable Digital Memory Characteristics of Nanoscale Thin Films of a Fully Conjugated Polymer

PARK Samdae, LEE, Taek Joon, HAHM, Suk Gyu, KIM, Dong Min, KIM, Kyungtae, KIM, Jinchul, KWON, Won-Sang, CHOI, Junman and REE, Moonhor*

*Department of Chemistry and Center for Electro-Photo Behaviours in Advanced Molecular Systems,
POSTECH, Pohang, Republic of Korea, 790-784*

**E-mail: ree@postech.edu*

This paper reports for the first time the programmable digital memory characteristics of the nanoscale thin films of a fully π -conjugated polymer, poly(diethyl dipropargylmalonate) (PDEDPM) in the absence of doping. This π -conjugated polymer was found to exhibit good solubility in organic solvents and to be easily processed to form nanoscale thin films through the use of conventional solution spin-, roll-, or dip-coating and subsequent drying. Films of the π -conjugated polymer with top and bottom metal electrodes exhibit excellent dynamic random access memory (DRAM) characteristics or write-once-read-many-times (WORM) memory behavior without polarity, depending on the film thickness. All the PI films are initially present in the OFF-state. Films with a thickness of 30 nm were found to exhibit very stable WORM memory characteristics without polarity and an ON/OFF current ratio of 10^6 , whereas films with a thickness of 62–120 nm were found to exhibit excellent DRAM characteristics without polarity and an ON/OFF current ratio as high as 10^8 . These memory characteristics are governed by trap-limited space-charge limited conduction and heterogeneously local filament formation. In these polymer films, both the ester units and the conjugated double bonds of the polymer backbone can act as charge trapping sites. The excellent bistable switching properties and processibility of this π -conjugated polymer mean that it is a promising material for the low-cost mass production of high density and very stable digital nonvolatile WORM memory and volatile DRAM devices.

Enhanced Device Performance of Organic Solar Cells via Reduction of the Crystallinity in the Donor Polymer

J. H. Park^a, J.-I. Park^b, D. H. Kim^b, J.-H. Kim^a, J. S. Kim^a, J. H. Lee^a,
M. Sim^a, S. Y. Lee^b, K. Cho^{a*} E-mail: kwcho@postech.ac.kr

^a*Department of Chemical Engineering /School of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang, 790-784, Korea*

^b*Display Laboratory, Samsung Advanced Institute of Technology, Yongin, 446-712, Korea*

A new π -conjugated polymer, poly(2,5-dioctyloxyphenylene vinylene-alt-3,3-dioctylquaterthiophene) (PPVQT-C8), consisting of alternating p-divinylene phenylene and 3,3-dialkylquaterthiophene units, was synthesized for use in organic solar cell devices. The crystallinity of poly(quaterthiophenes) (PQTs) was reduced by introducing p-divinylene phenylene units between pairs of quaterthiophene units. A well-mixed nanoscale morphology of PPVQT-C8:PCBM photoactive layer resulted from this modification, which increased the power conversion efficiency relative to devices based on highly crystalline PQTs. Bulk heterojunction solar cells based on PPVQT-C8:PC60BM blends with a 1:3 ratio presented the best photovoltaic performances, with a short-circuit current density (J_{sc}) of 6.7 mA/cm², an open-circuit voltage (V_{oc}) of 0.67 V, a fill factor (FF) of 0.62 and a power conversion efficiency (PCE) of 2.8% under illumination of AM 1.5 with light intensity of 100 mW/cm². The charge carrier mobility and morphology studies indicated that an optimized interpenetration network composed of PPVQT-C8:PCBM could be achieved in a blend ratio of 1:3.

P43

Charge transport anisotropy in the transistor of 6,13-bis(triisopropylsilylethynyl) pentacene single crystal with cofacial molecular stacks

Hyun Ho Choi, Do Hwan Kim, Wi Hyoung Lee, Jung Ah Lim, Donghoon Kwak and Kilwon Cho*

*Department of Chemical Engineering, Pohang University of Science and Technology,
Pohang, 790-784, Korea, E-mail: kwcho@postech.ac.kr*

Measuring the field-effect mobility anisotropy of the conjugated molecules with cofacial molecular stacks basically gives insight into the correlation between the charge transport and the stacking properties. Here, the anisotropic ratio of the field-effect mobility in 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS PEN) single crystal with cofacial molecular stacks in *a-b* basal plane was measured. Further, this anisotropic ratio was explained by the HOMOs level coupling and the various hopping routes. By classifying the various kinds of stacking types, it was recognized that the sequence of hopping routes is the origin of charge transport anisotropy. The calculation of the HOMOs level coupling is coincident with the measured anisotropic ratio of the field-effect mobility.

Bulk heterojunction solar cells based on preformed polythiophene nanowires via solubility-induced crystallization

J.-H. Kim^a, J. H. Park^b, J. H. Lee^a, J. S. Kim^a, M. Sim^b, C. Shim^a, K. Cho^{a,b,*}

*School of Environmental Science and Engineering,
Pohang University of Science and Technology, Pohang, Korea^a
Department of Chemical Engineering,
Pohang University of Science and Technology, Pohang, Korea^b
E-mail: kwcho@postech.ac.kr*

Here, we report the preparation of well-controlled nanoscale morphologies in photoactive thin films. The fabrication of bulk heterojunction structures in blend films of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) employed two steps to achieve first the *in-situ* formation of self-organized P3HT nanowires using a marginal solvent, and second, phase separation via mild thermal annealing. Morphological changes in the active layers that had been spin-cast from a marginal solvent, with varying annealing temperatures, were systematically studied and compared to the morphologies of films spin-cast from a good solvent. The interpenetrating nanowire structure yielded power conversion efficiencies as high as 4.07 % due to the enhanced charge transport. Hole and electron mobilities increased substantially to $1.6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, due to the two step process of P3HT crystallization by nanowire formation and subsequent phase separation. Photovoltaic performances improved with increasing film thickness up to 300 nm as a result of the interpenetrating donor/acceptor network structure.

High-Performance Organic Transistors from Soluble Acene-Polymer Blend Semiconductors

Wi Hyoung Lee, Donghoon Kwak, and Kilwon Cho*

*Department of Chemical Engineering, Pohang University of Science and Technology,
Pohang, 790-784, Korea, E-mail: kwcho@postech.ac.kr*

We report on the structural development and phase separation behavior of spin-cast difluorinated triethylsilylethynylanthradithiophene (F-TESADT) and poly(methyl methacrylate) (PMMA) blends and their application in field-effect transistors (FETs). Although F-TESADT is highly crystalline small-molecular semiconductor with excellent field-effect electronic properties, its use in FETs is limited by the dewetting of film especially when solvent with high boiling point is used for solution processing. For this reason, PMMA—insulating polymer with good film-forming characteristics—is blended with F-TESADT for enhancing processing window. Because F-TESADT—the phase with lower surface energy than PMMA—is preferentially segregated at the air-film surface during spin-casting, conducting channel is maintained in a direction parallel to the substrate. Morphological and structural characterizations confirm that highly crystalline F-TESADT crystals are formed on PMMA. The use of these phase-separated blend films as active layer leads to high mobility FETs with good environmental and electrical stability.

Participants

John Armonas
American Polymer
8680 Tyler Blvd.
Mentor, Ohio 44060
USA
+1-440-255-2211
apsc@ampolymer.com

Byungcheol Ahn
Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Hyungmin Ahn
Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Seonyoung Ahn
Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Rüdiger Berger
MPI for Polymer Research
Ackermannweg 10
55128 Mainz
Germany
(T) +49-6131-379-114 (F) +49-6131-379-100
berger@mpip-mainz.mpg.de

Guy. C. Berry
Carnegie Mellon Univ.
4400 Fifth Ave.
Pittsburg, PA 15221
USA
(T) +1-412-268-3131 (F) +1-412-268-6897
gcberry@andrew.cmu.edu

Taihyun Chang
Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea
+82-54-279-2109
tc@postech.ac.kr

Kookheon Char
Department of Chemical Engineering
Seoul National University
Seoul,
Republic of Korea
(T)+82-2-880-7431
khchar@snu.ac.kr

Jung-Hsuan Chen
Department of Microstructure and Characterization
Material and Chemical Research Lab.
Industrial Technology Research Institute
Rm. 166, Bldg. 77, 195, Sec. 4
Chung Hsing Rd., Chutung
Hsinchu, 31040
Taiwan
+886-3-5918242
jhc@itri.org.tw

H.N. Cheng
USDA /ARS /SRRC
1100 Robert E. Lee Blvd.
New Orleans, LA 70124
USA
+1-504-286-4450
hncheng100@gmail.com

Oscar Chiantore
University of Torino
Torino
Italy
oscar.chiantore@unito.it

Kilwon Cho
Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea
+82-54-279-2270
kwcho@posetech.ac.kr

Young Jin Cho
Department of Chemistry
Sejong University
98 Gunja-Dong, Gwangjin-Gu
Seoul, 143-747
Republic of Korea

Hyun Ho Choi
Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea

Il young Choi
Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Junman Choi
Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Sung Ho Choi
LG Chem, Ltd
LG Chem Research Park,
104-1, Moonji-dong, Yuseong-gu,
Daejeon, 305-380
Republic of Korea

Im Sik Chung
BioNanotechnology Research Center
Korea Research Institute of Bioscience &
Biotechnology (KRIBB)
52 Eoeun-Dong, Yuseong-Gu,
Daejeon 305-333
Korea
(T)+82-42-879-8448 (F)+82-42-879-8594
cis123@kribb.re.kr

Willem de Groot
Dow Chemical Co.
2301 Brazosport Blvd. B1470D
Freeport, TX 77531
USA
(F) +1-979-238-3306
adegroot@dow.com

Alexander Gorshkov
Laboratory of Liquid Phase and Interphase
Processes
The Department of Polymers and Composites
N.N. Semenov Institute of Chemical Physics
Russian Academy of Sciences
Kosygina 4, 119991, Moscow
Russian Federation
(T)+7-916 628 11 85 (F)+7-499 137 82 47
alex.gorshkov@gmail.com

Don Ho Gum
LG Chem, Ltd
LG Chem Research Park,
104-1, Moonji-dong, Yuseong-gu,
Daejeon, 305-380
Republic of Korea

Sei Kwang Hahn
Department of Materials Science & Engineering
Pohang University of Science and Technology
(POSTECH)
San31, Hyoja-dong, Nam-gu
Pohang, Gyeongbuk, 790-784
Republic of Korea
(T)+ 82-54-279-2159
skhanb@postech.ac.kr

Charles C. Han
Institute of Chemistry
Chinese Academy of Sciences
2 North First Street, Zhongguancun
Beijing, 100190
China
(T) +86-10-8261-8089
c.c.han@iccas.ac.cn

Jiyeon Han
Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Song-Yi Han
Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Dan He
School of Display and Chemical Engineering
Yeungnam University
214-1 Dae-dong
Gyeongsan, Gyeongbuk 712-749
Republic of Korea
+82-53-810-3557
danneyhe@hotmail.com

Tomohiro Hirano
University of Tokushima
2-1 Minami-josanjima
Tokushima 770-8506
Japan
(T)+81-88-656-7403 (F) +81-88-656-7404
hirano@chem.tokushima-u.ac.jp

Nguyen Thi Dieu Huyen
School of Display and Chemical Engineering
Yeungnam University
214-1 Dae-dong, Gyeongsan
Gyeongbuk 712-749
Republic of Korea
+82-53-810-3557
dieuhuyenmtd@yahoo.com

Josef Janca
Tomas Bata University
Nad Stranemi 1511
Zlin
Czech Republic
(F) +420 57 603 5141
jjanca@ft.utb.cz

Sangmin Jeon
Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea
(T)+82-54-279-2392
jeons@postech.ac.kr

Youn Cheol Jeong
Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Hiroshi Jinnai

Department of Macromolecular Science and Engineering
Kyoto Institute of Technology
Kyoto 606-8585
Japan
(T)+81-75-724-7846 (F) +81-75-724-7770
hjinnai@kit.jp

Hwan Min Jung

LG Chem, Ltd
LG Chem Research Park,
104-1, Moonji-dong, Yuseong-gu,
Daejeon, 305-380
Republic of Korea

Joeun Jung

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Jueun Jung

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Jungwoon Jung

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Namchul Jung

Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea

Sungmin Jung

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Tassilo Kaule

MPIP Mainz
Ackermann weg 10
Mainz, 55128
Germany
kaule@mpip-mainz.mpg.de

Mohd Yusuf Khan

School of Display and Chemical Engineering
Yeungnam University
214-1 Dae-dong
Gyeongsan, Gyeongbuk 712-749
Republic of Korea
+82-53-810-3557
Yusuf.ic@gmail.com

Bong Shik Kim

School of Display and Chemical Engineering
Yeungnam University
214-1 Dae-dong
Gyeongsan, Gyeongbuk 712-749
Korea
kimbs@yu.ac.kr

Dong Min Kim

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Hyemin Kim

Department of Materials Science & Engineering
POSTECH
Pohang, 790-784
Republic of Korea

Hyung Don Kim

Sam Bo Scientific Co.
418-221, Gaehwa-dong, Gangseo-gu
Seoul, 157-230
Republic of Korea
(T) +82-2-2665-8800 (F) +82-2-2667-0034
sambo@sambosc.com

Hyun Woo Kim

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Jihoon Kim

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Jin-san Kim

Department of Chemistry
Yonsei University
Wonju, Kangwon, 220-710
Korea
kimjinsan@yonsei.ac.kr

Jinseck Kim

Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea

Joo-Hyun Kim

Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea

Kihyun Kim

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Kyungtae Kim

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Mihee Kim

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Sin-Wook Kim

R&D Center, NCK Co., Ltd.
Display Materials Research Dept.
401 Chupal-ri, Paengsung-up,
Pyongtak, 401-805
Republic of Korea
(T)+82-31-691-7044 (F) +82-31-691-0725
swkim@nckco.kr

Sung Yeon Kim

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Won Kyong Kim

Sam Bo Scientific Co.
418-221, Gaehwa-dong, Gangseo-gu
Seoul, 157-230
Republic of Korea
(T) +82-2-2665-8800 (F) +82-2-2667-0034
sambo@sambosc.com

Sam Bo Scientific Co.

418-221, Gaehwa-dong, Gangseo-gu
Seoul, 157-230
Korea
(T) +82-2-2665-8800 (F) +82-2-2667-0034
sambo@sambosc.com

Won Jong Kim

Department of Chemistry
Pohang University of Science and Technology
(POSTECH)
San31, Hyoja-Dong, Nam-Gu,
Pohang, Gyeongbuk, 790-784
Republic of Korea
(T) +82-54-279-2104
wjkim@postech.ac.kr

Youngsuk Kim

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Yong-Gi Ko

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Pavel Kratochvil

Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic
162 06 Prague 6
Czech Republic
(T)+420-296 809 277 (F)+420-296 809 411
krat@imc.cas.cz

Wonsang Kwon

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Choong Hoon Lee

LG Chem, Ltd
LG Chem Research Park,
104-1, Moonji-dong, Yuseong-gu,
Daejeon, 305-380
Republic of Korea
(T)+ 82-42-866-2753 (F)+ 82-42-861-7146
choong@lgchem.com

Dongkyu Lee

Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea

Duhwan Lee

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Eun Jung Lee

LG Chem, Ltd
LG Chem Research Park,
104-1, Moonji-dong, Yuseong-gu,
Daejeon, 305-380
Republic of Korea

Hoik Lee

Dept. of Chemistry
Hanyang University
17 Haengdang-dong, Seongdong-gu
Seoul, 133-791
Republic of Korea
(T) +82-10-9740-1527 (F) +82-2299-0762
hoic0822@naver.com

Hyojoon Lee

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Junseok Lee

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Junyoung Lee

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Seung Goo Lee

Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea

Seung Hwa Lee

Korea Kumho Petrochemical Co., Ltd.
Kumho Petrochemical R&BD Center
57-1 Hwaam-dong, Yusung-gu, Daejeon, Republic
of Korea

Sunju Lee

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Wi Hyoung Lee

Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea

Sung Chul Lim

LG Chem, Ltd
LG Chem Research Park,
104-1, Moonji-dong, Yuseong-gu,
Daejeon, 305-380
Republic of Korea

Li-Jiaun Lin

Industrial Technology Research Institute
Bldg. 77, 195, Sec. 4
Chung Hsing Rd., Chutung
Hsinchu, 31040
Taiwan
(F)+886-3-5820288
ljlin@itri.org.tw

Jimmy Mays

Department of Chemistry
Univ. of Tennessee
Knoxville, TN 37996
USA
(T) +1-865-974-0747 (F)+1-865-974-9304
jimmymays@utk.edu

Hikaru Momose

University of Tokushima
2-1 Minami-josanjima
Tokushima 770-8506
Japan
(T)+81-88-656-7404 (F) +81-88-656-7404
momose@poly.chem.tokushima-u.ac.jp

Hye-Seon Moon

Korea Kumho Petrochemical Co., Ltd.
Kumho Petrochemical R&BD Center
57-1 Hwaam-dong, Yusung-gu, Daejeon, Republic
of Korea
(T)+82-42-865-8633 (F)+82-42-865-8704
hyea0310@hanmail.net

Myeong Hee Moon

Department of Chemistry
Yonsei University
Seoul, 120-749
Republic of Korea
(T)+82-2-2123-5634 (F)+ 82-2-364-7050
mhmoon@yonsei.ac.kr

Ken Nakajima

Nishi&Nakajima Lab.
WPI Advanced Institute for Materials Research
Tohoku University
2-1-1 Katahira Aoba-ku
Sendai, 980-8577
Japan
+81-22-217-5927
knakaji@wpi-aimr.tohoku.ac.jp

Ran Namgung

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Tatsuya Naono

University of Tokushima
2-1 Minami-josanjima
Tokushima 770-8506
Japan
(T)+81-88-656-7404 (F) +81-88-656-7404
naono@poly.chem.tokushima-u.ac.jp

Son Ok Oh

LG Chem, Ltd.
LG Chem Research Park,
104-1, Moonji-dong, Yuseong-gu,
Daejeon, 305-380
Republic of Korea

Hajime Ohtani

Department of Materials Science and Engineering
Graduate School of Engineering
Nagoya Institute of Technology
Nagoya 466-8555
Japan
(T/F) +81-52-735-7911
ohtani.hajime@nitech.ac.jp

Mohammad Omrani

Polymer Group
Technical Faculty
Univ. of Tehran
Enghelab St.
Tehran +98
Iran
917-7141731
Omrani.m1982@gmail.com

Jae Hoon Park

Korea Kumho Petrochemical Co., Ltd.
Kumho Petrochemical R&BD Center
57-1 Hwaam-dong, Yusung-gu, Daejeon, Republic
of Korea

Jong Hwan Park

Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea

Moon Jeong Park

Department of Chemistry
Pohang University of Science and Technology
(POSTECH)
San31, Hyoja-Dong, Nam-Gu,
Pohang 790-784
Republic of Korea
(T) +82.54.279.2342
moonpark@postech.ac.kr

Samdae Park

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea
Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Taiho Park

Department of Chemical Engineering
Pohang University of Science and Technology
(POSTECH)
San31, Hyoja-Dong, Nam-Gu,
Pohang 790-784
Republic of Korea
(T) +82.54.279.2394
taihohpark@postech.ac.kr

Harald Pasch

University of Stellenbosch
Private Bag X1
Stellenbosch, 7602
South Africa
+27-21-8084967
hpasch@sun.ac.za

Meshkat Razban

Polymer Faculty
Azad University of Mahshahr
Imam Blvd
Mahshahr +98
Iran
916-3539893
msh.razban@gmail.com

Moonhor Ree

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea
(T)+82-54-279-2120
ree@postech.ac.kr

Wayne Reed

Dept. of Physics
Tulane University
New Orleans, LA 70118
USA
(T)+1-504-862-3185 (F) +1-504-862-3185
wreed@tulane.edu

Yecheol Rho

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Jin Sook Ryu

LG Chem, Ltd
LG Chem Research Park,
104-1, Moonji-dong, Yuseong-gu,
Daejeon, 305-380
Republic of Korea
+82-42-866-5785
jsryu@lgchem.com

Kenji Sakamoto

R&D Center, NCK Co., Ltd.
Display Materials Research Dept.
401 Chupal-ri, Paengsung-up,
Pyongtak, 401-805
Republic of Korea
(T) +82-31-691-7044 (F) +82-31-691-0056
sakamoto@nckco.kr

Mitsuhiro Shibayama

University of Tokyo
5-1-5 Kashiwanoha
Kashiwa, 277-8581
Korea
(T/F) +81-4-7136-3418
sibayama@issp.u-tokyo.ac.jp

Sejin Son

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

In Young Song

Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea

A-Young Sung

Department of Ophthalmic Optics
Daebul University
72, Sanhori, Samhoeup, Youngamgun
Jeonnam, 526-702
Republic of Korea
(T) +82-61-469-1313 (F) +82-61-469-1313
say@mail.daebul.ac.kr

Atsushi Takahara

Institute for Materials Chemistry and Engineering
Kyushu University
Motooka 744, Nishi-ku,
Fukuoka 819-0395,
Japan
(T) +81-92-802-2517 (F) +81-92-802-2518
takahara@cstf.kyushu-u.ac.jp

Hiroshi Takayama

Nissan Chemical Industries, LTD.
Tsuboinishi 2-10-1
Funahashi-shi, Chiba
Japan
(T) +81-47-465-1117 (F) +81-47-461-0492
takayamah@nissanchem.co.jp

Jun Tamura

JEOL Ltd.
1-2 Musashino 3-Chome
Akishima, Tokyo 196-8558
Japan
(T)+81-42-542-2237 (F)+81-42-546-8068
tamura@jeol.co.jp

Koichi Ute

Univ. of Tokushima
2-1 Minami-josanjima
Tokushima, 770-8506
Japan
(T)+81-88-656-7401 (F) +81-88-656-7404
ute@chem.tokushima-u.ac.jp

G. Julius Vancso

University of Twente
P.O. Box 217
Enschede, 7500 AE
The Netherlands
+31-53-489-3823
g.j.vancso@utwente.nl

Yanwei Wang

Tech. Univ. of Denmark
DPC, DTU Byn 423 room 126
Kgs. Lyngby DK-2800
Denmark
+45 4525 6812
wyy@kt.dtu.dk

JeongA Yang

Department of Materials Science & Engineering
POSTECH
Pohang, 790-784
Republic of Korea

JuMi Yeo

Department of Chemistry
POSTECH
Pohang, 790-784
Republic of Korea

Jung Hyun Yun

Analysis Lab/Catalyst & Process R&D Center
SK Energy Institute of Technology
140-1 Wonchon-dong, Yuseong-gu
Daejeon 305-712
Republic of Korea
(T) +82-42-866-7132 (F) +82-42-866-7823
ashley@skenergy.com

Minhyuk Yun

Department of Chemical Engineering
POSTECH
Pohang, 790-784
Republic of Korea

Jiang Zhao

Institute of Chemistry
Chinese Academy of Sciences
2 North First Street, Zhongguancun
Beijing, 100190
China
(T/F) +86-10-8261-9487
ijzhao@iccas.ac.cn