Three-Dimensional Imaging in Polymer Science: Its Application to Block Copolymer Morphologies and Rubber Composites

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[Award Accounts: SPSJ Wiley Award (2006)] Vol. 39, No. 8, pp 749–758 (2007) New methods to visualize polymer morphologies in three-dimension (3D) are reviewed. Here, one such imaging technique, transmission electron microtomography, was used *for the first time* to characterize the morphological change in a silica particle/rubber composite under stretching. Aggregates of particles were broken down upon stretching and many voids were generated near and between the particles. Local stress was inferred from the image intensity of the 3D image. The thickness of the specimen after stretching was thinner than what is expected from the affine deformation.



### Novel Method to Protect Electronics Devices from Electrostatic Charging using Electrostatic Series of Polymers

M. KAWATA, T. HAYAKAWA, and M. KAKIMOTO

[Short Communication] Vol. 39, No. 8, pp 760–761 (2007) In manufacturing for electric devices, small and light chip devices stick on the cover tape of container when the cover tape is opened. This phenomenon caused by electrostatic charging of device, and the electrostatic gravity is generated between electric device and cover tape. We discover a simple method to adjust the electrostatic series at the surface of polymer blends as shown in Figure. By using this technique, the difference of the charging density between the surfaces of the packaging polymers and small electronics devices can be minimized to prevent damage by the electrostatic charging.



### Synthesis of Multifunctional Poly(calix-[4]resorcinarene)

J. JEERUPAN, G. KONISHI, T. NEMOTO, D. SHIN, and Y. NAKAMOTO

[Short Communication] Vol. 39, No. 8, pp 762–763 (2007) The preparation of a poly(calixresorcinarene) from calixresorcinarene permethyl ether (2), formaldehyde, and sodium bromide (NaBr) *via* simultaneous phenol-formaldehyde condensation and bromomethylation process is described. This polymer (3) consists of a calixarene as the cavity in the main chain and the bromomethylphenyl group as a reactive site attached to the backbone. The structure of 3 was confirmed by <sup>1</sup>H NMR, FT-IR spectra and elemental analysis. The molecular weight and thermal properties of 3 are also discussed.



Asymmetric Polymerization of (S)-N-Maleoyl-L-Leucine Allyl Ester and Chiral Recognition Ability of Its Polymer as Chiral Stationary Phase for HPLC

H. GAO, Y. ISOBE, K. ONIMURA, and T. OISHI

[Regular Article] Vol. 39, No. 8, pp 764–776 (2007) Asymmetric polymerizations were carried out to obtain optically active poly((S)-ALMI)s using the novel monomer (*S*)-*N*-Maleoyl-L-leucine allyl ester ((*S*)-ALMI). In anionic polymerization, the (*S*)-ALMI enables the double bonds in the maleimide moiety to be exclusively polymerized, retaining potentiality for polymerization or reaction of the other double bonds in the side group of the *N*-substituent. CD spectra analysis displayed that the anionically obtained poly((S)-ALMI)s with high levorotations possess asymmetric carbons in the main chain induced through the polymerizations in addition to that in the intrinsic *N*-substituent.



Asymmetric Anionic polymerization of (S)-ALMI

### Synthesis of Poly(*N*-fluoroalkyl benzamide) with Controlled Molecular Weight and Polydispersity Index

K. OHSHIMIZU, Y. SHIBASAKI, and M. UEDA

[Regular Article] Vol. 39, No. 8, pp 777–782 (2007) Poly(*N*-fluoroalkyl benzamide) with the controlled  $M_n$  and  $M_w/M_n$  was prepared by the chain-growth polycondensation of 4-(*N*-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorooctyl-amino)benzoylbenzoxazolin-2-thione initiated with *p*-nitrobenzoyl chloride using EtMgBr as an activator. The  $M_n$  was tailored up to 25,000 by changing the feed ratio of the monomer and initiator, while the  $M_w/M_n$  was maintained below 1.2. The contact angle of the polymer film against a water droplet was 105.0, which was higher than 91.0 for poly(*N*-octyl benzamide), indicating the monomer 3 could be applicable to prepare a novel amphiphilic block copolymer.



## Characterization of Wormlike Pentaoxyethylene Dodecyl Ether C<sub>12</sub>E<sub>5</sub> Micelles Containing *n*-Dodecanol

M. MIYAKE and Y. EINAGA

[Regular Article] Vol. 39, No. 8, pp 783–791 (2007) For the  $C_{10}E_5$ ,  $C_{12}E_5$ , and  $C_{12}E_6$  micelles containing *n*-dodecanol, the spacing *s* between the hydrophilic tails of adjacent surfactant molecules on the micellar surface decreased and the stiffness parameter  $\lambda^{-1}$  increased with increasing *n*-dodecanol content  $w_d$  in the micelles. They were substantially independent of the hydrophobic and hydrophilic chain length of the surfactant molecules.



# Wormlike Micelles of Hexaoxyethylene Decyl $C_{10}E_6$ and Tetradecyl $C_{14}E_6$ Ethers Containing *n*-Dodecanol

Y. EINAGA, M. EBIHARA, and R. UCHIDA

[Regular Article] Vol. 39, No. 8, pp 792–801 (2007) Molar mass  $M_w$  dependence of the apparent hydrodynamic radius  $R_{\text{H,app}}$  for the  $C_{10}E_6 + n$ -dodecanol + water system of  $w_d$  (dodecanol content in the micelles) = 0.0704 (a) and for the  $C_{14}E_6 + n$ -dodecanol + water system of  $w_d = 0.0195$  (b) at various temperatures *T* indicated; The solid and dashed lines represent the theoretical values of  $R_{\text{H,app}}$ , which include effects of growth in micellar size with concentration *c* along with hydrodynamic and direct collision interactions among micelles, and the hydrodynamic radius  $R_{\text{H}}$  for the isolated micelles, respectively.



## Effect of Carboxylic Acid Monomer Type on Particle Nucleation and Growth in Emulsifier-free Emulsion Copolymerization of Styrene-Carboxylic Acid Monomer

M. Abdollahi

[Regular Article] Vol. 39, No. 8, pp 802-812 (2007) Carboxylated polystyrene latexes were prepared by emulsifier-free emulsion copolymerization of styrene with various carboxylic acid monomers. DLS analysis and SEM observations showed that  $N_p$  increases with increasing the hydrophobicity of carboxylic acid monomers in the order of IA < AA < MAA. There was significant difference in the polymerization rate per particle in all the experiments also. The results revealed that the both particle nucleation and growth processes are dependent on the hydrophilic nature of carboxylic acid monomers.





## Synthesis of Tropolone-Containing Conjugated Polymers and Their Optical Properties

Novel tropolone-containing conjugated polymers were obtained by the palladium-catalyzed coupling polymerization. The polymer structure was characterized by <sup>1</sup>H NMR and IR spectra to support the formation of an intramolecular hydrogen bond. The optical properties of polymers bearing a protected hydroxyl group or a free hydroxyl group were investigated by measuring the UV and PL spectra.

K. TAKAGI, K. SAIKI, K. MORI, Y. YUKI, and M. SUZUKI

[Regular Article] Vol. 39, No. 8, pp 813–821 (2007)



One-Pot and Rapid Synthesis of Uniformed Silica Spheres *via* Mediation of Linear Poly(ethyleneimine)s and Dyes

R.-H. JIN and J.-J. YUAN

[Regular Article] Vol. 39, No. 8, pp 822–827 (2007) Uniformed silica spheres with bright dye emission feature were facilely mediated by poly(ethyleneimine)s with linear and star architectures. Diameters of the spheres were ranged from 50 to 600 nm depending upon the polymers' architectures and mediation conditions.



Mechanical and Dielectric Properties of a New Polymer Blend Composed of 1,2-Bis(vinylphenyl)ethane and Thermosetting Poly(phenylene ether) Copolymer Obtained from 2,6-Dimethylphenol and 2-Allyl-6-methylphenol A novel low-dielectric-loss thermosetting material was prepared by blending poly(2allyl-6-methylphenol-co-2,6-dimethylphenol) (Allyl-PPE) with 1,2-bis(vinylphenyl)ethane (BVPE). BVPE was effectively functioned as a cure promoter of Allyl-PPE, so that the cured temperature was under 250 °C, and it showed good thermal property and better thermomechanical properties than that of PPE-BVPE blended resin because of the better miscibility of the two components. The small domain was observed by EELS technique. The dielectric constant and dielectric loss were varied by changing the components ratio of Allyl-PPE and BVPE.

J. NUNOSHIGE, H. AKAHOSHI, Y. LIAO, S. HORIUCHI, Y. SHIBASAKI, and M. UEDA

[Regular Article] Vol. 39, No. 8, pp 828–833 (2007)



## Macroscopic Deformation and Failure of Ductile Polyethylene: The Dominant Role of Entangled Amorphous Network

B. NA, R. LV, Q. ZHANG, and Q. FU

[Regular Article] Vol. 39, No. 8, pp 834–840 (2007) The dominant role of entangled network in the macroscopic deformation and failure behaviors of ductile polyethylene has been demonstrated by tensile and fracture toughness (EWF) tests. Stiffer entangled network with higher molecular weight corresponds to lower strain at break as well as permanent strain. The fracture toughness of ductile polyethylene can be well correlated with the relaxation of the entangled amrophous networks.



Extremely Rapid Synthesis of Aliphatic Polyesters by Direct Polycondensation of 1:1 Mixtures of Dicarboxylic Acids and Diols Using Microwaves We report a rapid, environmentally benign, solvent-free method for the synthesis of aliphatic polyesters by the direct polycondensation of equimolar quantities of a dicarboxylic acid and a diol assisted by microwave irradiation in the presence tin(II) chloride as a catalyst.





S. VELMATHI, R. NAGAHATA, and K. TAKEUCHI

[Regular Article] Vol. 39, No. 8, pp 841–844 (2007) Curing Behavior of Epoxy Resin Initiated by Amine-Containing Inclusion Complexes

N. AMANOKURA, M. KANEKO, T. SAHARA, and R. SATO

[Regular Article] Vol. 39, No. 8, pp 845–852 (2007) Amine compounds form inclusion complexes with 1,1,2,2-tetrakis(4-hydroxyphenyl) ethane (**TEP**). When these inclusion complexes compounds are reacted with epoxy resins, curing acceleration, pot life extension, and higher curing temperatures are observed. An explanation for this curing behavior is that guest molecule "amine compounds" are trapped in inclusion complex crystals. X-ray crystal structure data shows the existence of O-H–N hydrogen bonding. With the imidazole molecule in the inclusion complex, hydrogen bonding prevents easy attack of the epoxy ring.



## Conformational Transformation of Poly-( $\beta$ -phenetyl-L-aspartate) in Block Copolymer with Polystyrene in 1,1,2,2-Tetrachloroethane

T. ITOH, T. IWAI, E. IHARA, and K. INOUE

[Regular Article] Vol. 39, No. 8, pp 853–860 (2007) Block copolymers where polystyrene (PS) was attached to N- or C-terminus of poly( $\beta$ -phenetyl-L-aspartate) (PA) were prepared. Temperature dependence of PA conformation in 1,1,2,2-tetrachloroethane were studied by <sup>1</sup>H NMR. N*H* proton signals indicate significant differences of the conformational behavior between the two types of the block copolymers.



Synthesis of A Main Chain-Type Polyrotaxane Consisting of Poly(crown ether) and *sec*-Ammonium Salt Axle and Its Application to Polyrotaxane Network

Y. KOHSAKA, G. KONISHI, and T. TAKATA

Vol. 39, No. 8, pp 861-873 (2007)

[Regular Article]

nium axle into poly(crown ether) to polypseudorotaxane followed by end-capping of the axle terminal with a bulky aromatic isocyanate. The complete pseudorotaxanation (> 99%) was achieved, while the incorporation ratio of the axle moiety was finely controllable. The polypseudorotaxane was utilized for the preparation of a new type of polyrotaxane network.

A main chain-type polyrotaxane was synthesized by the initial threading of sec-ammo-

Polypseudorotaxanation Polypseudorotaxanation Crosslinking Polyrotaxane network

Core Phase Transition of Radiation-The phase transition of core chains in the micelles of radiation-synthesized poly(meth-**Modified Polysilane Micelles as Revealed** yl-n-propylsilane)-graft-poly(acrylic-acid) copolymers was revealed from their therfrom Their Thermochromism mochromism. UV spectral change discloses that the solid core of the micelles changes into the molten state with increasing temperature. The molten state was found to be the H. TANAKA, N. SATO, T. MATSUYAMA, third state of the polysilane micelle core. It was also demonstrated that polysilane is R. INOUE, and T. KANAYA applicable as a stimuli-responsive optical probe molecule. [Note] **Polysilane micelle** Molten core Solid core Vol. 39, No. 8, pp 874-877 (2007) Abs. 2 Wavelength Cold

## Correlation of Morphology of Electrospun Fibers with Rheology of Linear Polyacrylamide Solution

A. A. VETCHER, R. GEARHEART, and V. N. MOROZOV

[Note] Vol. 39, No. 8, pp 878–881 (2007) The morphology of the products of electrospinning aqueous solutions of linear polyacrylamide (PAA) of different molecular weights was studied in a broad range of concentrations (from 0.01% to 13%), in search of conditions favoring formation of uniform bead-free electrospun fibers. It was shown by AFM and optical microscopy that electrospinning generates uniform fibers when the PAA concentration (C) exceeds the entanglement concentration ( $C_e$ ), and that the average diameter of the fibers is independent of molecular weight but is proportional to ( $C/C_e$ ).



## Synthesis of Sulfonated Poly(1,4-diphenoxybenzene) for Proton Exchange Membrane

K. MATSUMOTO, S. ANDO, and M. UEDA [Note]

Vol. 39, No. 8, pp 882-887 (2007)

A new synthetic method of polyphenylene (PP) has been developed. PP was easily prepared by oxidative coupling polymerization of 1,4-diphenoxybenzene with FeCl<sub>3</sub> as an oxidant with a number-average molecular weight of 11,000 Da. The sulfonated polymer with a ion-exchange capacity of 2.3 mequiv/g showed high proton conductivity of  $2 \times 10^{-1}$  S/cm at 80 °C and 95% relative humidity, which is comparable to that of Nafion N-115.

