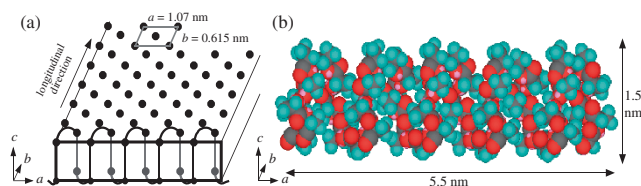


## AWARD ACCOUNTS

**SPSJ Mitsubishi Chemical Award Accounts**  
**Molecular, Structural, and Material Design of Bio-Based Polymers**

Polymeric materials prepared from renewable resources are now being accepted as “bio-based polymers.” We developed novel synthetic routes to bio-based polymers such as polylactides (PLA), poly(butylene succinate) (PBS) and their copolymers. Particularly, we focused on stereoblock polylactides (sb-PLA) consisting of different PLLA/PDLA sequences, forming stereocomplex crystals. The enantiomeric PLA molecules form various helical conformations in their crystallization by which their structure and properties are changed. We discovered an interesting doubly coiled conformation in a nano-band structure formed by block copolymers.



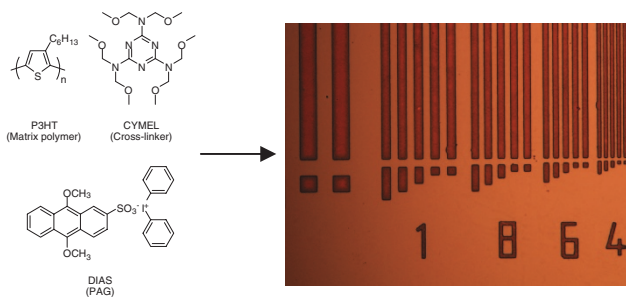
Y. KIMURA

*Vol. 41, No. 10, pp 797–807 (2009)*

## SHORT COMMUNICATION

**A Negative-Type Photosensitive Poly(3-hexylthiophene) with Cross-Linker and Photoacid Generator**

A novel patterning method of  $\pi$ -conjugated polymers ( $\pi$  CPs) involving chemically amplified photoresist based on poly(3-hexylthiophene) (P3HT), hexamethoxymethylmelamine (CYMEL) as a cross-linker, and diphenyliodonium-9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photoacid generator has been developed. The clear negative pattern with 4- $\mu$ m features was obtained on the 100-nm thick film consisting of P3HT (70 wt%), CYMEL (20 wt%), and DIAS (10 wt%). This method will be applied to patterning other  $\pi$ CPs.



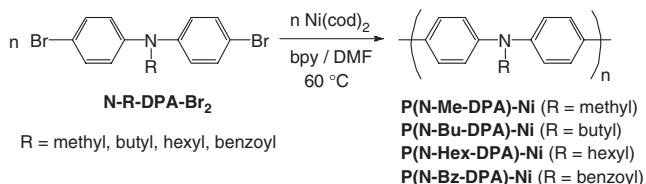
K. ENDO, T. OGURA, T. HIGASHIHARA, and M. UEDA

*Vol. 41, No. 10, pp 808–809 (2009)*

## REGULAR ARTICLE

**Synthesis and Chemical Properties of Poly(*N*-substituted diphenylamine-4,4'-diyl)s**

Poly(diphenylamine)s with substituents at the *N*-position,  $(C_6H_4-p-NR-C_6H_4-p)_n$  (R = methyl, butyl, hexyl, and benzoyl), have been prepared. They were soluble in organic solvents, and showed number average molecular weights ( $M_n$ ) of 3400–6100 with  $M_w/M_n$  ( $M_w$  = weight average molecular weight) of 1.9–2.4 in GPC analysis. The polymers exhibited photoluminescence (PL) with emission peaks at  $\lambda_{EM}$  = 408–425 nm in NMP solutions.

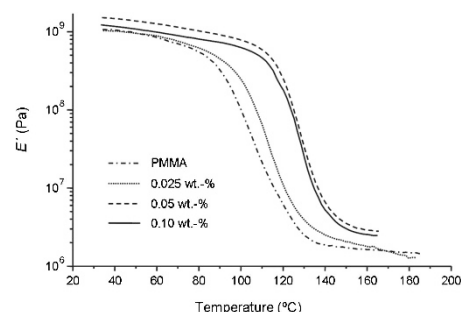


T. YAMAMOTO, S.-B. KIM, and T. KOIZUMI

*Vol. 41, No. 10, pp 810–815 (2009)*

### Thermal and Mechanical Analysis of Silver/Carbon Nanoparticle—PMMA Nanocomposites Obtained by Miniemulsion Polymerization

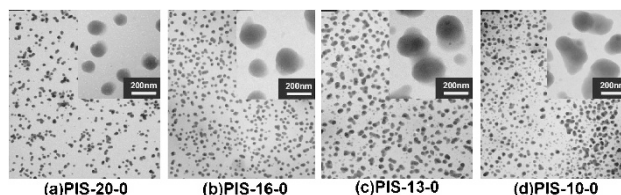
Elastic modulus ( $E'$ ) of Silver/Carbon nanoparticle—PMMA nanocomposites.



E. A. ZARAGOZA-CONTRERAS, C. A. HERNÁNDEZ-ESCOBAR,  
M. E. MENDOZA-DUARTE, S. G. FLORES-GALLARDO,  
R. IBARRA-GÓMEZ, and A. MÁRQUEZ-LUCERO  
*Vol. 41, No. 10, pp 816–821 (2009)*

### SiO<sub>2</sub> Reinforcement and Morphology of a Novel Poly-(imide-siloxane)-Based Thermal Plastic Elastomer Composite

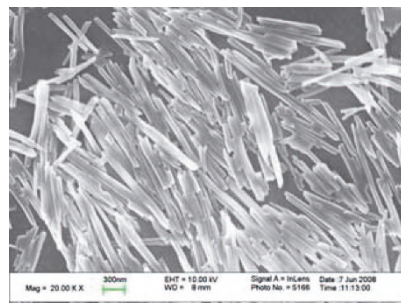
Silica (SiO<sub>2</sub>) was used for the reinforcement of the poly(imide-siloxane) (PIS)-based thermal plastic elastomer. Trimethylsilyl modified SiO<sub>2</sub> was incorporated in the PIS copolymer matrix to obtain reinforced composites. Excellent interfacial compatibility was observed and microphase separation was kept at desirable level. The obtained composites have improved thermal and mechanical properties than bare PIS copolymer. An elongation at break of 989% was obtained for the PIS/SiO<sub>2</sub> composite at silica content of 3 wt %.



W.-C. LIAW, Y.-L. CHENG, P.-C. HUANG,  
K.-P. CHEN, and L.-W. FU  
*Vol. 41, No. 10, pp 822–834 (2009)*

### Structure and Performance of Polyamide 6/Halloysite Nanotubes Nanocomposites

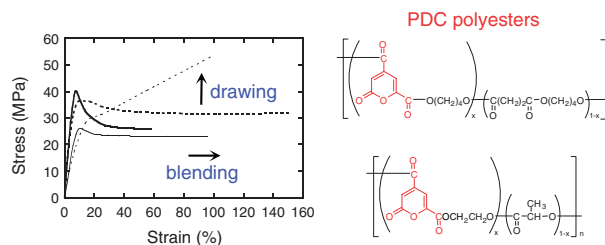
Structure and performance of polyamide 6 nanocomposites with silylated halloysite nanotubes (HNTs) are described. These modified HNTs show profound effects on the performance and polymorphism of polyamide 6.



B. GUO, Q. ZOU, Y. LEI, and D. JIA  
*Vol. 41, No. 10, pp 835–842 (2009)*

### Mechanical Properties of Poly(L-Lactide) Films Controlled by Blending with Polyesters of Lignin-Derived Stable Metabolic Intermediate, 2-Pyrone-4,6-Dicarboxylic Acid (PDC)

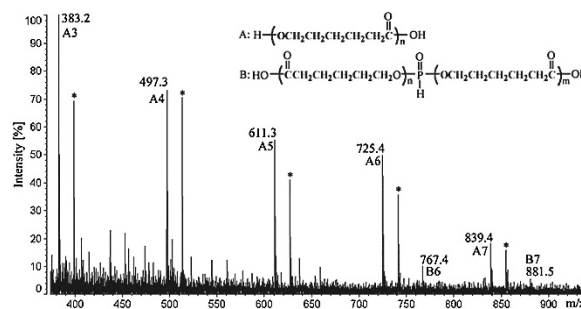
The mechanical properties of the blend films composed of PLLA and PDC polyesters were studied by tensile measurements. It was found that addition of <10 wt % of PDC polyesters improve the fracture strain and that drawing generally improves the tensile strength of the blend films containing <10 wt % of PDC polyesters. PDC-incorporated poly(butylene succinate) was a better additive than PDC-incorporated poly(L-lactic acid).



T. MICHINOBU, M. BITO, M. TANIMURA, Y. KATAYAMA, E. MASAI, M. NAKAMURA, Y. OTSUKA, S. OHARA, and K. SHIGEHARA  
*Vol. 41, No. 10, pp 843–848 (2009)*

### Microwave-assisted Ring-Opening Polymerization of $\epsilon$ -Caprolactone in Presence of Hydrogen Phosphonates

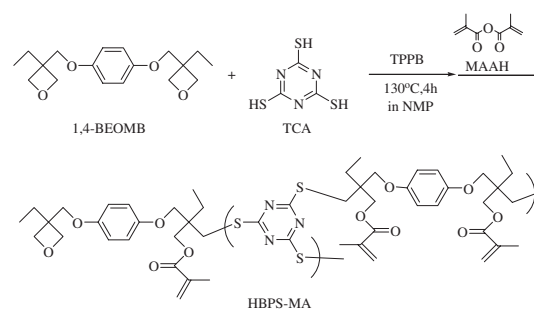
PCL was synthesized by a MROP of  $\epsilon$ -CL, using hydrogen phosphonate as the catalyst. It was found that the MROP of  $\epsilon$ -CL was first initiated by the trace water in the reaction mixture; a subsequent transesterification reaction occurred between the oligo( $\epsilon$ -CL) and diisopropyl hydrogen phosphonate at the early stage of the MROP, and the resulting oligo( $\epsilon$ -CL)-substituted hydrogen phosphonate could act as the catalyst during the MROP after diisopropyl hydrogen phosphonate was consumed out.



Y. TAN, S. J. CAI, L. Q. LIAO, Q. R. WANG, and L. J. LIU  
*Vol. 41, No. 10, pp 849–854 (2009)*

### Synthesis of Photocrosslinkable Hyperbranched Polysulfide Containing Methacryloyl Groups by the Reaction of Bis(oxetane) with Thiocyanuric Acid Followed by the Reaction with Methacrylic Anhydride

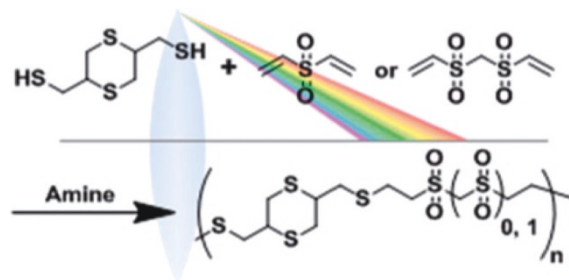
The synthesis and photopolymerization of hyperbranched polysulfide with pendant methacryloyl groups (HBPS-MA) were examined. The reaction of 1,4-bis[(3-ethoxy-3-oxetanyl)methoxy]benzene (1,4-BEOMB) with thiocyanuric acid (TCA) was carried out to give the soluble hyperbranched polysulfide (HBPS) in high yield. Furthermore, HBPS-MA was synthesized by the reaction of HBPS and methacrylic anhydride. The photoradical polymerization of HBPS-MA was examined in the presence of photoinitiator in the film state upon UV irradiation to afford the corresponding cured film quantitatively.



K. MARUYAMA, N. KOIKE, H. SUGIMOTO, H. KUDO, and T. NISHIKUBO  
*Vol. 41, No. 10, pp 855–859 (2009)*

### Synthesis of High Refractive Index Poly(thioether sulfone)s with High Abbe's Number Derived from 2,5-Bis(sulfanylmethyl)-1,4-Dithiane

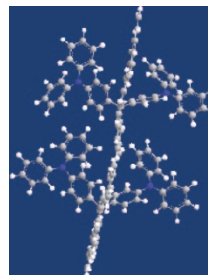
New thermoplastics, poly(thioether sulfone)s (PESs) with the high refractive indices and high Abbe's numbers have been developed by the simultaneous introduction of sulfide, sulfone, and alicyclic units in the polymer chains. The PESs with a high molecular weight was prepared by the Michael polyaddition of 2,5-bis(sulfanylmethyl)-1,4-dithiane (BMMD) with divinyl sulfone (DVS) or bis(vinylsulfonyl)methane (BVSM). Poly(BMMD-DVS) and poly(BMMD-BVSM) exhibited the high refractive index of 1.6512 and 1.6461, and the Abbe's number of 42.6 and 43.1 as thermoplastics.



Y. SUZUKI, T. HIGASHIHARA, S. ANDO, and M. UEDA  
*Vol. 41, No. 10, pp 860–865 (2009)*

### Synthesis and Characterization of a New Triphenylamine-substituted PFO/PPV Copolymer

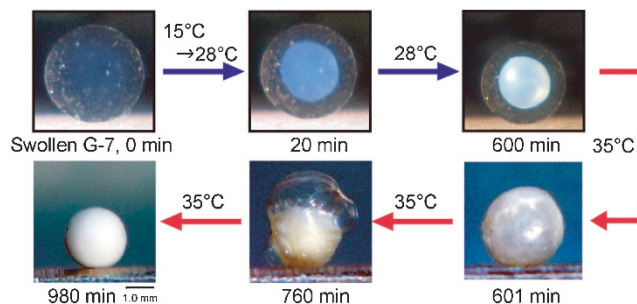
A highly soluble triphenylamine-substituted PFO/PPV alternating copolymer was synthesized by using a typical Heck-coupling reaction. This polymer exhibits strong photoluminescence with maximum emission peaks centered at 425 and 460 nm in benzonitrile. In deoxygenated dry benzonitrile, the fluorescence time profile of copolymer exhibited a bi-exponential decay with lifetime of 0.12 ns (98%) and 1.13 ns (2%).



L. GU, J. BAI, Y. CHEN, and Y. LIN  
*Vol. 41, No. 10, pp 866–871 (2009)*

### Synthesis of Core-Shell Type Gel Beads Consisting of Two Different Poly(*N*-alkylacrylamide) Gel Layers, and Their Thermosensitive Behavior

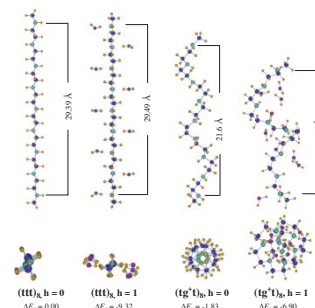
The mm size core-shell type gel bead (G-7) containing a poly(*N*-isopropylacrylamide) (PNIPA) shell and poly(*N*-*n*-propylacrylamide) core was prepared by two-step amidation of poly(acrylic acid) gel-1,8-diazabicyclo[5,4,0]undec-7-ene salt bead with the corresponding alkylamines. The swelling/de-swelling of the shell and core in G-7 occurred independently and isotropically in response to temperature changes, and the bead maintained its spherical shape during swelling/de-swelling, except for a case of appearance of squeeze effect in the de-swelling of the PNIPA shell in water at 35 °C.



T. IIZAWA, A. TERAOKA, T. ABE, M. OHUCHIDA, and Y. MATSUURA  
*Vol. 41, No. 10, pp 872–879 (2009)*

### Conformational Analysis for Hydrated Ethylene Imine Oligomer Models by Quantum Chemical Calculations

Hydrate effects on conformations of ethylene imine oligomers (1–8 mers) were examined using QCC with some hydrate ratios ( $h = \text{H}_2\text{O}/N_{\text{mol}}$ , 0–1). Hydrate energies ( $\Delta\mu_h$ ) for each conformer were negative and linearly decreased with increase of  $h$ . All  $(\text{tg}^+ \text{t})_x$  with  $h < 1$ , and the  $(\text{ttt})_x$  over 3 mers with  $h = 1$ , were the most stable. Each result corresponded to the results observed for non-hydrated and hydrated linear PEI crystal, respectively.

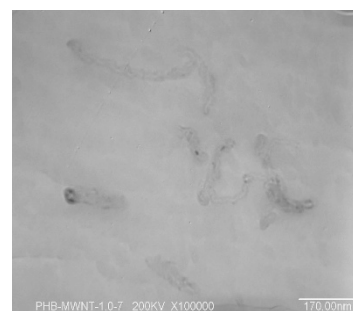


M. KOBAYASHI, M. TAKAHASHI, and H. SATO  
*Vol. 41, No. 10, pp 880–887 (2009)*

### NOTE

### Isothermal Melt Crystallization Kinetics Study of Bio-degradable Poly(3-hydroxybutyrate)/Multiwalled Carbon Nanotubes Nanocomposites

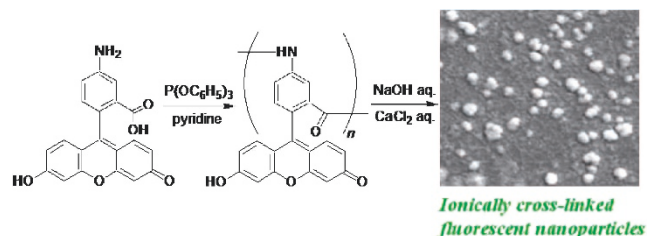
The overall crystallization rates are found to decrease with increasing crystallization temperature for both neat PHB and the PHB/MWNTs nanocomposites; moreover, the overall crystallization rates are higher in the nanocomposites than in neat PHB because of the heterogeneous nucleation effect induced by the presence of MWNTs. However, the crystal structure of PHB does not change in the nanocomposites. The depression of equilibrium melting points of PHB indicates that there is some limited miscibility between PHB and MWNTs in the nanocomposites.



C. XU and Z. QIU  
*Vol. 41, No. 10, pp 888–892 (2009)*

### Synthesis of Aromatic Polyamide Having Fluorescein Moieties in the Main-Chain and Its Conversion into Ionically Cross-Linked Nanoparticles with $\text{Ca}^{2+}$

Synthesis of an aromatic polyamide having fluorescein moieties in the main-chain was achieved by direct polycondensation of 5-aminofluorescein using triphenyl phosphite/pyridine system as a condensing agent. The TGA analysis of the polyamide supported its thermal stability. The polyamide was converted into ionically cross-linked fluorescent nanoparticles by treatment with  $\text{CaCl}_2$  aqueous solution. The nanoparticles were degraded by treating with EDTA.



J. KADOKAWA, T. NISHIKAWA, Y. SASAKI,  
Y. TANAKA, T. KATO, and Y. KANEKO  
*Vol. 41, No. 10, pp 893–897 (2009)*