Hybrid Polymer Nanoassemblies: Polymer Nanosheets Organized with Metal Nanoparticle Arrays for Surface Plasmon Photonics

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[Award Accounts: SPSJ Hitachi Chemical Award (2006)] Vol. 39, No. 5, pp 411–422 (2007) Hybrid polymer nanoassemblies were constructed by manipulating metal nanoparticle (Ag or Au) arrays with various photofunctional polymer nanosheets such as luminescent, redox active, and nonlinear optical active nanosheets. The polymer nanoarchitectures allow smooth and robust free-standing hybrid polymer nanosheets. Effective utilization of both isolated and coupled surface plasmon resonance from metal nanoparticles was demonstrated experimentally for optoelectronic applications.





#### Temperature Coefficients of Unperturbed Chain Dimensions for Polystyrene and Poly( $\alpha$ -methylstyrene)

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[Regular Article] Vol. 39, No. 5, pp 423–427 (2007) The temperature coefficient  $d \ln \langle R^2 \rangle_0 / dT$  of the unperturbed mean-square end-to-end distance  $\langle R^2 \rangle_0$  with *T* the absolute temperature was determined from light scattering measurements for atactic polystyrene with the fraction of racemic diads  $f_r = 0.59$  and atactic poly( $\alpha$ -methylstyrene) with  $f_r = 0.72$ , both in toluene and in the range of temperature 15.0–55.0 °C, on the assumption that the excluded-volume effect in good solvents is independent of *T*. As shown in a contour map of  $10^3 d \ln \langle R^2 \rangle_0 / dT$  at 300 K in a  $(\lambda^{-1}\kappa_0, \lambda^{-1}\tau_0)$ -plane, the experimental results for the two polymers may be well explained by the helical wormlike (HW) chain theory, where  $\lambda^{-1}\kappa_0$  and  $\lambda^{-1}\tau_0$  are the reduced differential-geometrical curvature and torsion, respectively, of the characteristic helix associated with the HW chain, the numbers attached to the contour lines indicate the theoretical values, and those in parentheses the observed ones.



## Monodispersed Carboxylated Composite Polymer Microspheres and Physical Immobilization of Biomolecules

H. AHMAD, Md. M. HOSSAIN, Md. M. RAHMAN, and M. A. J. MIAH

[Regular Article] Vol. 39, No. 5, pp 428–434 (2007) Monodispersed carboxyalated composite polymer particles were prepared by multi-steps seeded copolymerization. Carboxyl group density on the surface of polymer particles was dependent on the methods of preparation. These carboxyl functionalized polymer particles can be utilized as biomedical carrier. Figure shows the SEM photographs of PS/ P(MMA-EGDM)/P(MMA-MAA) composite polymer particles.



# Effect of Solvent on Morphological and Structural Change of Cellulose under Ball-Milling

M. AGO, T. ENDO, and K. OKAJIMA

[Regular Article] Vol. 39, No. 5, pp 435–441 (2007) The fibrous cellulose was converted to the globular particle or plate-like particle by the method of ball-milling with hydrophilic or hydrophobic solvent, as water, toluene and 1-butanol. The morphological and structural changes of the fibrous cellulose were attributed by the interaction between the cellulose and the solvents. The surface property of the product was tried to investigate by interposing a dye stuff, and characteristic color development of the cellulose/ dye was clearly distinguished depending on the solvent, cinnabar; without solvent (a), yellow; toluene (c) and yellowishgreen; water (b) or 1-butanol (d).



## A Negative Type Photosensitive Polymer Based on Poly(naphthylene ether), a Cross-Linker, and a Photoacid Generator with Low Dielectric Constant

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

[Regular Article] Vol. 39, No. 5, pp 442–447 (2007) A novel negative-working thermally stable photosensitive polymer based on poly-(naphthylene ether), a cross-linker hexa(methoxymethyl)melamine (CYMEL), and a photoacid generator (5-propylsulfonyl-oxyimino-5*H*-thiophen-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA). This photosensitive polymer showed a high sensitivity ( $D_{0.5}$ ) of 6.0 mJ cm<sup>-2</sup> and a high contrast ( $\gamma_{0.5}$ ) of 5.2, when it was exposed to a 436 nm light, post-exposure baked at 140 °C for 5 min, and developed with toluene. A negative image featuring 20 µm line and space patterns was obtained on a film exposed to 20 mJ cm<sup>-2</sup> of visible light at 436 nm by the contact-printed mode. The resulting polymer film had the low dielectric constant of 2.8 and high thermal stability.



## Synthesis and Photoluminescence of Novel Organo-Soluble Polyarylates Bearing (N-Carbazolyl)triphenylamine Moieties

G.-S. LIOU, S.-H. HSIAO, H.-M. HUANG, and C.-W. CHANG

[Regular Article] Vol. 39, No. 5, pp 448–457 (2007) A new series of blue photoluminescent aromatic polyesters (polyarylates) were synthesized from 4,4'-dicarboxy-4"-N-carbazolyltriphenylamine with various bisphenols. These polymers were amorphous and could be cast from chloroform solutions into transparent films due to their excellent solubility. These polyarylates exhibited high  $T_g$  values (234–287 °C). The maximum PL intensity of the solutions of polymer **3e** in NMP, chloroform, THF, and toluene solution, and its solid-state thin film appeared at 501, 481, 476, 447, and 468 nm, respectively. The photoluminescence exhibited solvent effect and was red-shifted in the polar solvent at room temperature.





H. MATSUMOTO, T. KAWAI, and S. TERAMACHI

[Regular Article] Vol. 39, No. 5, pp 458-463 (2007)

The direction of temperature gradient for normal-phase mode temperature gradient interaction chromatography (TGIC) in poly(methyl methacrylate) (PMMA) fractionation was studied by using System I (column: cyano-modified silica // eluent: 1,4-dioxane/n-hexane) and System II (bare silica // 1.4-dioxane/ CH<sub>2</sub>Cl<sub>2</sub>), respectively. It was found that PMMA samples were fractionated effectively not only by positive temperature gradietnt in System I but also by negative temperature gradient in System II as shown in the chromatogram.



## Hierarchically Structured Silica from Mediation of Linear Poly(ethyleneimine) Incorporated with Acidic/Basic Additives

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

[Regular Article] Vol. 39, No. 5, pp 464-470 (2007)

A unique hierarchically structured silica was directed by simple hydrolytic condensation of tetramethoxysilane (TMOS) on aggregates of linear poly(ethylenemine) (LPEI) incorporated with acidic and basic additives.



#### Syntheses of Poly[(tetraphenyl-p-silphenylenesiloxane)-co-(tetramethyl-p-silphenylenesiloxane)]s and the Physical Properties of Their Films

H. ITO, E. AKIYAMA, Y. NAGASE, and S. FUKUI

[Regular Article] Vol. 39, No. 5, pp 471-477 (2007)

Syntheses of the poly[(tetraphenyl-p-silphenylenesiloxane)-co-(tetramethyl-p-silphenylenesiloxane)]s and the physical properties of their films were investigated. Their  $T_{g}$ 's increased with the increase of the units based on 1,4-bis(diphenylhydroxysilyl)benzene. The highest  $T_g$  and  $T_{d5}$  of the copolymers were 127 °C and 524 °C, respectively. The gas permeability coefficients of the films were distinctly lower than that of a polydimethylsiloxane. The tensile strength and the density of the films increased with the increase of the units. These results indicated that dense and tough films were obtained from these copolymers.



 $T_{g} = 62 \text{ °C}$   $T_{d5} = 524 \text{ °C}$ Young's modulus = 4.5 MPa

# Effect of Structure of Bridging Group on Curing and Properties of Bisphenol-A Based Novolac Epoxy Resins

G. PAN, Z. DU, C. ZHANG, C. LI, X. YANG, and H. LI

[Regular Article] Vol. 39, No. 5, pp 478–487 (2007) Three bisphenol-A based epoxy resins with methylene, methine-phenyl and methinenaphthyl bridging groups were successfully designed and prepared *via* condensation of bisphenol-A with formaldehyde, benzaldehyde, 1-naphthaldehyde, respectively, followed by epoxidation with excess epichlorohydrin. The effect of bridging groups on the curing kinetics and properties of the epoxy resins were investigated. It was concluded that the methylene-bridged epoxy resin possessed the highest cure reaction reactivity toward DDS and the methine-naphthyl-bridged epoxy network possessed the highest storage modulus, glass transition temperatures, thermal stability, and moisture resistance.

