Development of Fluorinated Polymeric Functional Materials Using Fluorinated Organic Peroxide as Key Material

H. SAWADA

[Award Accounts: SPSJ Mitsubishi Chemical Award (2006)] Vol. 39, No. 7, pp 637–650 (2007) Fluoroalkanoyl peroxide is convenient for the synthesis of a wide variety of fluoroalkyl end-capped vinylsilane, acrylate, and methacrylate oligomers with carbon–carbon bond formation. These fluorinated oligomers were applied to surface modification of traditional organic polymers to exhibit a surface active characteristic imparted by fluorine. The oligomers form nanometer size-controlled self-assembled molecular aggregates with the agregation of terminal fluoroalkyl segments in aqueous and organic media. The fluorinated aggregates provide suitable host moieties to interact with guest molecules.

$$\begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$$

Guest molecules $\subset R_{F}$

Guest Molecules Nanocomposites

Poly(1-*n*-octadecylpyrrole) Films with 'Needle'-like Morphology

H. YAN, Y. HATTORI, J. FUJISATO, and N. TOSHIMA

[Short Communication] Vol. 39, No. 7, pp 652–653 (2007) Poly(1-*n*-octadecylpyrrole) films with 'needle'-like morphology were synthesized electrochemically at an applied potential of 9,000 mV vs. Ag/AgCl. The films were electrochemically inactive, and showed electrical conductivity of ca. 1 × 10⁻⁵ S cm⁻¹.

mer surface



Self-assembled Fluorinated Oligomeric Aggregates/

Preparation of Polyimide-Silica Nanocomposites from Nanoscale Colloidal Silica

J.-W. HUANG, Y.-L. WEN, C.-C. KANG, and M.-Y. YEH

[Regular Article] Vol. 39, No. 7, pp 654–658 (2007) The polyamic acid solutions prepared from pyromellitic anhydride (PMDA) and 4,4-oxydianiline (ODA) were blended directly with a commercial nanoscale colloidal silica sol, and converted to polyimides (PIs)/silica nanocomposite films. The nanoscale silica particles were dispersed well in PI and the nanocomposite films showed fairly good optical transparency up to 30 wt % of silica content. These PI/silica nanocomposite films exhibited better mechanical properties, higher glass transition temperature (T_{g}) , better thermal stability and lower coefficient of thermal expansion (CTE) with increasing silica content.



Photoinduced Holographic Gratings in Azobenzene-Functionalized Poly(amideimide)s

E. SCHAB-BALCERZAK, A. SOBOLEWSKA, A. MINIEWICZ, J. JURUSIK, and B. JARZABEK

[Regular Article] Vol. 39, No. 7, pp 659–669 (2007) The photoinduced holographic grating recording in poly(amideimide)s containing azobenzene moiety as side group were studied. Polymers differ in their backbone structure and in position in which azobenzene group is attached to polymer chain. The highest values of diffraction efficiencies showed polymer with azobenzene chromophores attached between amide linkages to polymer. The faster grating recording rates were observed for polymers with four methyl substituents in the backbone. The formation of SRG was observed.



Formation of β -Phase Crystalline Structure of PVDF Nanofiber by Electrospray Deposition: Additive Effect of Ionic Fluorinated Surfactant

M. NASIR, H. MATSUMOTO, M. MINAGAWA, A. TANIOKA, T. DANNO, and H. HORIBE

[Regular Article] Vol. 39, No. 7, pp 670–674 (2007) Poly(vinylidene fluoride) (PVDF) nanofibers were prepared by electrospray deposition (ESD). The addition of ionic fluorinated surfactants influenced morphology, diameter, and crystalline structure of PVDF nanofiber. Particularly, complete β -phase structure of PVDF nanofiber was formed during ESD by adding ionic fluorinated surfactants.



Triarylamine-Bearing Poly(1,4-phenylenevinylene): Facile Preparation and Its Durable Aminium Polyradical

T. KURATA, Y.-J. PU, and H. NISHIDE

[Regular Article] Vol. 39, No. 7, pp 675–683 (2007) Poly[2-{bis(4-methoxyphenyl)amino}phenyl]-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] with high-molecular weight was prepared by the Gilch polycondensation. The polymer showed a reversible redox attributed to the pendant arylamine moiety and afforded the corresponding aminium polyradical with an appreciable life-time under ambient conditions. The polyradical was in the high-spin state with an average spin quantum number of $\overline{S} = 3/2$ at low temperature. Its film formability would allow application of the polyradical to device formation.



Effects of Static and Dynamic Forces on Surface Viscoelastic Response of Polymer Films in Scanning Viscoelasticity Microscopy

K. AKABORI, K. TANAKA, N. SATOMI, T. NAGAMURA, A. TAKAHARA, and T. KAJIYAMA

[Regular Article] Vol. 39, No. 7, pp 684–689 (2007) Scanning viscoelasticity microscopy enables one to gain insights into local viscoelastic properties at polymer surfaces. We have examined an effect of tip modulation manner on surface viscoelastic response in polystyrene films. If dynamic and/or static forces were/was ill-chosen, non-linearity of viscoelastic response became dominant. On the contrary, if they were appropriately adjusted, linear viscoelastic measurement could be realized in the frequency range more than 2 decades. This lead to traditional rheological analysis even at the surface.



Synthesis and Properties of Helical Poly-(macromonomer) Consisting of Polyacetylene Main Chain and Poly(methyl methacrylate) Side Chains

M. SHIOTSUKI, W. ZHANG, and T. MASUDA

[Regular Article] Vol. 39, No. 7, pp 690–695 (2007) A helical poly(macromonomer) [poly(M-PMMA)] with a polyacetylene main chain and poly(methyl methacrylate) (PMMA) side chains was synthesized by the polymerization of an acetylene-terminated PMMA macromonomer (M-PMMA) in the presence of a Rh catalyst. M-PMMA was synthesized with a chiral acetylene-containing initiator 2-bromo-2-methylpropionic acid (*S*)-1-methylpropargyl ester (I) by atom transfer radical polymerization (ATRP) of methyl methacrylate. Poly(M-PMMA) exhibited strong CD effects at around 350–357 nm, indicating that it possessed a predominantly onehanded helical conformation. Poly(M-PMMA) had stable helical conformation irrespective of solvents and temperature.



Studies on the Thermal Properties and Flame Retardancy of Epoxy Resins Modified with Polysiloxane Containing Organophosphorus and Epoxide Groups

M. HOU, W. LIU, Q. SU, and Y. LIU

[Regular Article] Vol. 39, No. 7, pp 696–702 (2007) A novel epoxy resin modifier, phosphorus-containing epoxide siloxane (PES), was synthesized by the ring-opening reaction of epoxy-siloxane with 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. PES was employed to modify an epoxy resin using 4, 4'-diaminodiphenylmethane as curing agent. The thermal, thermomechanical, and flame-retardant properties of all cured samples were investigated by differential scanning calorimetry, dynamic mechanical analysis, thermogravimetric analysis, limited oxygen index, and cone calorimetry. The results showed that the epoxy resins modified with PES exhibited excellent thermal properties and flame retardancy.

$$\begin{array}{c} \begin{array}{c} CH_{3} \\ H_{3} \\ CH_{3} \\ -Si \\ -O \\ CH_{3} \\$$



Edge view WAXD pattern of press-dried Low-Substituted Hydroxypropylcellulose LHPC film: film was placed parallel to the beam stopper.

Preparations of Aromatic Diamine Monomers and Copolyamides Containing Phosphorylcholine Moiety and the Biocompatibility of Copolyamides

Y. NAGASE, M. OKU, Y. IWASAKI, and K. ISHIHARA

[Regular Article] Vol. 39, No. 7, pp 712–721 (2007) The synthesis of a novel aromatic diamine compound containing phosphorylcholine (PC) group was carried out to prepare aromatic copolyamides with PC moiety. The obtained copolyamides exhibited the high thermal stability, and also the excellent biocompatibility even though the PC content was around 20 mol%. Therefore, the introduction of PC group in the side chain of aromatic polyamide was effective to develop the biocompatibility, which would be due to the surface property covered with polar PC units.



Fig. SEM pictures of polymer film surfaces after contact with PRP.

Crystallization Behavior of Polypropylene Filled with Modified Carbon Black

J. CHEN, X. LI, and C. WU

[Regular Article] Vol. 39, No. 7, pp 722–730 (2007) A novel method was employed to modify the surface of carbon black (CB) by organic small molecules. The results were shown that organic small molecules were grafted onto the surface of modified CB (MCB) and the particle size of MCB reduced markedly. Then it was found both CB and MCB can influence the crystallization behavior of polypropylene (PP). However, MCB accelerated the crystallization rate and increased the crystallization peak temperature of PP more evidently than CB did.



Synthesis and Property of Poly(arylene sulfone)s Containing 9,9-Diarylfluorene Moiety in the Main Chain

S. SEESUKPHRONRARAK and T. TAKATA

[Regular Article] Vol. 39, No. 7, pp 731–736 (2007)





Micromorphology Memory in Amphiphilic Polypeptides

T. KANEKO, T. SHIMOKURI, S. TANAKA, and M. AKASHI

[Regular Article] Vol. 39, No. 7, pp 737–744 (2007) Thin film of poly{peptide-*block*-ethylene oxide (EG)-*block*-peptide} formed multi-spherulites which melted upon heating but recrystallized by successive cooling, thereby changing the spherulite interface morphology. The water-immersion of recrystallized films recovered the once-disappeared spherulite morphologies under the control of the peptide-block conformation.



Polymer Possessing Diaza-18-crown 6-Ether Linked by π -Conjugated Aminopenta-2,4-dienylidene Groups Generated by Ring-opening of Pyridinium Ring

I. YAMAGUCHI, S. SHINGAI, and M. SATO

[Note] [Note] [Vol. 39, No. 7, pp 745–748 (2007)

Reactions of *N*-(2,4-dinitrophenyl)pyridinium chloride with 4,13-diaza-18-crown 6ether (DA18C6) and piperadine gave **polymer-1** and **polymer-2** that were consisted of the 5-alkane-penta-2,4-dienylideneammonium chloride unit. The corresponding model compounds were also obtained. The ¹H NMR spectra suggested that the π electrons of the penta-2,4-dienylideneammonium group of the polymers and model compounds were delocalized. The electric conductivity measurements indicated that the DA18C6 of **polymer-1** was able to include Ag⁺ in solution. The polymers and model compounds were electrochemically active in solutions, as revealed by cyclic voltammetry.

