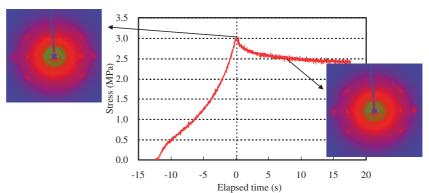
Strain-Induced Crystallization of Crosslinked Natural Rubber As Revealed by X-ray Diffraction Using Synchrotron Radiation

M. Tosaka

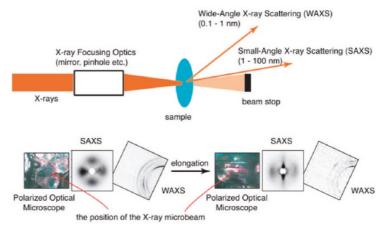
[Special Issues -Synchrotron Radiation and Neutron Beam- Review Article] Vol. 39, No. 12, pp 1207–1220 (2007) Strain-induced crystallization (SIC) of natural rubber (NR) has been extensively studied even before the advent of macromolecular physics. However, there are still some unsolved basic issues in this field. In this review article, classic studies on SIC of NR are briefly introduced, and then recent synchrotron X-ray diffraction studies are summarized and some unsolved issues are discussed. The experimental results in separate papers by different authors were categorized and interpreted on the basis of the molecular models.



Application of Microbeam Small- and Wide-angle X-ray Scattering to Polymeric Material Characterization

Y. Nozue, Y. Shinohara, and Y. Amemiya

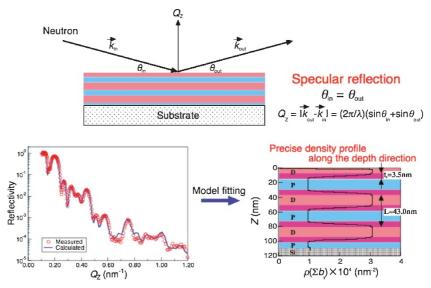
[Special Issues -Synchrotron Radiation and Neutron Beam- Review Article] Vol. 39, No. 12, pp 1221–1237 (2007) Microbeam X-ray scattering is a unique and powerful tool that provides abundant information on local structures, such as the spatial inhomogeneity of materials and the structural change at a local position. In this review, the representative applications of microbeam X-ray scattering to polymer crystallization, spatial inhomogeneity analyses, stress transfer under external field and the microphase separated structure analyses in block copolymer systems are introduced.



Neutron Reflectometry on Interfacial Structures of the Thin Films of Polymer and Lipid

N. TORIKAI, N. L. YAMADA, A. NORO, M. HARADA, D. KAWAGUCHI, A. TAKANO, and Y. MATSUSHITA

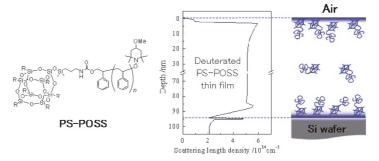
[Special Issues -Synchrotron Radiation and Neutron Beam- Review Article] Vol. 39, No. 12, pp 1238–1246 (2007) Neutron reflectometry is a very powerful and essential technique for the studies on material interfaces due to its high spatial resolution along the depth direction. The scattering contrast can be produced in hydrogenous soft-materials without big changes in their physical and chemical properties by substituting all or part of their hydrogen atoms with deuterium. Also, the neutron reflectometry can explore deeply-buried interfaces in a non-destructive way, and make *in situ* measurements combined with various sample environments due to its high transmission to the materials.



Dewetting Inhibition and Interfacial Structures of Silsesquioxane-terminated Polystyrene Thin Films

K. MIYAMOTO, N. HOSAKA, M. KOBAYASHI, H. OTSUKA, N. YAMADA, N. TORIKAI, and A. TAKAHARA

[Special Issues -Synchrotron Radiation and Neutron Beam- Regular Article] Vol. 39, No. 12, pp 1247–1252 (2007) Thermal stability of thin films composed of polyhedral oligomeric silsesquioxane (POSS)-terminated polystyrene (PS-POSS) was investigated. The introduction of POSS as a PS end group can actually stabilize PS films against dewetting. Neutron reflectivity measurement revealed that the POSS moiety of PS-POSS formed enrichment layer at the interfaces of the film, and the segregation of POSS end groups at the filmsubstrate interface seems to be an important factor in the dewetting inhibition effect.

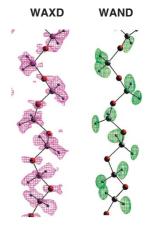


Structural Refinement and Extraction of Hydrogen Atomic Positions in Polyoxymethylene Crystal Based on the First Successful Measurements of 2-Dimensional High-Energy Synchrotron X-ray Diffraction and Wide-Angle Neutron Diffraction Patterns of Hydrogenated and Deuterated Species

K. Tashiro, M. Hanesaka, T. Ohhara, T. Ozeki, T. Kitano, T. Nishu, K. Kurihara, T. Tamada, R. Kuroki,

S. FUJIWARA, I. TANAKA, and N. NIIMURA

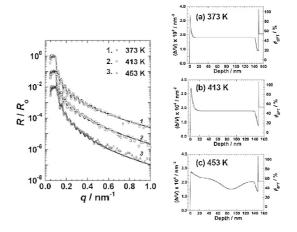
[Special Issues -Synchrotron Radiation and Neutron Beam- Regular Article] Vol. 39, No. 12, pp 1253–1273 (2007) Refiement of polyoxymethylene crystal structure has been successfully performed using more than 700 reflections which were collected by a synchrotronsourced X-ray diffraction measurement at -150 °C as well as at room temperature. The wide-angle neutron diffraction data were collected for both the deuterated and hydrogenated POM samples, from which the hydrogen atomic positions have been extracted clearly through the Fourier synthesis. The detailed analysis, including the observation of 00l reflections, supports the (29/16)helical model preferably than the conventional (9/5) helical model.



Temperature Dependence of Surface Segregation in Miscible Polymer Blend of Poly(4-trimethylsilylstyrene)/Polyisoprene

D. KAWAGUCHI, M. OHYA, N. TORIKAI, A. TAKANO, and Y. MATSUSHITA

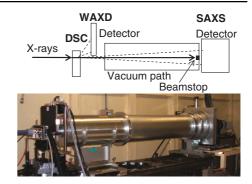
[Special Issues -Synchrotron Radiation and Neutron Beam- Regular Article] Vol. 39, No. 12, pp 1274–1280 (2007) Surface segregation behavior in miscible polymer blend thin film of partially deuterated poly(4-trimethylsilylstyrene) (dPT)/polyisoprene (PI) was investigated as a function of temperatures based on neutron reflectivity measurements. For all temperatures employed, dPT, being a lower surface energy component, was preferentially segregated at the surface. With increasing temperature, a concentration fluctuation in dPT/PI blend thin film even below the LCST was induced by the surface segregation of PT component in blend thin film.



Development of Synchrotron DSC/WAXD/SAXS Simultaneous Measurement System for Polymeric Materials at the BL40B2 in SPring-8 and its Application to the Study of Crystal Phase Transitions of Fluorine Polymers

H. MASUNAGA, S. SASAKI, K. TASHIRO, M. HANESAKA, M. TAKATA, K. INOUE, N. OHTA, and N. YAGI

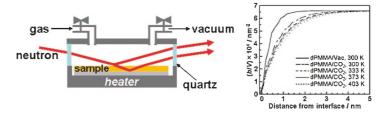
[Special Issues -Synchrotron Radiation and Neutron Beam- Regular Article] Vol. 39, No. 12, pp 1281–1289 (2007) A new system of DSC/WAXD/SAXS simultaneous measurements with twodimensional detectors has been successfully developed at the BL40B2 in SPring-8, Japan. The experimental data about the phase transitions of the crystal form I of poly(vinylidene fluoride) have been presented as actual examples, where the phase transitions from the polar crystal consisting of planar-zigzag chains to the unpolar and gauche-type HT phase have been confirmed definitely and the remarkable change in lamellar stacking structure could be detected in the temperature region just below the melting point.



Gas Sorption into Surface of Poly(methyl methacrylate) Films at Atmospheric Pressure

Y. FUJII, H. ATARASHI, N. YAMADA, N. TORIKAI, T. NAGAMURA, and K. TANAKA

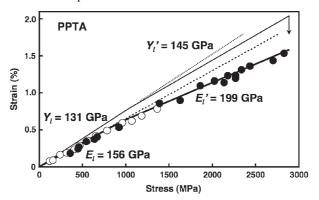
[Special Issues -Synchrotron Radiation and Neutron Beam- Regular Article] Vol. 39, No. 12, pp 1290–1294 (2007) Structure of deuterated poly(methyl methacrylate) (dPMMA) and polystyrene (dPS) at the interfaces with gases such as carbon dioxide and nitrogen under the pressure of 0.1 MPa were discussed by neutron reflectivity. Surface relaxation behavior for the dPMMA and dPS films under the gases was also discussed on the basis of lateral force measurement.



Elastic Modulus of the Crystalline Regions of Poly (*p*-phenylene terephthalamide) Single Fiber Using SPring-8 Synchrotron Radiation

M. KOTERA, A. NAKAI, M. SAITO, T. IZU, and T. NISHINO

[Special Issues -Synchrotron Radiation and Neutron Beam- Regular Article] Vol. 39, No. 12, pp 1295–1299 (2007) The elastic modulus E_l of the crystalline regions poly (p-phenylene terephthalamide) (PPTA) single fiber was measured by SPring-8 synchrotron radiation. The stress hardening of PPTA crystalline regions was observed during the tensile deformation process. The E_l value of PPTA single fiber was obtained as 156 GPa in the initial slope of stress–strain curve, and 199 GPa in the higher stress region. Stress hardening was also observed macroscopically. The stress hardening in the crystal lattice was found to directly affect the macroscopic tensile deformation.

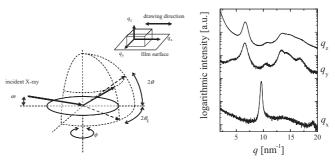


Side-Chain Effects on Friction-Transferred Polymer Orientation

S. NAGAMATSU, M. MISAKI, T. KIMURA, Y. YOSHIDA, R. AZUMI, N. TANIGAKI, and K. YASE

N. TANIGAKI, aliu K. TASE

[Special Issues -Synchrotron Radiation and Neutron Beam- Regular Article] Vol. 39, No. 12, pp 1300–1305 (2007) Effects of substituted side-chains of poly(2,5-dialkoxy-1,4-phenylenevinylene) derivatives (PPV) on polymer orientation have been studied using polarized optical spectroscopy and synchrotron-sourced grazing incidence X-ray diffraction (GIXD) analysis. The results of polarized optical spectroscopy indicate that the symmetrically substituted PPV is suitable for homogeneous oriented film preparation by friction-transfer technique. The formed film of poly(2,5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (BEHPPV) exhibited large light emission dichroism of up to 42.0.



Single-Crystal-like Structure of Poly(9,9dioctylfluorene) Thin Films Evaluated by Synchrotron-Sourced Grazing-Incidence X-ray Diffraction

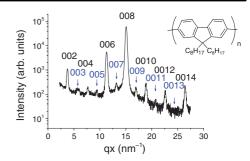
M. MISAKI, S. NAGAMATSU,

M. CHIKAMATSU, Y. YOSHIDA,

R. AZUMI, N. TANIGAKI,

Y. UEDA, and K. YASE

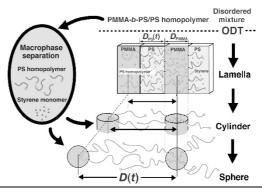
[Special Issues -Synchrotron Radiation and Neutron Beam- Regular Article] Vol. 39, No. 12, pp 1306–1311 (2007) The structures of friction-transferred poly(9,9-dioctylfluorene) (PFO) films and subsequently thermal-treated films were studied using synchrotron-sourced grazing-incidence X-rav diffraction (GIXD). The in-plnae diffraction and rocking profiles clearly showed the different film structures of PFO that depends on the annealing processes. These results suggest the ability of friction transfer for obtaining single-crystal-like thin films and the importance of carefully designed annealing process for the applications of the films to various optoelectronic devices.



Living Polymerization Induced Microphase Separation and Microdomain Investigated by Focusing Ultra-small-angle Neutron Scattering

R. MOTOKAWA, Y. IIDA, Y. ZHAO, T. HASHIMOTO, and S. KOIZUMI

[Special Issues -Synchrotron Radiation and Neutron Beam- Regular Article] Vol. 39, No. 12, pp 1312–1318 (2007) We performed *in situ* and time-resolved focusing ultra-small-angle neutron scattering (USANS) measurements on living radical RAFT polymerization of poly (methyl methacrylate)-*block*-polystyrene (PMMA-*b*-PS), the PS block chain is growing from the end of PMMA block chain. Focusing USANS, which is realized by a biconcave refractive lens and high resolution cross-wired photo-multiplier with ZnS/⁶LiF scintillater, plays an important role to determine the microdomain and macrodomain structures, appearing in the polymerization solution.

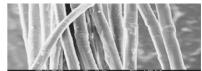


Grafting of Flax Fiber (*Linum usitatissimum*) with Vinyl Monomers for Enhancement of Properties of Flax-Phenolic Composites

B. S. KAITH and S. KALIA

[Regular Article] *Vol. 39, No. 12, pp 1319–1327 (2007)*

Binary vinyl monomers such as methyl-(MMA)/Ethylacrylate methacrylate (EA), MMA/Acrylonitrile (AN) and MMA/Acrylic acid (AA) have been graft co-polymerized onto flax fibers under the influence of microwave radiations (MWR). Various reaction parameters have been optimized and maximum grafting (25%) was observed in reaction time of 30 minutes at 210 W microwave power. Flax-g-copolymers thus prepared were used as reinforcing material in the preparation of flax-phenolic composites. Phenol-formaldehyde (PF) composites reinforced with graft co-polymers of flax fibers showed better mechanical properties in comparison to composites reinforced with raw flax fibers.

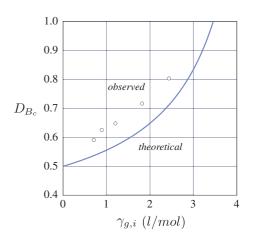


Theory of Gel Formation Drop-wise Addition of $R-A_f$ Solution onto $R-B_g$ Solution

K. SUEMATSU

[Regular Article] *Vol. 39, No. 12, pp 1328–1336 (2007)*

A branching process is investigated for the drop-wise addition polymerization. It is noteworthy that the cluster distribution function with no rings has the same form as that in the multiple link system. In this point of view the drop-wise addition polymerization is equivalent to the multi-link polymerization. Upon taking cyclization into consideration, however, the situation changes. The concentration of cyclic species varies depending on the dilution ratio r, in strong contrast to the conventional polymerization where the cyclic concentration remains invariable above the critical concentration c^* for varying monomer concentration and is a function of the extent of the advancement of the reaction alone. The dropwise addition polymerization is an only system known so far that dodges this invariance principle. The theoretical result was compared with experimental data. The general feature of the theoretical prediction is in good accord with the observed gel points (see Figure). There is appreciable numerical difference between the theory and the observations, which, however, can be reasonably explained by the side reaction effects.



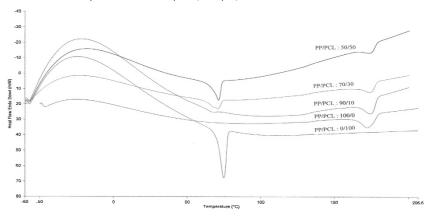
Gel points as against initial dilution. O: Observed points; (-): theoretical line by eq. (44).

Study on Properties of Polymer Blends from Polypropylene with Polycaprolactone and Their Biodegradability

I. M. ARCANA, B. BUNDJALI, I. YUDISTIRA, B. JARIAH, and L. SUKRIA

[Regular Article] Vol. 39, No. 12, pp 1337-1344 (2007)

DSC curves of polymer blends show two peaks associated with the melting temperatures of their component polymers indicating that the oxidized PP and PCL are immiscible polymer blends. The observed fusion enthalpy of oxidized PP and PCL phases are lower than the calculated fusion enthalpy due to the presence of a small amount of oxidized PP and PCL to form compatible polymer blends. Based on the difference between calculated and observed fusion enthalpies, the percentage of compatible polymer blends can be predicted, and the highest percentage of the compatible polymer blends is obtained in PP/PCL ratio of 70/30 (% w/w).



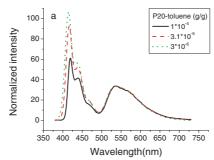
Studies of Green Emission in Polyfluorenes Using a Model Polymer

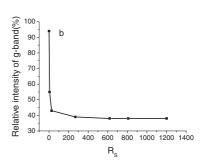
B. HE, J. LI, Z. BO, and Y. HUANG

[Regular Article]

Vol. 39, No. 12, pp 1345-1350 (2007)

A novel model polymer poly(9,9'-dioctylfluorene) with only one foluorenone unit in each chain was designed to clarify the exact nature of the green emission ("g-band") in polyfluorenes. The spectral properties of the model molecule in solution and film are investigated in detail. All the experimental evidence obtained demonstrates g-band in polyfluorene is attributed to the mono-chain fluorenone; more important, the aggregation of the chains suppresses the blue emission and enhances g-band.





Synthesis and Structure of Optically Active Polyesters Containing C2 Chiral Spirobifluorene Moieties in the Main Chain

R. Seto, T. Maeda, G. Konishi, and T. TAKATA

[Regular Article] Vol. 39, No. 12, pp 1351-1359 (2007)

Three optically active polyesters $\bf 3$ possessing C_2 chiral spirobifluorene $\bf 1$ moieties in the main chains were prepared and their structural feature was discussed mainly by the UV-vis and CD spectral characteristics. In the UV-vis and CD spectra of the polymers 3 bisignate Cotton effect was observed in the UV-vis absorption region of optically inactive diacid part of the repeating unit in any case. The results obtained and the structure simulation of 3 suggested their helical conformation.

$$R = \frac{1}{\sqrt{N}} \frac{1}{$$

Network Formation of Interlocked Copolymer Obtained from Copolymerization of 1,2-Dithiane and Lipoic Acid by Metal Salt

T. YAMANAKA and K. ENDO

[Regular Article] *Vol. 39, No. 12, pp 1360–1364 (2007)*

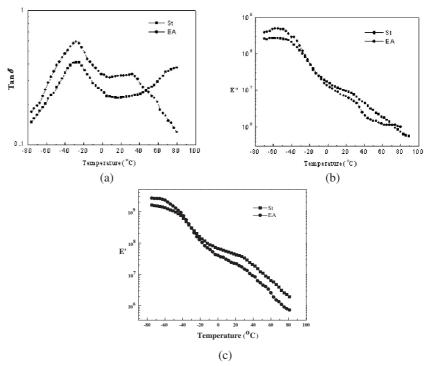
Network structure containing polycatenane was constructed under mild conditions by only mixing of Zn(acetate)₂ and the copolymer obtained from the thermal ring-opening copolymerization of 1,2-dithiane (DT) and liopic acid (LPA) without any initiators.

Compatibility of Polyurethane/(vinyl ester resin)(ethyl acrylate) Interpenetrating Polymer Network

C. QIN, Z. JIN, X. BAI, H. JIANG, and W. CAI

[Regular Article] Vol. 39, No. 12, pp 1365–1372 (2007)

A novel Polyurethane/poly(vinyl ester resin) Interpenetrating Polymer Network(PU/VER IPN), was synthesized at room temperature by polymerizing ethyl acrylate (EA) instead of the conventionally used styrene(St) as a comonomer with simultaneous interpenetration. The respective compatibilities of PU/VER(EA)IPN and PU/VER-(St)IPN were studied by ATR-FT/IR, TEM, AFM, DSC and DMA. The results showed that, compared with PU/VER(St)IPN, the substitution of St by EA resulted in better compatibility between the PU network and VER network and PU/VER(EA)IPN showed better damping properties.



A Monte Carlo Study of the Intrinsic Viscosity of Semiflexible Regular Three-Arm **Star Polymers**

D. IDA and T. YOSHIZAKI

[Regular Article]

Vol. 39, No. 12, pp 1373-1382 (2007)

The behavior of the ratio g_{η} of the intrinsic viscosity for an unperturbed regular threearm star freely rotating chain to that of a linear one, both having the same total chain length, was examined by a Monte Carlo simulation as a function of the reduced contour length λL as defined as the total contour length L of the corresponding Kratky-Porod wormlike chain divided by its stiffness parameter λ^{-1} . It is found that the value of g_{η} calculated in the Kirkwood–Riseman approximation, which is designated $g_{\eta}^{(KR)}$ (\bigcirc), lies between the values of upper and lower bounds, which are designated $g_{\eta}^{(U)}$ and $g_{\eta}^{(L)}$, respectively, and are represented by the upper and lower ends, respectively, of each vertical error bar, and further that $g_{\eta}^{(KR)}$ may give a good approximate value for semiflexible or stiff chains with small λ^{I} semiflexible or stiff chains with small $\lambda \tilde{L}$.

