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Selected Papers

Photoinduced Change in Mechanical Properties of Anthracene Polymers Containing Flexible Side Chains

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Anthracene polymers containing flexible side chains were prepared and their photomechanical properties were investigated. The glass transition temperature of the polymers decreased and the photoreactivity at room temperature was enhanced with an increase of the flexible side chain content. When the polymer was formed into a fiber shape and illuminated with UV light, it bent toward the actinic light source. The deformation was investigated using a thermomechanical analyzer, which revealed that the polymers undergo fast expansion and slow contraction in response to UV light, due to the thermal expansion and photodimerization of the anthracene moiety, respectively.

Photomobile materials show macroscopic deformation in response to light and generate mechanical work directly from light energy.[1] The energy supply for deformation of photomobilie materials is simple in comparison to other stimuli-responsive materials, and they have been intensively investigated with the development of several applications.[2–5] Inducement of microscopic changes in the material is necessary for photoinduced movement, and various changes, such as electrical,[6] thermal,[7] and structural,[8–10] have been proposed. Photodimerization, which changes the structure, has attracted much attention with regard to photomechanical effects, because dimerization induces migration of the photoactive moiety, so that a large deformation is expected. In addition, the reacted compounds are thermally stable, enabling stepwise measurement of the photoreaction, which can be easily traced using spectroscopy. These properties are suitable for photocurable shape memory polymers and such photodimerizable compounds, as cinnamic groups,[11] and coumarin[12] have been used. On the other hand, Zhao et al. reported the photoinduced bending of a supramolecular film driven by the photodimerization of coumarin moieties.[13] In this study, we have focused on the photodimerization of anthracene. Anthracene is a conventional photoreactive compound that can undergo [4 + 4] intermolecular dimerization upon irradiation with UV light (Figure 1).[14,15] The change in structure in anthracene is sufficiently large to demonstrate macroscopic movement in the crystal state.[16] We have previously demonstrated the photoinduced bending of anthracene-containing polymer fibers that was mainly induced by the photodimerization of anthracene moieties.[17] When the sample was heated above the glass transition temperature T_g (>110 °C), the photoreactivity of the sample was enhanced in addition to the deformation ratio. In this study, we synthesized anthracene polymers containing flexible side chains to investigate the influence of T_g on the photomechanical properties. The influence of the copolymerization ratio on the thermal properties and the photoresponsive behavior of the copolymer fibers were explored by thermomechanical analysis and dynamic mechanical analysis.

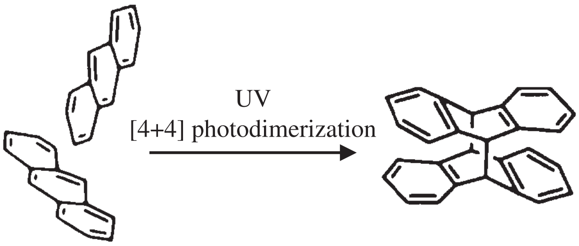

Figure 1. Photodimerization of anthracene.

Experimental

Materials. Figure 2 shows the chemical structure of the copolymer used in this study. Copolymers were synthesized by radical polymerization in tetrahydrofuran (THF) solution using azobisisobutyronitrile (AIBN) as an initiator. The monomer feed ratio was adjusted to control the copolymer composition. Table 1 summarizes the composition, molecular weight, and thermal properties of the copolymers. The number-average molecular weight (M_n), weight-average molecular mass (M_w), and their ratio (M_w/M_n) were determined for the anthracene polymer using gel permeation chromatography (GPC) with polystyrene standards for calibration. The copolymerization ratio was confirmed by 500 MHz ^{1}H nuclear magnetic resonance spectroscopy (NMR, Bruker DRX500). The thermo-

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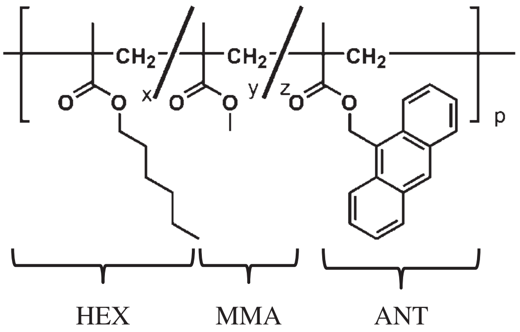

Figure 2. Chemical structure of the (co)polymer used in this study. The (co)polymers composed of methyl- (MMA), *n*-hexyl- (HEX), and 9-anthracenylmethyl (ANT) methacrylate.

Table 1. Composition, Molecular Weight, and Thermal Properties of the Copolymers

Sample	Composition[a] (x:y:z)	M_n[b] ($\times 10^4$)	M_w/M_n[b]	T_g[c]/°C
P091	0:90:10	3.0	1.9	117
P181	10:80:10	2.7	1.8	97
P271	20:70:10	2.2	2.0	74
P361	30:60:10	2.3	1.9	54
P451	40:50:10	3.8	1.8	40
PMMA	0:100:0	0.76	1.6	96

a) Determined by ^{1}H NMR. b) Measured using GPC with polystyrene standards. c) Determined by DSC.

dynamic properties of the polymer were analyzed using differential scanning calorimetry (DSC, Seiko I&E SSC-5200 and DSC220C) at heating and cooling rates of 10 °C min^{-1}. The sample abbreviations used indicate the content of units (*n*-hexyl methacrylate: HEX, methyl methacrylate: MMA, and 9-anthracenylmethyl methacrylate: ANT) in the polymer, as calculated from integration of the ^{1}H NMR spectra. For example, **P091** is composed of HEX:MMA:ANT at 0:90:10 (mol %).

Preparation and Characterization of the Polymer Fibers and Films. The polymer fiber was prepared according to previously reported syntheses.[18,19] A small amount of polymer was heated above T_g (>130 °C) on a glass substrate placed on a hot stage (Linkam TH-600PM). The fibers were drawn by dipping the tip of a pick and pulling it quickly. The optical anisotropy of the fiber was observed using a polarizing optical microscope (POM, Olympus BX51P). An absorption spectrum was measured with a UV–vis spectrometer (Hitachi U-3010) using a thin polymer film, which was prepared by spin coating from a THF solution. Photoinduced motion of the fibers was observed upon irradiation with UV light at 365 nm from a UV-LED irradiator (Keyence UV-400 with UV-50H) and recorded with a digital camera. The degree of contraction of the fibers was measured with a thermomechanical analyzer (Seiko SS6100) using the static stretch mode under photoirradiation. The fiber was fixed at both ends on the apparatus with instant glue and loaded at 3 mN as initial stress. The change in the viscoelastic properties during photodeformation was measured with a dynamic mechanical analyzer (UBM DVE-V4) using a tension clamp. The clamp assembly consists of a fixed lower clamp and a mobile upper clamp. The fiber was positioned between the two clamps and held under a preload of 15 mN. The force was oscillated at a frequency of 110 Hz, and the corresponding average stress–strain values were measured for 30 s. The change in surface height of the spin-coated samples was analyzed using atomic force microscopy (AFM, Seiko NPX1000) in damping mode. Commercial silicon cantilever with an average tip radius of less than 20 nm and a spring constant of 30 N m^{-1}, were oscillated at their fundamental frequency (200 kHz).

Results and Discussion

All (co)polymers shown in Figure 2 were synthesized by free-radical copolymerization. The feed ratio of the three methacrylate monomers was adjusted to control the copolymerization ratio. Table 1 summarizes the molecular weights and the thermal properties of the synthesized copolymers. T_g was found to decrease as the content of the HEX groups increased. We investigated the effect of the photochemical reaction on the polymers by absorption spectroscopy with a thin film (<1 µm) on a quartz substrate. Irradiating a copolymer film with UV light induced the [4 + 4] photodimerization of the anthracene groups. All copolymer films became insoluble after exposure, which indicated that photocrosslinking occurred. Figure 3a represents changes in the absorbance of the **P091** polymer film under photoirradiation; the anthracene absorption around 350–400 nm decreased slowly and did not recover. The degree of photodimerization (ΔP) is defined as,

$$\Delta P = \frac{A_0 - A_{\mathrm{UV}}}{A_0} \times 100(\%) \qquad (1)$$

where A_0 and A_{UV} indicate the absorbance at 367 nm before and after photoirradiation, respectively. The change in ΔP of the polymers at room temperature as a function of supplied energy is displayed in Figure 3b. This indicates that all the polymers cannot undergo 100% reaction and photoreaction requires only a small amount of energy when the content of the HEX groups is increased. Since the mobility of the polymer backbones has a strong affect on the photoreactivity, the same experiment was performed with heating of the polymers to their respective T_g values (Figure 3c). Photodimerization proceeded more effectively and photoreactivity became almost the same regardless of content of HEX moiety. It can be presumed that the HEX units enhance the [4 + 4] photoreaction of the anthracene polymers because they increase flexibility of the polymer backbones.

The prepared fibers show high anisotropy along the fiber axis and diameter of them were 200 µm (see Supporting Information). Figure 4 shows a typical macroscopic deformation of the anthracene polymer fiber (**P451**). The fiber bent toward the actinic light source upon exposure to UV light at 30 mW cm^{-2} for 30 s. This bending behavior was similar to that previously reported using **P091** fiber[17] indicating that the [4 + 4] photoreaction induced the deformation of the stretched fiber. The change in the length of the fiber axis upon photoirradiating was measured by thermomechanical analysis to further evaluate this bending behavior. Figure 5a shows a schematic illustration of the experimental setup. For evaluating

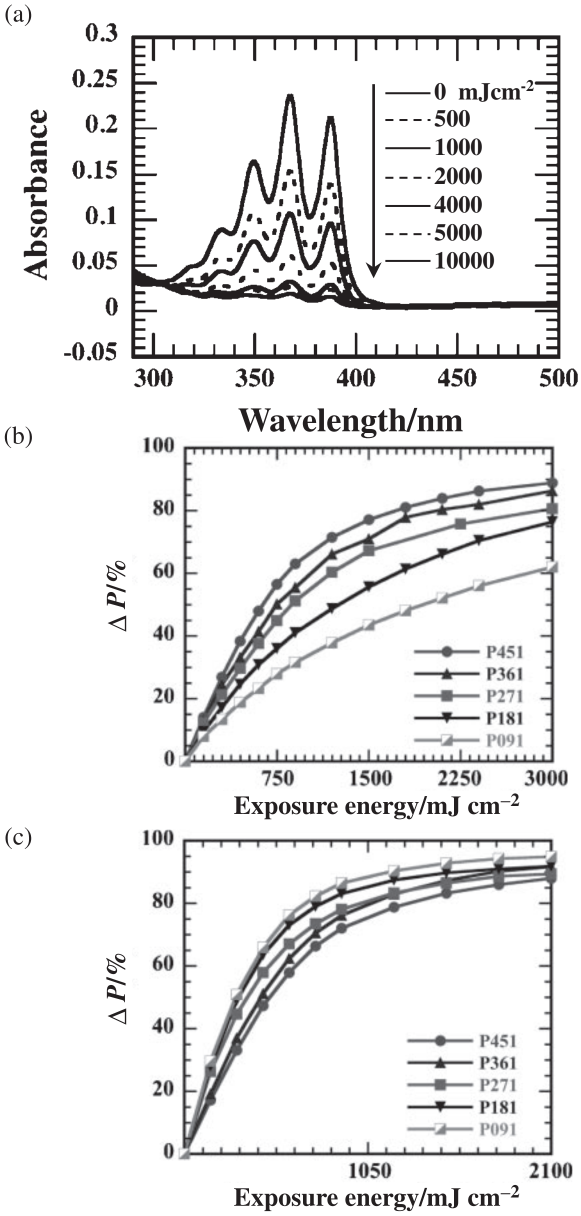

Figure 3. Photoreaction of the polymer film upon illumination with UV light: (a) change in the absorption spectrum of the **P091** film, (b) degree of photoreaction at room temperature and (c) at the glass transition temperature, as calculated from the change in absorbance at 367 nm.

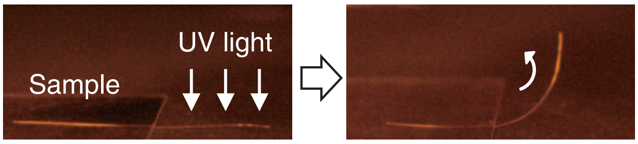

Figure 4. Photographs of **P451** fiber exhibiting bending behavior in response to UV light (365 nm, 30 mW cm^{-2}). White dash lines indicate edges of the fiber.

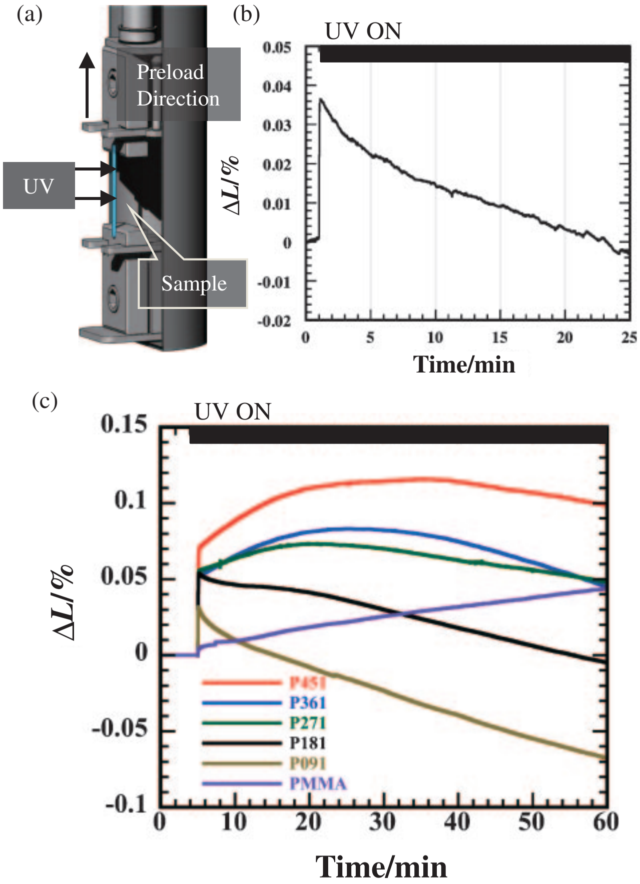

Figure 5. Thermomechanical analysis of the polymer fibers under photoirradiation: (a) schematic illustration of the experimental setup, (b) change in the length along the fiber axis of **P091**, and (c) various anthracene polymer fibers in response to UV light (365 nm, 150 mW cm^{-2}) at room temperature. Size of the fibers: Ø0.2 × 6 mm.

the photomechanical properties, the degree of contraction upon exposure to UV light was defined as follows,

$$\Delta L = \frac{L_{\mathrm{UV}} - L_0}{L_0} \times 100(\%) \tag{2}$$

where L_0 and L_{UV} represent the lengths of the film before and after photoirradiation, respectively. Figure 5b shows the change in ΔL for **P091** fiber in response to UV light. It revealed a fast expansion at the beginning of photodeformation followed by a slow contraction. The change in ΔL for all the polymers is summarized in Figure 5c. All polymer fibers containing anthracene side chains show fast expansion and slow contraction. On the other hand, PMMA fiber exhibited small photoresponsive behavior, which showed very small elongation upon exposure to UV light for long time. These results indicate the photoreaction of the anthracene moieties causes both fast and slow mechanical responses.

The change in ΔL of the polymers was evaluated under periodic irradiation to explore the fast photoresponsive behavior in detail (Figure 6). It was found that ΔL increased 0.02% to 0.05% within 5 s and decreased immediately when the sample was returned to the dark condition. The ΔL value increased with an increase in HEX moieties, which indicates that the enhancement of flexibility improves the photoresponsive behavior. The changes in ΔL for the polymers showed no obvious fatigue in the tested fibers. The repeatability of the fast

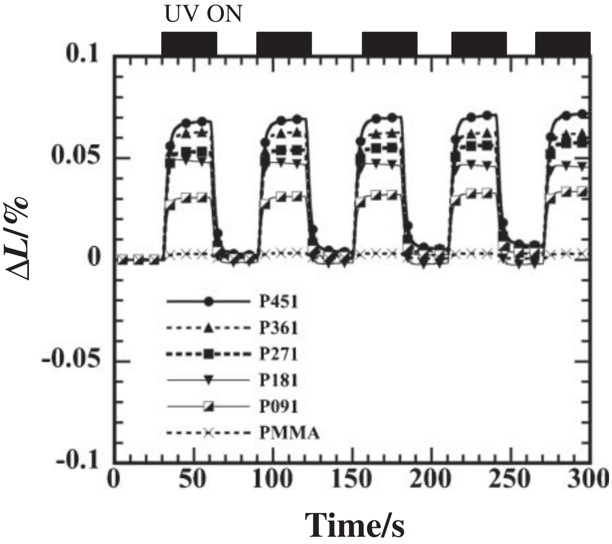

Figure 6. Change in the length along the fiber axis of the polymers upon periodic irradiation with UV light. Size of the fiber: Ø0.2 × 6 mm.

expansion was almost the same for the polymers. The fast reversible response appeared to be similar to that for an interpenetrated polymer film containing azobenzene moieties,[20] which displayed a fast resonant vibration between the *trans*- and *cis*-forms leading to a decrease in the elastic modulus, thereby creating free volume for elongation. However, the absorption spectroscopy indicated that no significant photodimerization occurred during short time UV-irradiation.

For further insight into this fast response upon photoirradiation, the viscoelastic properties were measured in response to UV light using dynamic mechanical analysis. Figures 7a and 7b show the logarithmic changes in the storage modulus ($\log E'$) and loss modulus ($\log E''$), respectively, in response to UV light. The parameters of the anthracene polymer shifted upon irradiation with the actinic beam, while the PMMA fiber showed no change, which indicates that the change in the viscoelastic properties involved fast photoresponsive behavior. On the other hand, the slow contraction due to photodimerization did not influence the $\log E'$ and $\log E''$ values of the samples. It is presumed that the change due to the slow contraction is small, slow and only occurs at the irradiated surface during the measurement time (30 s), so that the change in the viscoelastic properties is negligible, whereas the fast expansion is instantaneously induced in the entire fiber. Srikhirin et al. studied a photoinduced change in the viscoelastic properties of a PMMA film with dispersed azobenzene moieties.[21] They reported an increase in the storage modulus of the film upon irradiation at 485 nm, which suggests that high-intensity actinic light gives rise to rapid *trans–cis–trans* cycling, which can slightly stiffen the material due to local stress in the matrix. In contrast, no structural change was found in the photoactive anthracene moiety unless dimerization occurred and there was a low concentration of anthracene moieties, which resulted in small and completely opposite changes in the viscoelastic properties. Considering these results, the fast expansion results from photothermal effects that are observed in other photomobile materials.[22]

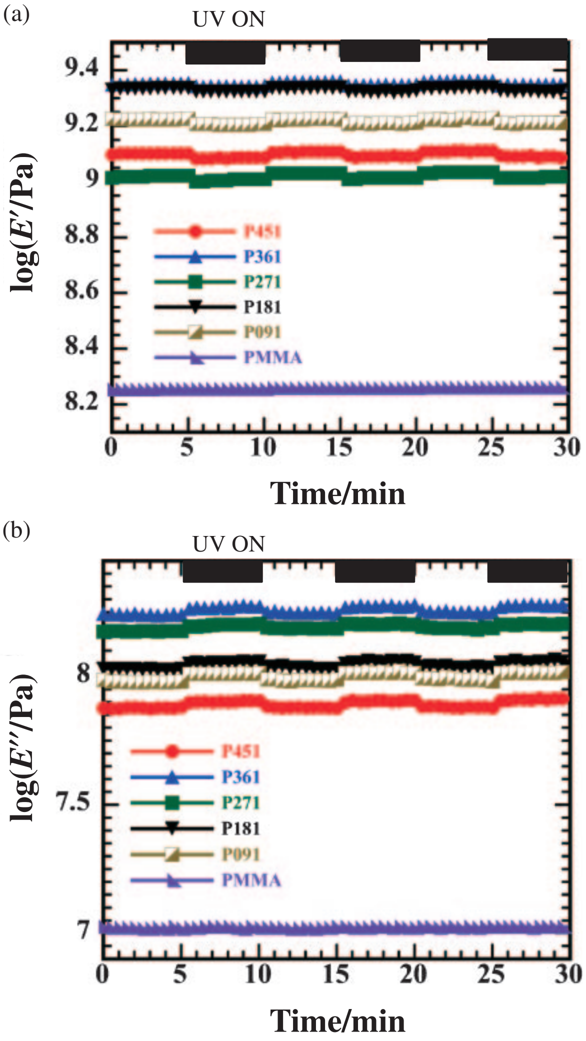

Figure 7. Dynamic mechanical analysis of the polymer fibers upon irradiation with UV light: (a) storage modulus and (b) loss modulus. Size of the fibers: Ø0.2 × 6 mm.

Fast expansion could not be observed on a macroscopic level, even for thin fibers (ca. 50 µm diameter); therefore, the surface image of the film was observed using AFM to trace the change upon photoirradiation. Figure 8a shows a schematic illustration of the experimental setup. The film was illuminated with UV light during measurement of the surface profile. Figure 8b shows a cross-sectional AFM image of the **P091** film. The film showed no obvious surface profile prior to irradiation, but its height immediately increased upon irradiation with UV light, and recovered when the light was turned off, resulting in the repetitive pattern seen in Figure 8c. Figure 8d shows the surface profile of the film after 20 exposures to UV-irradiation. Fast deformation was also observed for the PMMA film, although the value was small (<6 nm).

Summary

Anthracene polymers with different content of HEX moieties were prepared and the photoresponsive behavior was investigated. The glass transition temperature of the polymer

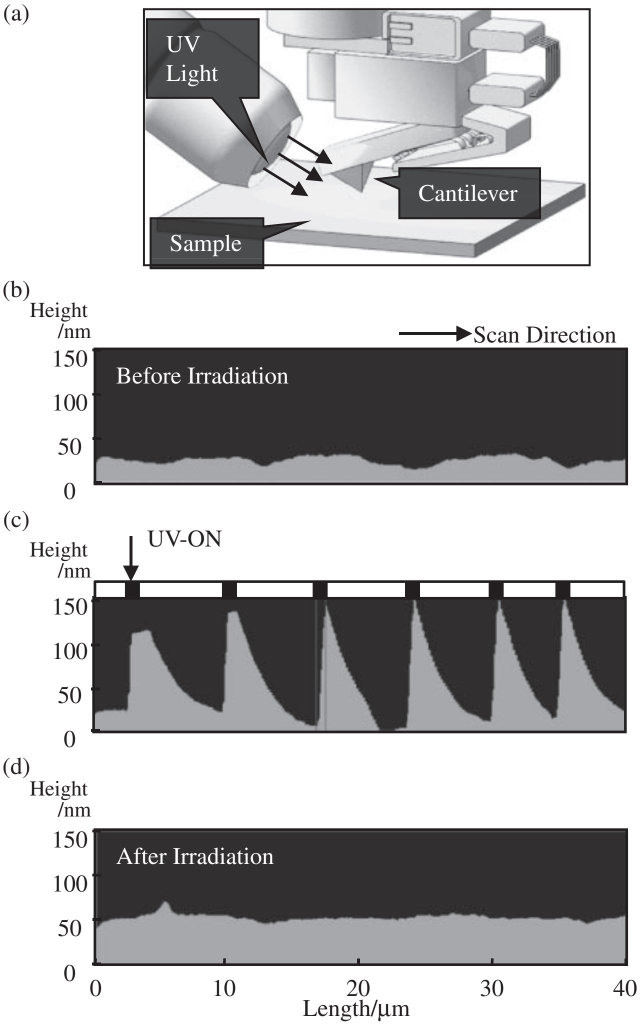

Figure 8. Observation of fast expansion in the anthracene polymer: (a) schematic illustration of the experimental setup, change in the height of the **P091** film (b) before irradiation and (c) upon repeated irradiation with UV light (365 nm, 150 mW cm^{-2}) at room temperature, and (d) after 20 exposures to UV irradiation.

decreased with increasing HEX content. The polymers exhibited similar photoresponsive behavior at the glass transition temperature. Upon exposure to UV light, fast expansion and slow contraction were observed, due to thermal expansion and photodimerization, respectively. The contraction became smaller and slower with increasing HEX content, due to increased flexibility, while little change in the expansion was observed. The fast expansion is due to optical absorption by the chromophore. Such films could therefore be patterned using a photomask and the fast-expansion properties utilized for many optical and micromechanical applications.

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Supporting Information

Polarizing optical micrographs of the polymer fibers. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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