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Photo-Induced Photonic Band Gap Shift of SiO_2 Inverse Opal Films Infiltrated by Azo-Tolane Copolymer

Tomomi Shirota [a], Masaki Moritsugu [b], Shoichi Kubo [c], Tomonari Ogata [a], Takamasa Nonaka [a], Osamu Sato [d] & Seiji Kurihara [a]

[a] Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, Kumamoto-shi, Kumamoto, Japan

[b] Innovative Collaboration Organization, Kumamoto University, Kumamoto-shi, Kumamoto, Japan

[c] Chemical Resource Laboratory, Tokyo Institute of Technology, Midori-ku, Yokohama, Japan

[d] Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga-shi, Fukuoka, Japan

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Photo-Induced Photonic Band Gap Shift of SiO_2 Inverse Opal Films Infiltrated by Azo-Tolane Copolymer

TOMOMI SHIROTA,[1] MASAKI MORITSUGU,[2] SHOICHI KUBO,[3] TOMONARI OGATA,[1] TAKAMASA NONAKA,[1] OSAMU SATO,[4] AND SEIJI KURIHARA[1]

[1]Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, Kumamoto-shi, Kumamoto, Japan
[2]Innovative Collaboration Organization, Kumamoto University, Kumamoto-shi, Kumamoto, Japan
[3]Chemical Resource Laboratory, Tokyo Institute of Technology, Midori-ku, Yokohama, Japan
[4]Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga-shi, Fukuoka, Japan

Photochemically tunable photonic band gap materials were prepared by the infiltration of liquid crystal polymers with azobenzene side chains and tolane side chains indicating larger birefringence into voids of SiO_2 inverse opal films. Linearly polarized light irradiation resulted in transformation from random to anisotropic molecular orientation of azobenzene and tolane side chains, then the azobenzene-tolane copolymer film showed larger birefringence. Thus, the reflection band of the SiO_2 inverse opal films infiltrated with the azobenzene-tolane copolymers was shifted to longer wavelength region by the irradiation of linearly polarized light.

Keywords Azobenzene; birefringence; photonic crystal; tolane

Introduction

Photonic crystals having a periodic structure have attracted much attention from both fundamental and practical points of view, because of their unique properties in controlling the propagation of light [1]. A typical photonic crystal material can be prepared by self assembling of nano spheres, which is generally called opal. In the case of the opal, Bragg's diffraction expressed by Eq. (1) under normal incident condition is observed due to the quasi-photonic band gap,

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Address correspondence to Seiji Kurihara, Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, 2-39-1 Kumamoto-shi, Kumamoto 860-8555, Japan. E-mail: kurihara@kumamoto-u.ac.jp

$$\lambda = 2\sqrt{\frac{2}{3}}d\sqrt{n_{sphere}^2 f + n_{void}^2(1-f)} \tag{1}$$

where λ is the peak wavelength of the reflection, d is the diameter of the sphere, n_{sphere} and n_{void} are the refractive indices of the sphere and the medium in the voids of opal, respectively, and f is the volume fraction of the sphere. In this way, λ can be tuned by two approaches: control of the diameter of the sphere and control of the refractive index.

In our previous work, a photo-tunable photonic crystal was prepared by infiltration of azobenzene liquid crystal polymers into a SiO_2 inverse opal film. The molecular orientation of the azobenzene liquid crystal polymers was controlled by the irradiation of linearly polarized (LP) and circularly polarized (CP) light, giving change in the birefringence ($\Delta n = n_e - n_0$) [2]. In this system, the LP and CP light irradiation caused the reversible transformation between anisotropic and random molecular orientation of azo-chromophores in the voids, leading to the reversible and stable shift of the reflection band [3,4]. However, the switching properties such as magnitude of the change in the wavelength were not enough. The shift width of reflection band depends on the birefringence of materials infiltrated in the SiO_2 inverse opal. So, it is expected that larger shift of the reflection band will be achieved by using of liquid crystal polymers with higher birefringence as infiltration materials into the SiO_2 inverse opal.

It is well known that tolane compounds have larger birefringence because of its rigid π-conjugated electronic structure [5,6]. In this work, therefore, we prepared the SiO_2 inverse opal films containing acrylate polymers with azobenzene and tolane groups [7], and investigated the effect of tolane group on their photoresponse properties.

Experimental

Materials

Monodispersed polystyrene (PS) spheres (a diameter of 300 nm), were purchased from Duke Scientific Corp. Alcoholic colloidal solution of SiO_2 nanospheres (a diameter of 12 nm) were kindly supplied from Catalysis and Chemical Industries Co., Ltd. (Japan). Other reagents were purchased and used without further purification.

Syntheses of Copolymers

Azobenzene acrylate monomer, **MAz6Ac**, tolane acrylate monomer **MTo6Ac** were synthesized according to the reported previously, and used in this study [7,9]. The structure of polymers is shown in Figure 1. Synthesis of poly(**MAz6Ac**-*co*-**MTo6Ac**), which is named A*m*T*n* (m, n; molar ratio of **MAz6Ac** and **MTo6Ac**, respectively), was carried out as follows; 0.75 mmol of MAz6Ac, 0.75 mmol of MTo6Ac and 0.015 g (0.125 mmol) of benzylthiol as chain transfer agent were dissolved in 10 ml of dimethylformamide in a glass tube, and 10 mg (0.06 mmol) of 2,2′-azobisisobutyronitrile was also added to the solution. After purge with nitrogen, the tube was sealed and shaken in a water bath at 60°C for 48 h. The reaction mixture was poured into excess methanol. The precipitate was collected and dissolved in chloroform again. After repeating this reprecipitation cycle several times, copolymer was collected and dried in vacuum.

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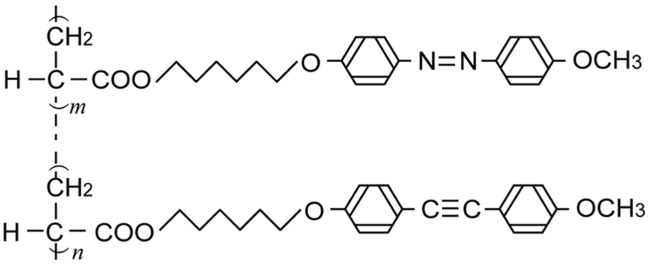

Figure 1. Structure of *Am*T*n* (*m, n*; molar ratio of **MAz6Ac** and **MTo6Ac**, respectively).

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Properties of Copolymers

Thermal properties of the copolymers were examined by means of differential scanning calorimetry (DSC; Seiko SSC-5020) and polarizing microscopic observation (Olympus BHSP polarizing microscope; Mettler FP80 and FP82 hot stage and controller). The scan rate of DSC measurements was 10°C/min of heating. Molecular weight was determined by gel permeation chromatography (GPC; Jasco 870-UV detector at 254 nm, Shodex KF-804 L column, tetrahydrohuran, as eluent). Copolymerization ratio was determined based on the absorption (358 nm) of the azobenzene groups in the copolymers by using a UV-vis spectrometer (Shimadzu UV-1600).

Photochemical Properties of Copolymers

Copolymer solid films (thickness 100 ~ 200 nm) were prepared by spin-coating using toluene solutions of the copolymers (5 wt%) on a glass substrate.

A change in the birefringence of the copolymer films was investigated by using a pump-probe method at various temperatures as follows; the solid films of the copolymers were placed between crossed polarizers where the polarizing directions of the polarizer were set at an angle of 45° with respect to the polarizing direction of a pumping laser light. An Ar^+ laser (488 nm, 80 mW/cm^2) and a He-Ne laser (633 nm) were used as the pumping and probe lights, respectively. Polarization of the pumping light was controlled by using a linear polarizer for LP light or a quarter plate for CP light. A change in intensity of transmitted light of the probe laser was monitored by a photo-detector. The photoinduced birefringence (Δn) of the copolymer solid films were estimated according to the method reported previously [10].

Preparation of Copolymer/SiO_2 Composite Inverse Opal Films

The SiO_2 inverse opal films were fabricated on a glass substrate according to the method reported earlier [11,12]. Typical procedure was as follows; a hydrophilic glass substrate was vertically immersed into a suspension containing 0.5 vol% of monodispersed PS spheres (a diameter of 300 nm) and maintained at 50°C for 3 days to allow evaporation of the solvent. This PS opal film was completely dried at room temperature, and heated at 80°C for 30 min to enhance the connection between the PS spheres or between the spheres and the glass substrate. Then, the film was immersed in an alcoholic colloidal dispersion of SiO_2 spheres (a diameter of 12 nm) and lifted with a rate of 8 μm/s, leading to the infiltration of SiO_2 spheres in the voids of the PS spheres. Finally, the PS opal film infiltrated with SiO_2 spheres

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was annealed at 500°C for 5 h to remove the PS spheres giving an inverse opal film consisting of SiO_2. Then, the copolymers were infiltrated into the voids of the SiO_2 inverse opal film above the melting point of each copolymer, and resulting composite films were cooled to room temperature to obtain a film of inverse SiO_2 opal films infiltrated with copolymers.

Photochemical Properties of Copolymer/SiO_2 Composite Inverse Opal Films

The reflection spectra of the copolymer/SiO_2 composite inverse opal films were measured with a CCD spectrometer (Ocean Optics USB2000). The changes in reflection peak of the copolymer/SiO_2 composite inverse opal films were measured with/without the irradiation of LP light with Ar^+ laser (488 nm, 80 mW/cm^2) at various temperatures.

Result and Discussion

Characterization of Copolymers

The copolymers having azobenzene and tolane groups as side chain groups were synthesized. The copolymerization ratio, the molecular weight and the phase transition temperatures of the copolymers obtained are shown in Table 1. The copolymerization ratio was controlled by adjusting the feed ratio of the azobenzene monomer and the tolane monomer.

Photo-Induced Birefringence of Copolymer Thin Films

Changes in the birefringence of the copolymer films by the irradiation of LP and CP lights of Ar^+ laser at various temperatures are shown in Figures 2(a)–(c). The birefringence of the copolymer films was increased by the irradiation of LP light, and was decreased by the following irradiation of CP light at all the temperatures studied. These results were arisen from reversible transformation of side chain groups between the uniaxial orientational state and random state by LP and CP light irradiation. The highest value of the birefringence was observed for A7T3 film ($\Delta n = 0.18$), which has moderate content of tolane group, because the photo-orientation of azobenzene side chains was suppressed at higher tolane contents due to the rigid and plane tolane side groups. The photo-induced increase in the birefringence of all the copolymers was remarkably depressed over the glass transition temperature (Tg). On the basis of the results, it is assumed that the temperature dependence of the photo-induced birefringence is related to the flexibility and mobility of the copolymer chain segments. Namely, the higher flexibility and

Table 1. Result of polymerization

Sample	MAz6Ac : MTo6Ac (found : mol%)	Mn ($\times 10^3$)	Mw ($\times 10^3$)	Phase transition temperatures (°C)
A7T3	75 : 25	3.9	5.0	G 48 S 73 N 103 I
A5T5	51 : 49	3.6	4.6	G 47 S 70 N 111 I
A2T8	16 : 84	3.3	5.0	G 44 S 65 N 93 I

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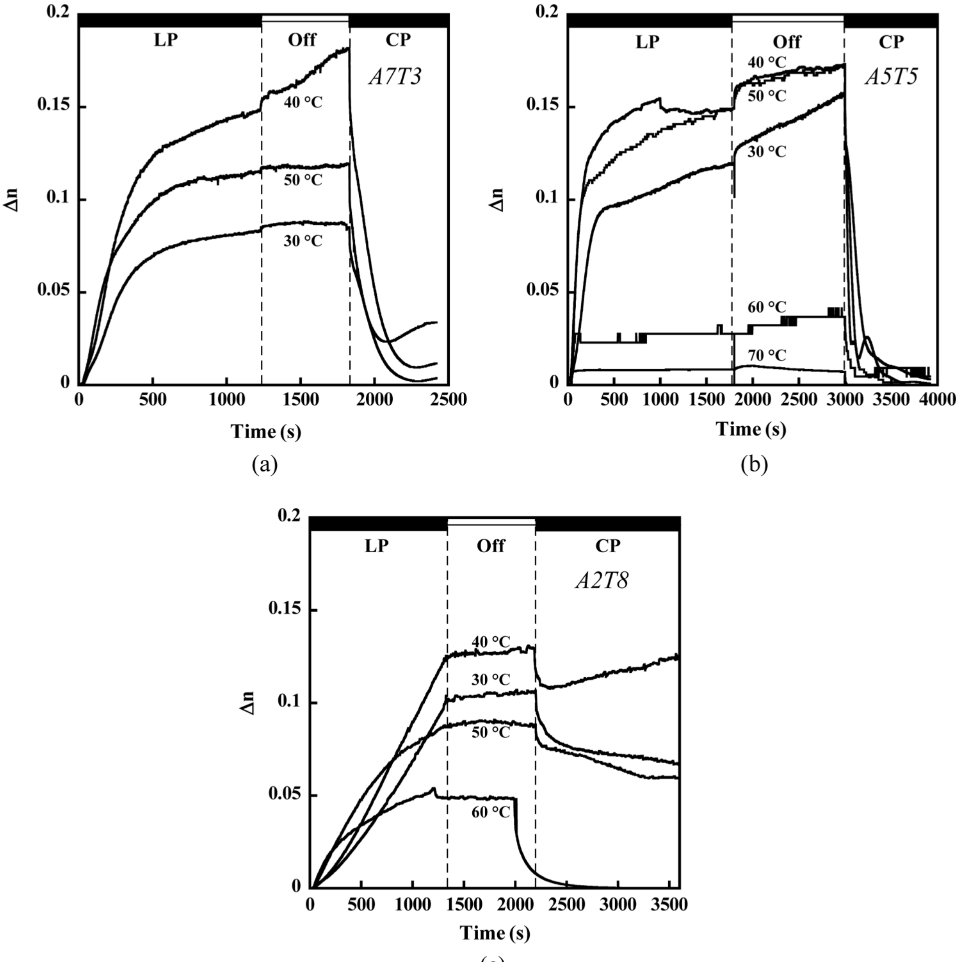

(a) (b)

(c)

Figure 2. Changes in birefringence of (a) A7T3, (b) A5T5 and (c) A2T8 copolymer films by irradiation of LP and CP light of Ar^+ laser at various temperatures.

mobility of polymer chains becomes, the birefringence increases. However, micro-Brownian motion of the polymer main chain segments causes lowering of the stability of molecular orientation of the side groups above Tg of the copolymers. Consequently, the decrease of the birefringence was caused above Tg. In addition, the apparent increase of the birefringence was observed after turn off the light. Although the reason for these phenomena is not clear at the present stage, one of reasons maybe fluctuating of orientation of azobenzene and tolane side chains caused by the continuous photoisomerization of azobenzene groups during the irradiation of Ar^+ laser [13]. In the dark state after irradiation of LP light, it seems that the incompletely-oriented chromophores tend to align parallel to the dominant molecular orientation direction due to the cooperation effect. The incomplete orientation under irradiation and cooperation effect in a dark are attributed to the curious increase in the birefringence after turn off LP light.

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Photochemical Properties of Copolymer/SiO_2 Composite Inverse Opal Films

In order to investigate the effect of the photoinduced orientation of azobenzene and tolane groups on the reflection spectra of the SiO_2 inverse opal films, LP light at 488 nm with Ar^+ laser was irradiated on copolymer/SiO_2 composite inverse opal films. Figure 3 shows reflection spectra of the A7T3/SiO_2 composite inverse opal film before and after irradiation of LP light at room temperature. The significant change in the reflection spectra was observed by the irradiation of the LP light for 60 min, resulting a shift of the reflection peak toward longer wavelength about 19 nm. In addition, the wavelength of the reflection peak was returned to the initial position by the irradiation of CP light.

As shown in Figure 3, a small shoulder appeared at the shorter wavelength side of the reflection band after the LP light irradiation. We have already reported that the peak shift and appearance of shoulder peak in the reflection band after the LP light irradiation were related to the combination of two reflection bands observed with perpendicular and parallel polarizers to the polarization direction of the light irradiated [3]. According to the Bragg's law, it is proposed that the small peak appeared at shorter wavelength region should be related to lower refractive index, n_o, corresponding to the short molecular axis of chromophores, and the reflection peak at longer wavelength region is attributed to higher refractive index, n_e, along long molecular axis of the chromophores. Therefore, the reversible shift of the reflection peak is interpreted in terms of the reversible transformation between anisotropic and random molecular orientations of azobenzene and tolane groups in the polymers by the LP and CP light irradiation [3].

The shift width ($\Delta\lambda$) in the reflection peak wavelength of A*m*T*n* composite inverse opal films after LP light with Ar^+ laser was plotted as a function of irradiation time in Figures 4(a)–(c). It is clear that $\Delta\lambda$ is decreased with increase in

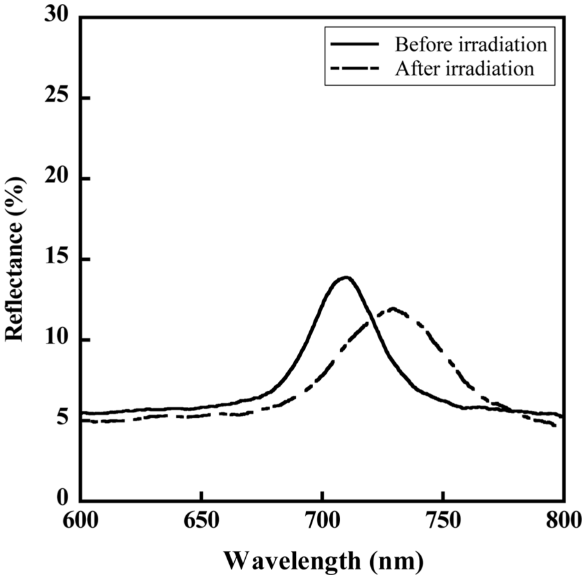

Figure 3. Reflection spectra of A7T3/SiO_2 composite inverse opal films before (solid line) and after (dashed line) irradiation of LP light of Ar^+ laser.

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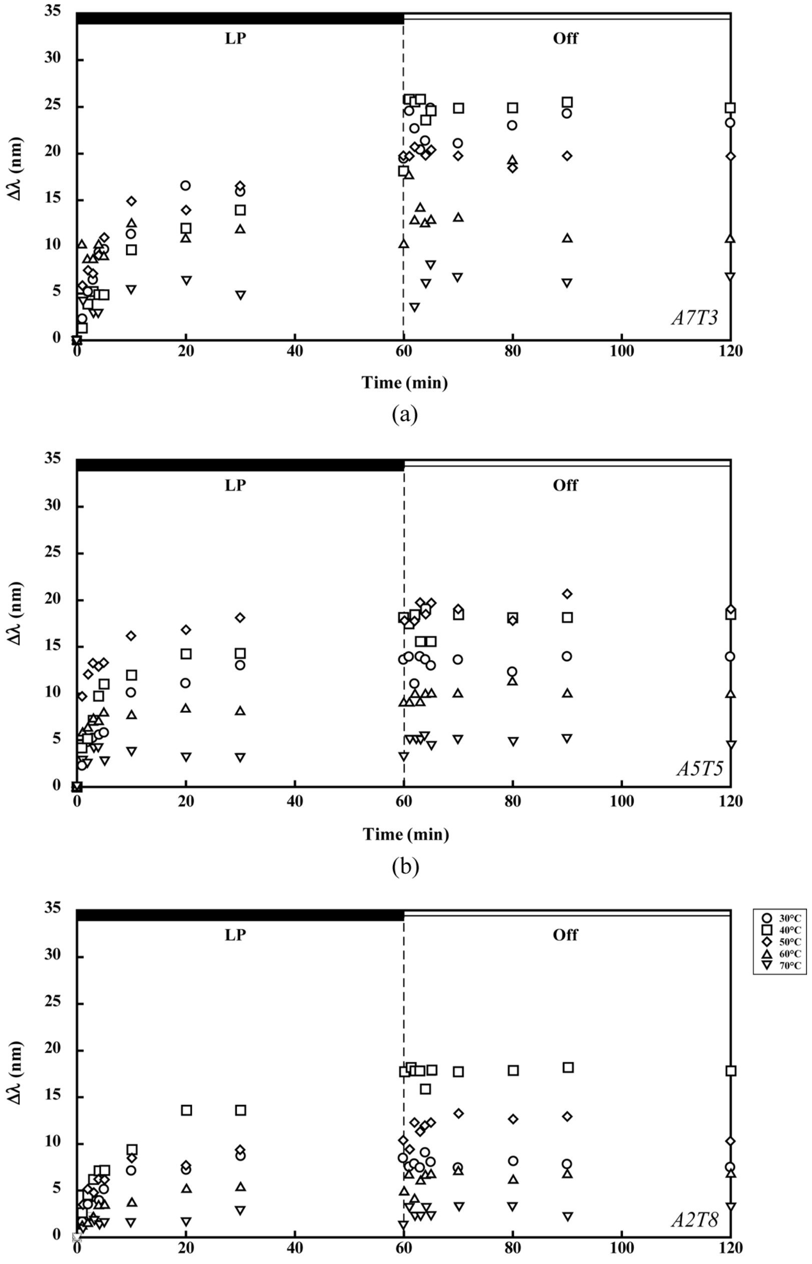

(a)

(b)

(c)

Figure 4. Changes of (a) A7T3, (b) A5T5 and (c) A2T8 composite inverse opal films by irradiation of linearly-polarized (LP) light of Ar^+ laser at 30°C (○), 40°C (□), 50°C (◇), 60°C (Δ) and 70°C (▽).

the ratio of tolane groups in the copolymers. This may be due to the presence of the rigid and plane structure, and non-photoresponsive ability of tolane groups, as previously described. In addition, width of peak shift was found to be strongly suppressed above Tg. This temperature dependences is reminiscent of the change in the photo-induced birefringence as shown in Figure 2. The flexibility and mobility of the copolymers is one of important factors influencing the photoresponse properties of the composite materials. A7T3 showed better photoresponse properties than others; $\Delta\lambda$ was 30 nm for A7T3 at 40°C.

Conclusion

We have fabricated photochemically tunable photonic crystal by infiltration of the liquid crystal copolymers having azobenzene and tolane groups in the SiO_2 inverse opal structure. The LP and CP light irradiation resulted in the reversible transformation between the anisotropic and random molecular orientations of azobenzene and tolane groups in the copolymers, consequently, the reversible and stable shift of the reflection band to longer wavelength was achieved. The highest values of Δn and $\Delta\lambda$ were observed for A7T3 copolymer. This is related to the rigid structure of tolane groups and its less photo-orientation property due to its strong laterally intermolecular interaction. On the other hand, the photoresponse properties are found to depend on the flexibility and mobility of the side chain of the copolymers in relating to the thermal properties.

References

[1] Yabolovitch, E. (1987). *Phys. Rev. Lett.*, *58*, 2059.
[2] Natansohn, A., Xie, S., & Rochon, P. (1992). *Macromolecules*, *25*, 5531.
[3] Moritsugu, M., Kim, S.-N., Ogata, T., Nonaka, T., Kurihara, S., Kubo, S., Segawa, H., & Sato, O. (2006). *Appl. Phys. Lett.*, *89*, 153131/1.
[4] Kurihara, S., Moritsugu, M., Kubo, S., Kim, S.-N., Ogata, T., Nonaka, T., & Sato, O. (2007). *European Polymer Journal*, *43*, 4951.
[5] Ozaki, M., Yoshida, Y., Kasano, M., & Yoshino, K. (2002). *Adv. Mater.*, *14*, 514.
[6] Loenard, S. W., Mondia, J. P., van Driel, H. M., Toader, O., John, S., Busch, K., Bimer, A., Gösele, U., & Lehmann, V. (2000). *Phys. Rev. B*, *61*, R2389.
[7] Ikeda, T., Horiuchi, S., Karanjit, D. B., Kurihara, S., & Tazuke, S. (2007). *Macromolecules*, *23*, 332.
[8] Okano, K., Shishido, A., & Ikeda, T. (2006). *Adv. Mater.*, *18*, 523.
[9] González-Rojas, C. H., Oprunenko, Yu. F., & Morales, G. E. (2004). *Russ. Chem. Bull. Int. Ed.*, *53*, 474.
[10] González-Rojas, C. H., Oprunenko, Yu. F., & Morales, G. E. (2004). *Russ. Chem. Bull. Int. Ed.*, *53*, 474.
[11] Kubo, S., Gu, Z. Z., Takahashi, K., Fujishima, A., Segawa, H., & Sato, O. (2004). *J. Am. Chem. Soc.*, *126*, 8314.
[12] Kubo, S., Gu, Z. Z., Takahashi, K., Fujishima, A., Segawa, H., & Sato, O. (2005). *Chem. Mater.*, *17*, 2298.
[13] Nathansohn, A. & Rochon, P. (2002). *Chem. Rev.*, *102*, 4139.

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