Photoinduced alignment behavior of polymer liquid crystals containing azobenzene moieties in the side chain*

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Abstract: Azobenzene-containing polymeric systems are being developed as materials for photonic applications. The present work deals with the photoinduced two-dimensional (2-D) and three-dimensional (3-D) alignment behavior of polymer liquid crystals (PLCs) with azobenzene moieties in the side chain. 2-D alignment of the PLCs was brought about on irradiation of linearly polarized light. The effects of various factors such as experimental conditions and structural parameters of the PLCs on the 2-D alignment behavior have been explored in detail. The response was enhanced by two methods: chemically tailoring structure of the PLCs and physically modifying the alignment procedure. 3-D alignment of the azobenzene moieties was achieved on irradiation of unpolarized light. It was revealed that the azobenzene moieties were aligned along the propagation direction of the irradiation light. Inert mesogens underwent reorientation together with azobenzene moieties in the 2-D as well as 3-D alignment process.

INTRODUCTION

Aromatic azo-dyes are the most frequently used kind of dye, since their isomerization behavior is a well studied phenomenon [1,2]. Azo aromatic groups can exist in two configurations, the *cis* form and the more stable *trans* form. When exposed to light of a certain wavelength, the stable *trans* form can be photoisomerized to *cis* form. *Cis-trans* isomerization can occur thermally and/or photochemically. Recent year, the generation of anisotropy induced by linearly polarized light (LPL) in polymeric systems containing azobenzene moieties has attracted increasing attention because of the practical applications such as waveguide and optical storage [3–17]. Side-chain polymer liquid crystals (PLCs) show unique combination of the functionality of conventional liquid crystals and the properties of macromolecules. Photoinduced alignment in PLCs is of special interest, because the property of self-organization offers the possibility of cooperative behavior that can amplify relatively weak photochemical effects.

Although the details of the orientation mechanism and underlying processes are not yet to be agreed, a simple physical picture may be proposed. Azobenzene moieties having the transition moment approximately parallel to the molecular long axis exhibit angular-dependent absorbance of the LPL. Only the azobenzene moieties with the transition moment perpendicular to the polarization direction of the incident light are inactive, but the others will be activated to undergo *trans-cis* photoisomerization and subsequent *cis-trans* back-isomerization. By repetition of these *trans-cis-trans* isomerization cycles and motion of the transition moment, the optic axis of azobenzene groups becomes aligned perpendicular to the electric field vector of the polarized actinic light. Inert mesogens undergo reorientation together with azobenzene moieties due to cooperative motion.
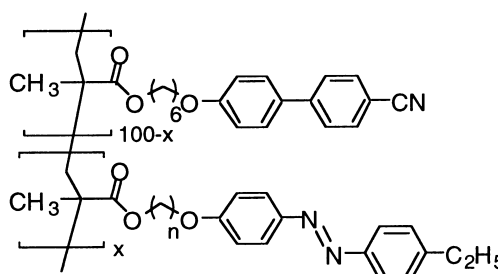
During the two-dimensional (2-D) alignment process, photoinduced biaxiality of azobenzene moieties was observed in PLCs [5,6], amorphous azo polymers [7,8], and LB systems [9]. It was interpreted in terms of the alignment of azobenzene moieties along the propagation direction of the irradiation light [7]. When the azobenzene moieties are aligned with the molecular long axis along the propagation direction of irradiation light, the photoisomerization does hardly take place, since the propagation direction of light is always perpendicular to its electric field vector. With unpolarized light, only the propagation direction is perpendicular to the electric field vector. Thus, in principle, we may align azobenzene moieties in the propagation direction of irradiation light and manipulate the PLCs three-dimensionally (3-D) by changing the direction of the incident light.

In the present work, we systematically studied the effects of experimental conditions and structural factors of PLCs on 2-D alignment behavior. The writing rate was improved through either chemically tailoring the structure of the azobenzene moieties or physical modification of the alignment procedure. 3-D alignment of the PLCs was proposed by the use of unpolarized light.

EXPERIMENTAL SECTION

Figure 1 shows the chemical structure of a series of PLCs in which photoinduced alignment was investigated. Unoriented polymer films were prepared by casting dilute solutions of the PLCs in THF onto freshly cleaned glass substrates. The typical sample thickness was $2\,\mu m$. Optical experiments were performed with the setup similar to the literature [10]. Photoirradiation was performed with a 500-W high-pressure Hg lamp. Light at 366 or 436 nm was selected by a combination of glass filters. The intensity was indicated in each section. A probe light (He-Ne laser, 633 nm) was polarized at 45° with respect to the polarization direction of the irradiation light, passed through crossed polarizers, and was used to probe the induced anisotropy. The induced order parameter, $S = (A_\perp - A_\parallel)/(A_\perp + 2A_\parallel)$, was obtained by using polarized UV and IR spectroscopy, where $A_\perp$ and $A_\parallel$ are the absorbance measured with the polarized beam perpendicular and parallel to the polarization direction of the irradiation light, respectively.

polymer	x	n	phase transition temp. (°C)
MACB-AB3	7	3	G 51 N 114 I
MACB-AB6	6	6	G 44 N 115 I
MACB-AB11	7	11	G 36 N 113 I
AB6	100	6	G 95 S 118 I

Fig. 1 Chemical structures, compositions and phase transition temperatures of a series of polymer liquid crystals used in this study.

RESULTS AND DISCUSSION

Two-dimensional alignment with linearly polarized light

2-D alignment change was induced in the PLC containing very low contents of the azobenzene moieties in initial polydomain state on irradiation of LPL with relatively low intensity [11]. Figure 2 shows the angular-dependent UV absorbance of azobenzene moieties at 360 nm and IR absorbance of cyano groups at $2225\,cm^{-1}$. Before irradiation, the absorbance did not change with the polarization direction of measurement beams. After irradiation, an optical anisotropy was evidently brought about: when the polarization direction of measurement beam was perpendicular to that of the irradiation light, the absorbance reached the maximum; when those directions were parallel to each other, the absorbance was at the minimum. The preferential orientation of azobenzene moieties and inert cyanobiphenyl mesogens is perpendicular to the electric vector of the irradiation light.
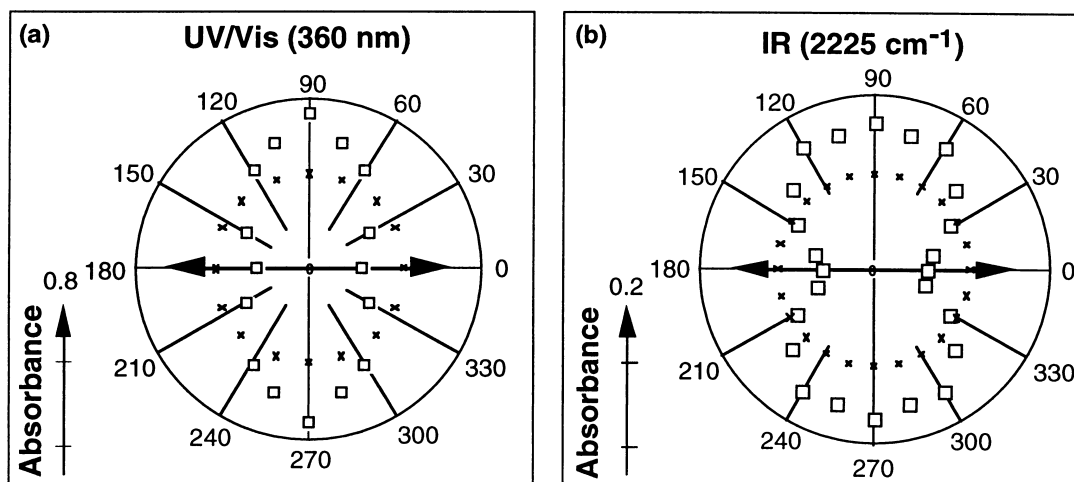
Fig. 2 Angular dependence of the UV absorbance at 360 nm (azobenzene moieties) and the IR absorbance at 2225 cm^{-1} (cyanobiphenyl mesogens) of a **MACB-AB6** film: ($\times$) in the initial state, ($\square$) after irradiation with 366-nm LPL (2.8 mW·cm^{-2}) at 95 °C for 30 min. The double-ended arrow indicates the polarization direction of the irradiation light.

Effect of intensity of irradiation light

A study on the effect of light intensity on alignment behavior indicated that not only the level of the induced anisotropy increased with increase of the intensity of irradiation light, but also the time required to achieve the saturated anisotropy was different at different intensity [11,12]. Figure 3 shows the induced order parameters of azobenzene and cyanobiphenyl moieties at various intensities of the irradiation light. High order parameters (0.45) of the azobenzene and cyanobiphenyl mesogens were generated on irradiation of LPL at 2.8 mW·cm^{-2}. Alignment change was induced even at the intensity of 0.7 mW·cm^{-2}. It is interesting that small anisotropy of the azobenzene moieties was induced at the intensity of 0.3 mW·cm^{-2}, while no macroscopic anisotropy of the inert mesogens was induced.
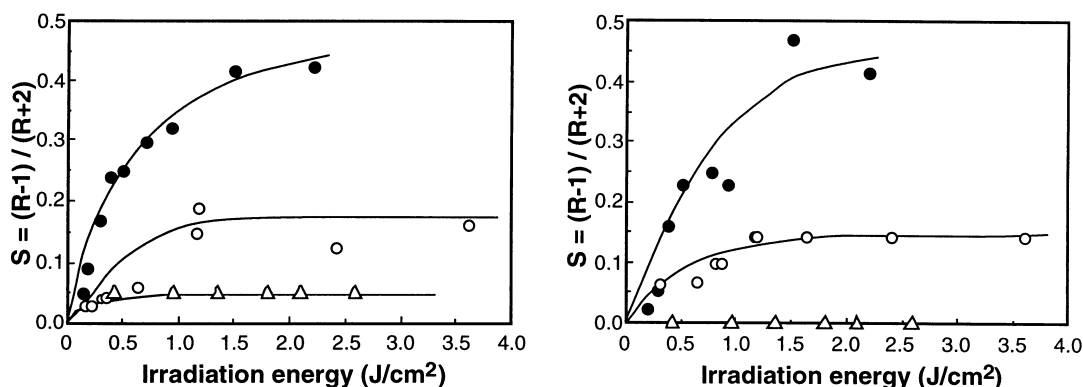

Fig. 3 Order parameters of azobenzene (left) and cyanobiphenyl (right) moieties as a function of the irradiation energy at 95 °C at various intensities of irradiation light (366 nm). ($\triangle$) 0.3 mW·cm^{-2}; ($\bigcirc$) 0.7 mW·cm^{-2}; ($\bullet$) 2.8 mW·cm^{-2}.

Effect of spacer length of azobenzene unit

Spacer length not only directly influences the mobility of the side chain but also usually affects the stability of mesophase which has effect on the mobility of mesogens as well. To avoid the effect of stability of mesophase, three PLCs with nearly the same enthalpic stability but different spacer length of azobenzene unit were designed. Experiments showed that alignment change in the PLC **MACB-AB3** possessing a short spacer was more difficult to be generated [13]. When the spacer length is long enough, such as six methylene units, the increase of the spacer length did not affect the alignment efficiency any more. It was found that the spacer length showed no effect on the *trans-cis-trans* isomerization

behavior of the azobenzene moieties. We considered the reason as the restriction of polymer main chain through spacer on the mobility of azobenzene moieties. The rate $(1.1 \times 10^{-3}\,\mathrm{s}^{-1})$ for alignment change, which was defined as the reciprocal of the required time to achieve 90% value of the saturated transmittance, was in the same order of magnitude as that of the *cis-trans* isomerization $(8.5 \times 10^{-3}\,\mathrm{s}^{-1})$. Therefore, the step of *cis-trans* isomerization may dominate, or at least has a significant effect on, the alignment process. The *cis*-azobenzenes produced by LPL isomerize to the *trans* form through two processes (the rate constants are defined as k_2 and k_3), as illustrated in Fig. 4. The restriction of polymer backbone may increase k_3 and decrease k_2; therefore, decrease the alignment efficiency. It should be noted that this kind of effect may not be obvious in the PLCs containing donor-acceptor type azobenzene moieties, because (i) the *cis-trans* thermal isomerization takes place quickly, and (ii) the *cis-trans* isomerization may be activated by light.
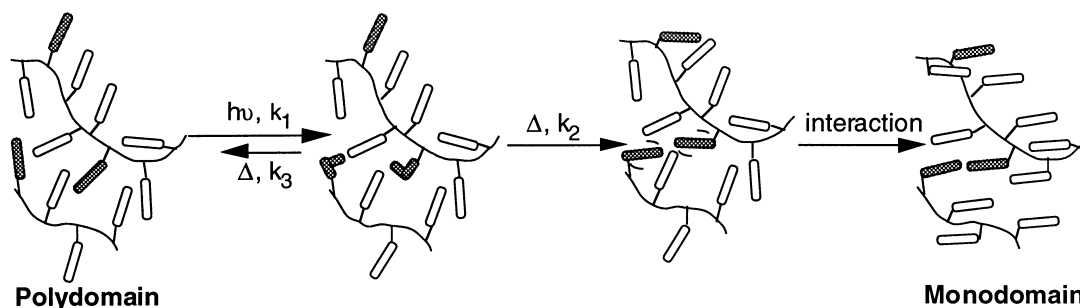

Fig. 4 Schematic representation of the mechanism of photoinduced alignment in polymer liquid crystals. k_1, rate constant of *trans-cis* photoisomerization; k_2 and k_3, rate constants of *cis-trans* thermal back-isomerization.

Effect of structure of azobenzene moieties

To investigate the effect of structure of photochromic moieties, a series of PLCs containing different azobenzene units in the side chain were synthesized (Fig. 5). With increase of the strength of donor and acceptor at 4 and $4'$ positions of the azobenzene groups, the possibility of an alignment change in the PLCs having the same methacrylic backbone decreased, although the *cis-trans* isomerization rate increased [14]. For example, compared with **MACB-AB6**, alignment change with lower efficiency was induced in **MACB-CNAB6**, and no alignment change was generated in **MACB-NAB6** and **MACB-ABA6**. The reasons were considered as the slightly increased enthalpic stability of the mesophase and the significantly decreased concentration of the *cis*-azobenzene.
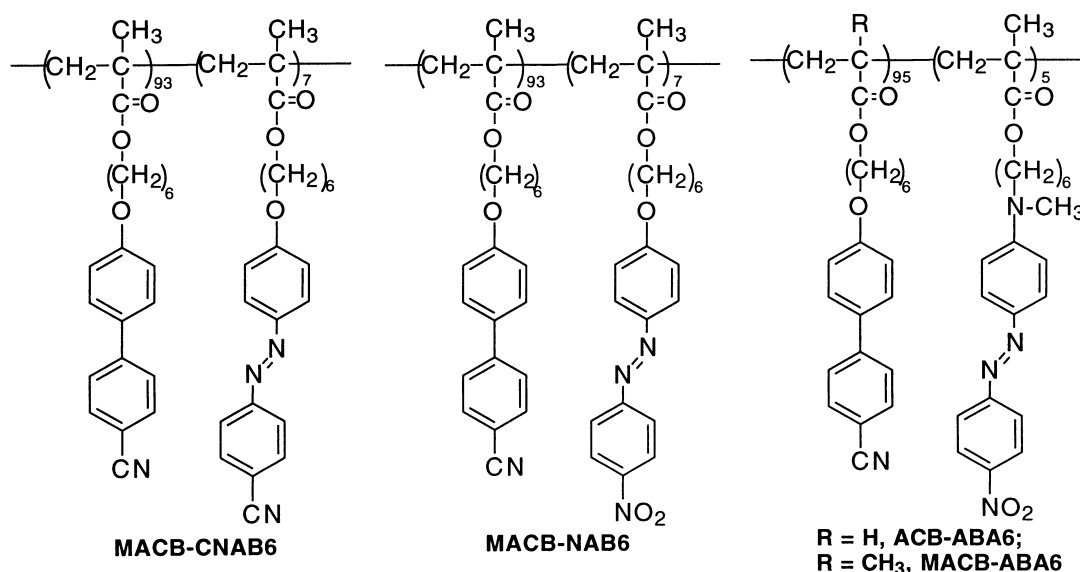

Fig. 5 Chemical structures of the polymer liquid crystals containing different azobenzene moieties.

Enhancement of the response

The response was improved by two methods [14,15]. First, the writing rate was remarkably increased through chemically tailoring structure of the PLC. By using the knowledge mentioned above, a PLC **ACB-ABA6** was designed, which contained a strong donor-acceptor type azobenzene group and exhibited low enthalpic stability of the mesophase. As shown in Fig. 6 (left), alignment change was induced within 90 s at 90 °C under steady-state irradiation. The other method to improve the response is modification of the alignment procedure (Fig. 6, right). Before exposed to LPL at 436 nm, the polydomain film was irradiated with unpolarized light at 366 nm to generate isotropic film. Large anisotropy with relatively high writing rate was observed in the photochemically decoupled film (curve a). The enhancement of the response was ascribed to the improvement of the mobility of the mesogens for alignment change due to the low stability of mesophase (former) or the isotropic state (latter). Moreover, the rate of *cis-trans* isomerization was increased as well.
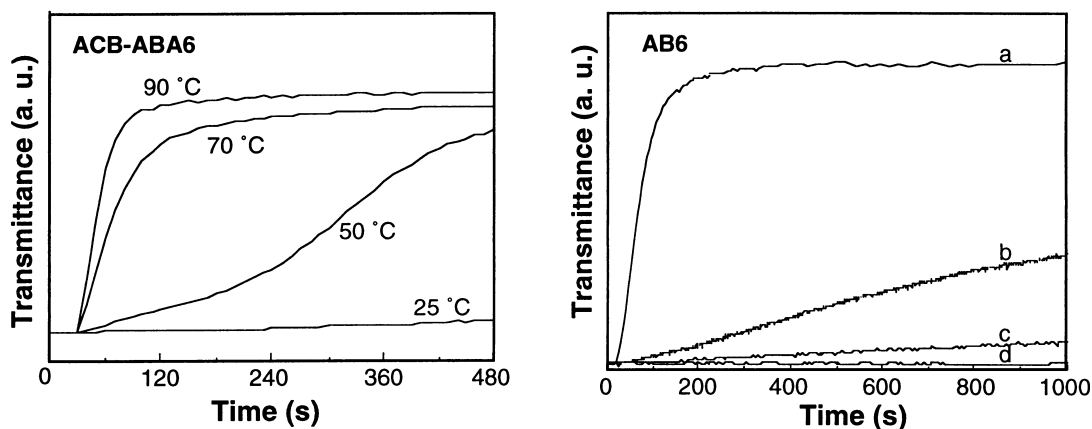

Fig. 6 Change in transmittance through crossed polarizers with a polymer film between them as a function of irradiation time. Left, **ACB-ABA6**. Films were exposed to LPL at the wavelength longer than 400 nm (intensity, 2.4 mW·cm^{-2} at 436 nm). Right, **AB6**. Experiments were performed at room temperature by using different methods. (a), the film was exposed to LPL at 436 nm (10 mW·cm^{-2}) immediately after photochemically decoupling the initial order using 366-nm unpolarized light; (b), the film was exposed to LPL at 436 nm after quickly quenching from isotropic state to glass state; (c), polydomain film was exposed to LPL at 436 nm directly; (d), polydomain film was exposed to LPL at 366 nm (2.8 mW·cm^{-2}) directly.

Three-dimensional alignment with unpolarized light

The 3-D alignment change was directly observed with polarizing microscopy under the conoscopic mode [16]. Figure 7 shows the images which were taken at 5 months after the alignment change had been induced. The cross-point, which represents the optic axis of the liquid-crystalline phase, appeared on irradiation, and changed position according to the incident angle of the irradiation light. These results indicate not only that alignment change was generated in the polymer film by use of the unpolarized light but also that the alignment direction was controlled by the propagation direction of the irradiation. The azobenzene moieties were well aligned in the propagation direction of the irradiation light. A study on a liquid-crystalline copolymer revealed that inert mesogens underwent 3-D reorientation together with the azobenzene moieties efficiently [17]. These results were supported by spectroscopic investigations. Induced anisotropy was large, stable and reversible. This may not only decrease the cost of energy but also provide a new system for high-density data storage with information being stored as changes in the orientation direction of the mesogens.

CONCLUSIONS

Large anisotropy was generated in initially unoriented PLC films on irradiation of LPL at relatively low intensity, although the contents of azobenzene units were only 6 mol%. The details in 2-D alignment behavior were explored from various points of view. The alignment efficiency depended on many factors,
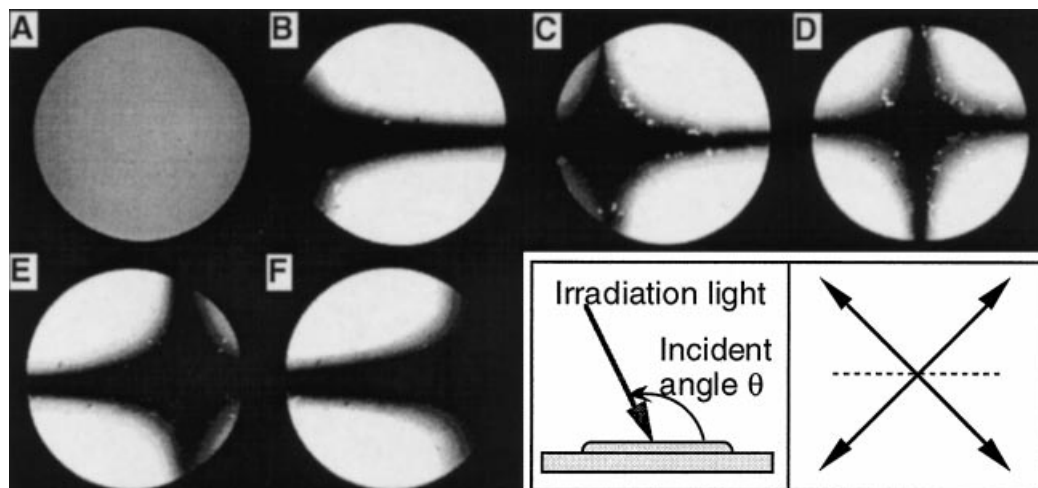
Fig. 7 Conoscopic observation of the alignment change in an **AB6** film as a function of the incident angle. The polarization directions of the polarizers (double-ended arrows) was 45° with respect to the projection of irradiation light (dash line). (A) Before irradiation (polydomain state). (B–F) After irradiation with 436 nm unpolarized light at room temperature (10 min) at the incident angle of 30° (B), 60° (C), 90° (D), 120° (E), and 150° (F).

such as sample temperature, light intensity, spacer length, stability of the mesophase, concentration of the *cis*-azobenzene, and so on. By optimizing these conditions, it is anticipated that the azobenzene-containing PLCs could be developed as materials for photonic applications. A relatively new result is that 3-D alignment of the PLCs was achieved on irradiation of unpolarized light. This may open a promising way for optical storage.

REFERENCES

1   G. S. Kumar, D. C. Neckers. *Chem. Rev.* **89**, 1915 (1989).

2   S. Xie, A. Natansohn, P. Rochon. *Chem. Mater.* **5**, 403 (1993).

3   T. Todorov, N. Tomova, L. Nikolova. *Opt. Commun.* **47**, 123 (1983).

4   M. Eich, J. H. Wendorff, B. Reck, H. Ringsdorf. *Makromol. Chem., Rapid Commun.* **8**, 59 (1987).

5   U. Wiesner, N. Reynolds, C. Boeffel, H. W. Spiess. *Liq. Cryst.* **11**, 251 (1992).

6   T. Fischer, L. Läsker, S. Czapla, J. Rübner, J. Stumpe. *Mol. Cryst. Liq. Cryst.* **298**, 213 (1997).

7   P. Rochon, J. Gosselin, A. Natansohn, S. Xie. *Appl. Phys. Lett.* **60**, 4 (1992).

8   K. Ichimura, S. Morino, H. Akiyama. *Appl. Phys. Lett.* **73**, 921 (1998).

9   M. Schönhoff, M. Mertesdorf, M. Lösche. *J. Phys. Chem.* **100**, 7558 (1996).

10   T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara, S. Tazuke. *Macromolecules* **23**, 42 (1990).

11   Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda. *Macromolecules* **31**, 349 (1998).

12   Y. Wu, A. Kanazawa, T. Shiono, T. Ikeda, Q. Zhang. *Polymer* **40**, 4787 (1999).

13   Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda. *Macromolecules* **31**, 1104 (1998).

14   Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda. *Macromolecules* **31**, 4457 (1998).

15   Y. Wu, Q. Zhang, A. Kanazawa, T. Shiono, T. Ikeda, Y. Nagase. *Macromolecules* **32**, 3951 (1999).

16   Y. Wu, T. Ikeda, Q. Zhang. *Adv. Mater.* **11**, 300 (1999).

17   Y. Wu, J. Mamiya, A. Kanazawa, T. Shiono, T. Ikeda, Q. Zhang. *Macromolecules* **32**, 8829 (1999).