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HOLOGRAPHIC IMAGE STORAGE IN POLYMER AZOBENZENE LIQUID CRYSTALS

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Unique characteristics were observed in phase-type gratings which were formed in polymer liquid crystal (PLC) films. We have investigated the formation and the properties of the holographic gratings recorded in PLCs with azobenzene moieties (photoresponsive unit). Two types of PLCs were examined: homopolymers of azobenzene monomers (PALC) and copolymers with a tolane moiety (mesogenic unit with a high birefringence) in the side chain. The diffraction efficiency (η) was enhanced in the LC phase. We obtained the value of η of 31% while it was less than 1% in a glassy state in the Raman-Nath regime. This difference may be due to the modulation of refractive index (Δn) based on alignment change of mesogens in the PLC film. In addition, we attempted the holographic image storage of three-dimensional (3-D) objects in the PLC film. The 3-D object was reconstructed with high resolution (>5,000 lines/mm).

Keywords: holographic image storage; photoinduced refractive-index modulation; azobenzene; polymer liquid crystals

INTRODUCTION

Recently, intensive research activities have been directed towards development of materials for holography due to scientific and industrial interest. Holography is expected to be a promising candidate for storage of high-density information as well as recording of three-dimensional (3-D) objects. In recording phase-type holograms, light-induced large modulations either in surface structure or in refractive index are necessary to acquire high efficiency.

Liquid crystals (LCs) are typical self-organizing materials with unique and excellent properties such as 1) self-organizing nature at certain temperature range with fluidity, 2) cooperative effect, 3) large optical anisotropy, and 4) alignment change by external field. Owing to these excellent properties, LC materials are expected to be used not only in LC

displays but also in various photonic applications. Especially, the large optical anisotropy is favorable for fabrication of phase-type gratings with high efficiency. In fact, Wendorff *et al.* demonstrated holographic data storage in polymer liquid crystals (PLCs) with side-chain azobenzene moieties in 1987. It was reported that the formation of phase-type gratings based on difference in the refractive index between *trans*-azobenzene and *cis*-azobenzene could be achieved in PLCs with azobenzene moiety [1].

The holographic data storage process has been extensively studied using functionalized polymers with side-chain azobenzene groups [2–12]. All the polymers reported had high glass transition temperature, and stored information was fairly stable at room temperature. This feature is favorable to apply polymers to recording materials. In these studies, however, effects of photoinduced refractive-index modulation (Δn) have not been fully discussed because the modulation was very small. As mentioned above, LC is a supramolecular assembly and shows various unique characteristics. In this paper, we report holographic data storage in PLCs with an azobenzene moiety. It was expected that additional properties which could not be observed in the conventional surface-relief gratings would emerge in this study: Δn might become an important factor.

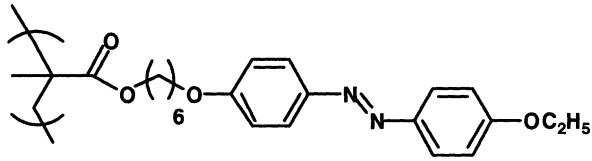
EXPERIMENTAL

Materials

Figure 1 shows the structure, molecular weight and thermodynamic property of PLCs with azobenzene moieties as well as their abbreviation used in this study. These polymers were prepared using a procedure similar to the literature [13,14]. Sample films were prepared by casting a THF solution of the polymer onto a glass substrate which had been coated with an alignment layer and rubbed to align mesogens. Homogeneously aligned films were obtained after annealing. Thickness of the sample films were measured as about $500 \sim 1600$ nm with a profile measurement microscope.

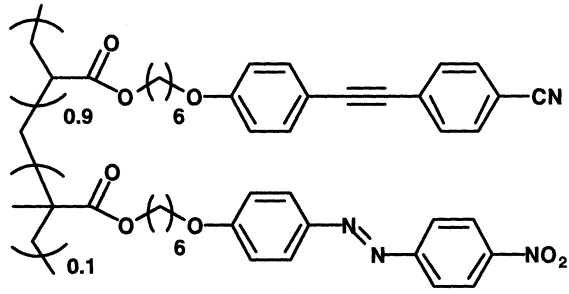
Formation of Holographic Gratings

Formation of grating in the PLCs was performed by a following procedure Figure 2 (A). In this study, two beams from an Ar^+ laser at 488 nm were used as writing beams. The incident angle of the writing beams was fixed at $\theta = 7.$ (fringe spacing (Λ): 2 μm). Diffraction efficiency (η) was defined as the ratio of the intensity of the first-order diffraction beam (He-Ne laser



PM6AB2

Mn = 18,000 G 68 N 150 I



T-AB

Mn = 9,000 G 33 N 95 I

FIGURE 1 Chemical structures and properties of PLCs used in this study. Mn, number-average molecular weight; G, glass; N, nematic; I, isotropic phase.

at 633 nm) to that of the transmitted beam through the film in the absence of the writing beams. Photoinduced refractive-index modulation of PLCs was investigated as follows Figure 2 (B). The sample film placed in a thermostated block was irradiated with light from an Ar^+ laser. Intensity of the probe light from a He-Ne laser transmitted through a pair of crossed polarizers, with the sample film between them, was measured with a photodiode.

Atomic Force Microscope (AFM) Measurements

After grating formation, the surface structure of the PLC films was investigated with an AFM (Shimadzu, SPM-9500 J2). Photoirradiation was performed at different temperatures. After grating was recorded in an N phase and those in a glassy state, the films were cooled to room temperature, and then observation of the films was carried out at room temperature.

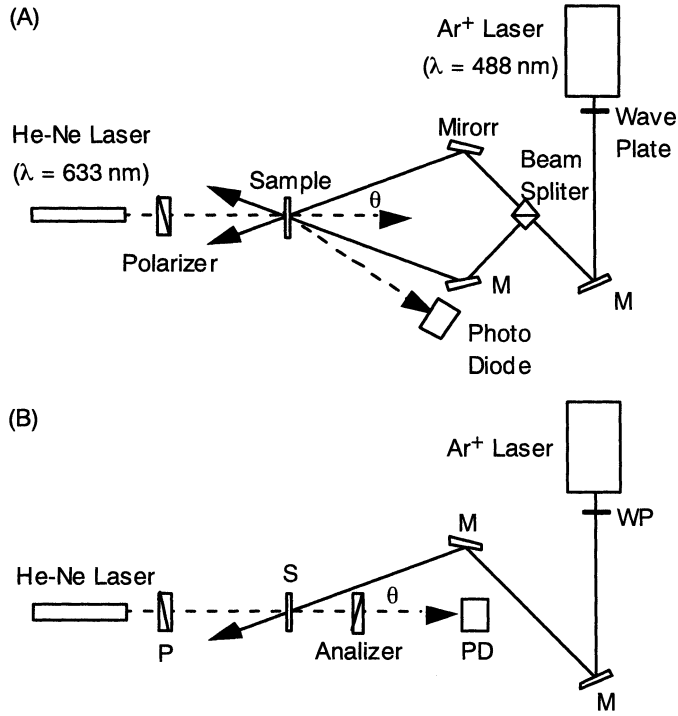


FIGURE 2 Optical setup for grating formation (A) and photoinduced refractive-index modulation (B) in the PLCs film.

RESULTS AND DISCUSSION

Dynamics of the First-Order Diffraction Beam

Figure 3 shows typical profiles of the first-order diffraction efficiency as a function of time at various temperatures (line (A)) in the **PM6AB2** films. The experiments were performed at $\theta = 7°$, corresponding to $\Lambda = 2\,\mu m$. Total power density of the writing beams was $120\,mW/cm^2$. The diffraction beams were immediately observed when the writing beams were turned on. Dynamics of the diffraction beam was much influenced by temperature. The response time of the diffraction beam became shorter as temperature increased. η reached to its maximum value within several tens seconds at these temperatures. This is much faster response than those previously reported [9–11]. In the previous studies, very long-time exposure, at least several hundreds seconds or several minutes, was necessary for the grating formation because large surface modulations must be induced. Faster

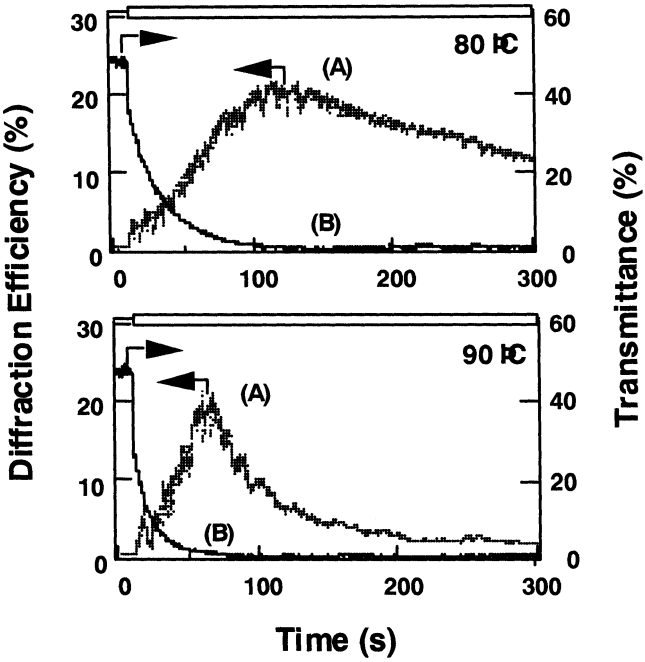


FIGURE 3 Typical profiles of the first-order diffraction efficiency (A) and the transmittance (B) as a function of time at various temperatures.

response is favorable for development of high-sensitivity materials and dynamic holography.

Figure 3 also shows the change in intensity of the probe light transmitted through crossed polarizers on irradiation of the pumping light at various temperatures (line (B)). On exposure to the beam, the transmittance immediately decreased. It was caused by the photochemical N to I phase transition of **PM6AB2** due to *trans-cis* photoisomerization of the azobenzene moiety [15]. This phase transition was also influenced by temperature. It was found that the time necessary to obtain the highest value of η almost coincided with the time required for the photochemical N to I phase transition at each temperature. We speculated that the I phase was induced photochemically in the bright areas of the interference pattern. It is assumed that this large-scale change in the molecular alignment is associated with the grating formation and the enhancement of η.

Effect of Polarization of Reading Beam on Diffraction Efficiency

Todorov *et al.* explored the η and its dependence on polarization of the reading beam for gratings produced in poly(vinyl alcohol) doped with

methyl orange [16]. They reported that the efficiency depends strongly on the polarization of the reading beam. We can expect that the same anisotropy would be obtained in the present system. Figure 4 shows the experimental configuration used for evaluation of the anisotropy. The linearly polarized reading beam is incident on the sample at normal, and the polarization direction of the beam has an angle to the horizontal axis. In Figure 4, symbols i) and ii) denote rubbing directions. In the rubbing direction i), a relation of $\alpha = 90$ and 270° means that the polarization direction is parallel to the rubbing direction, and also parallel to the grooves. On the other hand, the polarization is perpendicular to the rubbing direction at $\alpha = 0$, 180 and 360°. Figure 4 i) shows experimental results obtained for this rubbing direction. It is clearly seen that the diffraction efficiency showed strong anisotropy with respect to the polarization direction of the reading beam. η showed the maximum value at $\alpha = 90$ and 270°, and the minimum value at $\alpha = 0$, 180 and 360°. Such anisotropy has not been reported in the study of surface-relief gratings. Therefore, we can conclude that this is caused by the spatial modulation of the molecular alignment. Even though the relief structure was formed on the film, the grating would be also made up by alternate arrangement of the N and the I

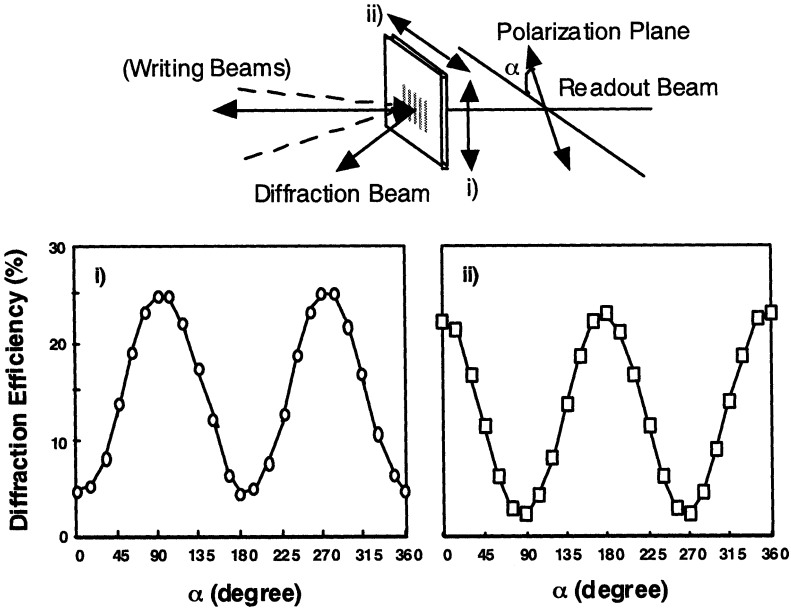


FIGURE 4 Experimental configuration for evaluation of the anisotropy in the η and experimental results obtained for rubbing direction i) and ii).

phases. As shown in Figure 4, two phases may be present periodically under the relief structure.

The diffraction of the linearly polarized reading beam occurs on the basis of Δn as well as the surface modulation. It is well known that general LCs show the following relationship,

$$n_e > n > n_o$$

and Δn can be expressed as

$$| n_e - n | > | n_o - n |, \quad (1)$$

where n_e and n_o are the refractive index of LCs for an extraordinary ray and an ordinary ray, respectively, and n is the index of an I phase. Taking the relationship of Eq. (1) into consideration, it is expected that the value of η is larger with $|n_e - n|$ than with $|n_o - n|$ in Eq. (1). In Figure 4 i), the reading beam was diffracted on the basis of $\Delta n = |n_e - n|$ at $\alpha = 90$ and 270°, and in terms of $\Delta n = |n_o - n|$ at $\alpha = 0$, 180 and 360°. Actually, larger values were obtained at $\Delta n = |n_e - n|$. This result obviously indicates that the N phase is preserved in the dark areas. Recently, similar results were reported by Simoni and co-workers in dye-doped polymer-dispersed LCs [17]. They speculated that this anisotropy would originate from photo-alignment of LC droplets containing dye molecules in the bright areas. They also showed the plausible grating structure comprising of ordered and disordered alignment.

Effect of the Birefringence of LCs on Grating Formation

Natansohn *et al.*, Tripathy *et al.* and others explored the mechanism of surface relief gratings (SRGs) on azopolymer films [8–12]. The behavior of the grating formation differs according to the polarization configuration of the writing beams. Two s-polarized ($\mathbf{s} + \mathbf{s}$) configuration produces a very small surface modulation, nearly negligible (<few nm), and shows the smallest value of η (<0.1%) due to SRG in the Raman-Nath regime (theoretical maximum value of η: 33.9%). In this study, we explored the surface modulation of the **T-AB** films under the ($\mathbf{s} + \mathbf{s}$) configuration to discuss an origin of Δn in the formation of grating. Detail of the surface modulation is shown in Figure 5. A periodic structure of the surface relief was about 2 μm wide in each case while its height was about 12 nm (60°C) and 7 nm (25°C), respectively. In an N phase, the value of η was 31% while it was less than 1% in a glassy state under this experimental condition.

This difference may arise from the Δn due to the photoinduced alignment change of mesogens in the PLC film. Figure 6 shows the change in transmittance upon photoirradiation at different temperatures. The transmittance little changed at 25°C, while it gradually decreased and finally

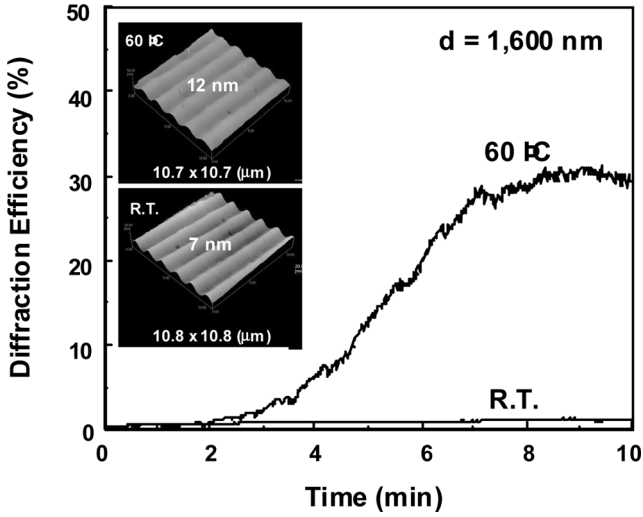


FIGURE 5 Change in the intensity of diffracted light and AFM 3-D views of the gratings recorded in an N phase (60°C) and a glassy state (R.T.) in the **T-AB** film, upon photoirradiation. Film thickness, 1,600 nm; light intensity, 80 mW/cm^2.

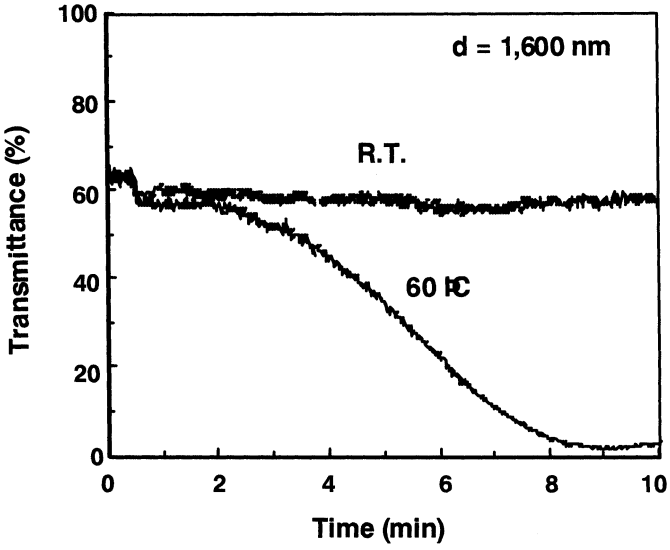


FIGURE 6 Change in the transmittance of probe light in the **T-AB** film in an N phase (60°C) and a glassy state (R.T.) in the **T-AB** film upon photoirradiation. Film thickness, 1,600 nm; light intensity, 80 mW/cm^2.

reached zero at 60°C. This means that the birefringence disappeared and a large value of Δn, which is necessary to obtain a high value of η, was induced in the N phase (60°C) upon photoirradiation. This result indicates that high value of η can be achieved with a slight change in alignment of mesogens when PLCs with high birefringence are used. In any event, the ratio of the height of the relief to the film thickness was very small (less than 1.0%), and the contribution of SRG to the Δn was negligible in the PLCs film.

Holographic Image Storage

Based on these results, we attempted holographic image storage of three-dimensional (3-D) objects in the **T-AB** film with a reflection-type optical setup. The optical setup used is shown in Figure 7 (A). We employed a coin as an object. The intensity of the writing beams was 100 mW/cm^2. Figure 7 (B) also shows the reconstructed image. The fringe spacing (Λ) for the reflection grating is given by the following equation:

$$\Lambda = \lambda/2n\sin(\theta'/2), \tag{2}$$

where λ is the wavelength of writing beams, n is the average refractive index of the sample, θ' is the angle between a object beam and a reference beam. In the present study, $\lambda = 488$, $n = 1.6$, $\theta' = 160$ then the fringe

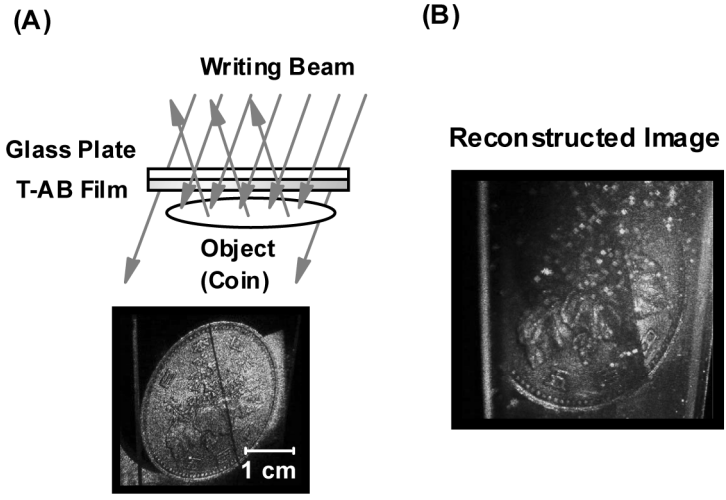


FIGURE 7 Optical setup for holographic image storage of the 3-D object (A) and reconstructed image from the hologram stored in the **T-AB** film (B). Reconstruction of the hologram was conducted with the same setup without the original object.

spacing is about 160 nm. It is evident that the object was reconstructed with high resolution (>5,000 lines/mm) in the **T-AB** film. In reflection holograms, the SRG was not observed by polarizing microscopy and AFM measurements. The recording and erasure of images were reversible by the control of temperature. The stored image remained unchanged after 2 years when the films were kept at room temperature.

CONCLUSION

We explored the formation of phase-type gratings in the PLCs films. Large enhancement in the η and the faster response were observed in the N phase. It is considered that these results are attributed to the spatial modulation of the refractive index. The grating formation resulted from the photochemical N to I phase transition. Strong anisotropy was observed in the η with respect to polarization of the reading beam. This indicates that the Δn, which resulted from the periodic induction of the photochemical phase transition, would mainly contribute to the grating formation. It was found that the grating formation is also strongly affected by the structure of the mesogenic unit. The effect of birefringence of PLCs on the formation of gratings indicates that considerable enhancement of η can be achieved by using PLC with a tolane moiety. Furthermore, η and Δn showed the largest values of 31% and 0.08, respectively, in the $(\mathbf{s}+\mathbf{s})$ polarization configuration. These values are equal to or larger than those observed under other polarization conditions. In addition, we could perform the holographic 3-D image storage. We believe that these results will contribute to development of various holographic applications such as optical data storage.

REFERENCES

[1] Eich, M., Wendorff, J. H., Reck, B., & Ringsdorf, H. (1987). *Makromol. Chem., Rapid. Commun.*, *8*, 59. Eich, M. & Wendorff, J. H. (1987). *Makromol. Chem., Rapid. Commun.*, *8*, 467. Eich, M. & Wendorff, J. H. (1990). *J. Opt. Soc. Am. B*, *7*, 1428. Anderle, K. & Wendorff, J. H. (1994). *Mol. Cryst. Liq. Cryst.*, *243*, 51.

[2] Hvilsted, S., Andruzzi, F., Kulinna, C., Siesler, H. W., & Ramanujam, P. S. (1995). *Macromolecules*, *28*, 2172.

[3] Andruzzi, F., Altomare, A., Ciardelli, F., Solaro, R., Hvilsted, S. & Ramanujam, P. S. (1999). *Macromolecules*, *32*, 448.

[4] Hasegawa, M., Yamamoto, T., Kanazawa, A., Shiono, T., & Ikeda, T. (1999). *Chem. Mater.*, *11*, 2745. Hasegawa, M., Yamamoto, T., Kanazawa, A., Shiono, T., & Ikeda, T. (1999). *J. Mater. Chem.*, *9*, 2765.

[5] Yamamoto, T., Hasegawa, M., Kanazawa, A., Shiono, T., & Ikeda, T. (1999). *J. Phys. Chem. B*, *103*, 9873. Yamamoto, T., Hasegawa, M., Kanazawa, A., Shiono, T., & Ikeda, T. (2000). *J. Mater. Chem.*, *10*, 337.

[6] Berg, R. H., Hvilsted, S., & Ramanujam, P. S. (1996). *Nature*, *383*, 505.

[7] Rasmussen, P. H., Ramanujam, P. S., Hvilsted, S., & Berg, R. H. (1999). *J. Am. Chem. Soc.*, *121*, 4738.
[8] Rochon, P., Batalla, E., & Natansohn, A. (1995). *Appl. Phys. Lett.*, *66*, 136.
[9] Barrett, C. J., Natansohn, A., & Rochon, P. (1996). *J. Phys. Chem.*, *100*, 8836.
[10] Lagugne, L. F., Rochon, P., & Natansohn, A. (1999). *Appl. Phys. Lett.*, *75*, 1377. Lagugne, L. F., Buffeteau, T., & Sourisseau, C. (1999). *J. Phys. Chem. B*, *103*, 6690.
[11] Kim, D. Y., Tripathy, S. K., & Kumar, J. (1995). *Appl. Phys. Lett.*, *66*, 1166. Kim, D. Y., Li, L., Jiang, X. L., Shivshankar, V., Kumar, J., & Tripathy, S. K. (1995). *Macromolecules*, *28*, 8835.
[12] Viswanathan, N. K., Balasubramanian, S., Li, L., Kumar, J., & Tripathy, S. K. (1998). *J. Phys. Chem. B*, *102*, 6064.
[13] Angeloni, A. S., Caretti, D., Carlini, C., Chiellni, G., Galli, G., Altomare, A., & Solaro, R. (1989). *Liq. Cryst.*, *4*, 513.
[14] Hall, H. K. Jr., Kuo, T., & Leslie, T. M. (1989). *Macromolecules*, *22*, 3525.
[15] Ikeda, T. & Tsutsumi, O. (1995). *Science*, *268*, 1873.
[16] Todorov, T., Nikolova, L. & Tomova, N. (1984). *Appl. Opt. 23*, 4588.
[17] Simoni, F., Francescangeli, O., Reznikov, Y., & Slussarenko, S. (1997). *Opt. Lett.*, *22*, 549.