

Photochemically Induced Birefringence in Polyurethanes Containing Donor–Acceptor Azobenzenes as Photoresponsive Moieties

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ABSTRACT: Three kinds of photoresponsive polyurethanes containing slightly different azobenzene moieties [i.e., disperse red 19 (DR19), 2-position-substituted DR19, and 2,2'-position-substituted DR19] were prepared, and their photoinduced birefringence behavior was examined. These polyurethanes showed nearly the same molecular weights, glass transition temperatures, viscosities, and absorption coefficients at the wavelength of the light used to induce the photoresponse. Irradiation of these polymer films with a linearly polarized Ar⁺ laser induced birefringence due to reorientation of the azobenzene moieties through multiple trans–cis–trans isomerization cycles. Despite the slight difference in the chemical structure of the azobenzene moiety, a large difference in the growth behavior of the

photoinduced birefringence was observed among these polymers. Because of the small differences in the characteristics of these polymers, we concluded that the isomerization behavior of the azobenzene moiety was the main factor for the results obtained in this study. In addition, the saturated value of the induced birefringence differed to a great extent among these polymers. It was suggested that such a phenomenon could be related to the reorientation behavior induced by the introduction of two methyl groups. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 17–22, 2002

Key words: amorphous; polyurethanes; donor–acceptor azobenzene moiety; isomerization; birefringence; alignment; azopolymers

INTRODUCTION

In recent years, polymers containing azobenzene groups have been attracting a great deal of attention because of their potential use in two- or three-dimensional optical data storage media and various other photonic applications.^{1–29} It has been known for more than a decade that linearly polarized light can induce a reorientation of the azobenzene groups in such polymers.^{1,2} The accepted mechanism for photoinduced birefringence involves the photochemical trans–cis isomerization, subsequent thermal and/or photochemical cis–trans back-isomerization, and angular redistribution connected by rotational diffusion resulting from thermally induced Brownian motion.^{24,25} By repetition of these trans–cis–trans isomerization cycles and the motion of the azobenzene moiety, the long molecular axis becomes aligned perpendicular to the electric field vector of the polarized actinic light. This process results in optical anisotropy induced by the orientation of the azobenzene groups. The resulting anisotropy can be removed by irradiation with a circularly polarized light or unpolarized light and then introduced again with lin-

early polarized light. Because of their unique properties, the polymers with azobenzene groups are expected to be the most attractive materials for reversible optical data storage media, and several azobenzene-containing polymeric systems have been proposed by various researchers.^{1–6,8,9,11,15–29}

Systematic studies of the optically induced birefringence for amorphous high glass transition temperature (T_g) polymers containing azobenzene moieties have been performed by Natansohn and coworkers.^{15–22} In their series of samples, a rapid and large change in the refractive index of the polymer film was induced on irradiation with linearly polarized light with the samples at a temperature below T_g . The polymers showed long-term stability in their optical anisotropy induced at room temperature. The birefringence behavior is expected to depend on several factors, such as the dipolar interaction of the azobenzenes,¹⁹ the packing structure of the azobenzene groups,²⁰ the light intensity,¹⁵ and the film thickness (d).¹⁷ To our knowledge, only a few articles have detailed the effect of the introduction of substituents to the azobenzene moieties in amorphous polymer systems.^{16,20–22} An evaluation of the photoinduced birefringence behavior following the introduction of substituents to chromophores is generally difficult because of changes in the ultraviolet–visible (UV–vis) absorption spectra and the absorption coefficient at

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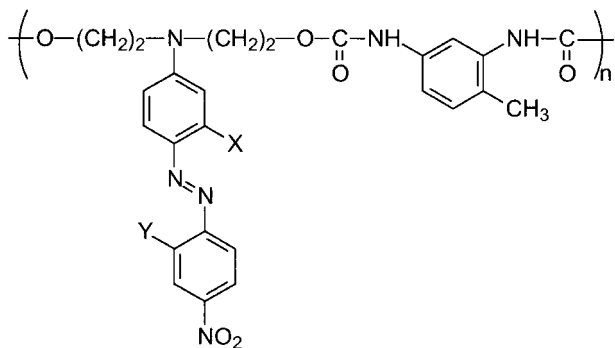


Figure 1 Chemical structures of the photoresponsive polyurethanes 1–3.

the wavelength of the irradiated light. Moreover, in a polymeric system, the molecular weight and T_g of the polymer would also be expected to have an influence.²⁸ In our previous work, we synthesized urethane–urea copolymers and polyurethanes containing several kinds of donor–acceptor-substituted azobenzenes, and we investigated their nonlinear optical, electro-optical, and polarization-multiplexed optical recording properties.^{30–33} However, the photochemically induced birefringence of photoresponsive polyurethanes has not been studied. Furthermore, our polyurethanes showed nearly the same UV–vis absorption spectra, absorption coefficients, molecular weights, and T_g 's. This article presents a comparison of the photochemically induced birefringence behaviors for three kinds of amorphous polyurethanes: a disperse red 19 (DR19)-containing polymer, a 2-position-substituted DR19-containing polymer, and a 2,2'-position-substituted DR19-containing polymer.

EXPERIMENTAL

Figure 1 shows the chemical structures of the photoresponsive polyurethanes 1–3 used in this study. The synthetic route of polymer 3 is described in our previous work,^{30,31} and the other polymers were prepared according to similar methods. The number-average molecular weights (M_n 's) and weight-average molecular weights (M_w 's) of the polymers were determined by gel permeation chromatography (GPC; Tosoh SC-8010; column, Shodex OhpakSB-G + SB-

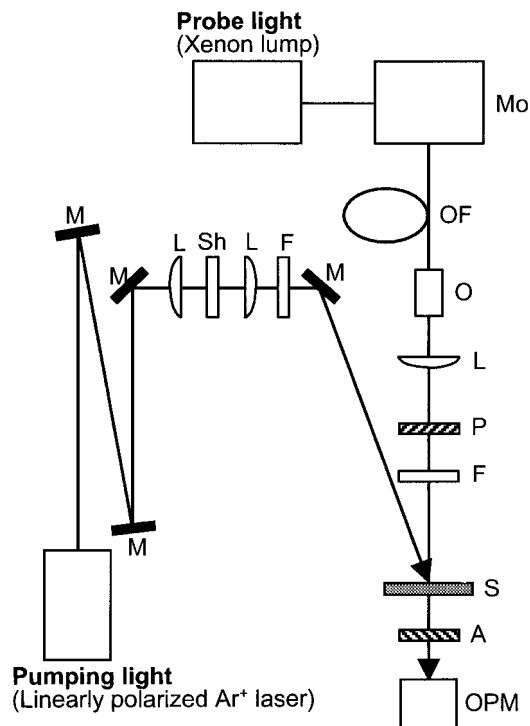


Figure 2 Schematic illustration of the experimental setup. M = mirror; F = filter; P = polarizer; A = analyzer; L = lens; Sh = shutter; OPM = optical power meter; S = sample; Mo = monochromator; OF = optical fiber; O = microscope objective.

806M HQ \times 2; eluent, *N,N'*-dimethylformamide) (Tokyo, Japan) calibrated with standard poly(ethylene glycol). T_g was determined by differential scanning calorimetry (DSC; PerkinElmer (Wellesley, MA) DSC-7 and TAC 7/DX thermal controller; heating rate, 10°C/min). The general properties of these polymers are summarized in Table I.

Sample films (\sim 0.2 μm thick) were prepared via spin coating from approximately 5 wt % pyridine solutions of each polymer. These solutions were passed through a 0.20- μm filter (Millipore, Bedford, MA) for the removal of particulate impurities before spin coating. Optically clear films were formed on glass substrates at a rotation speed of 2000 rpm, and these were placed in a vacuum oven at 120°C for over 24 h to obtain solvent-free samples.

TABLE I
Compositions, Molecular Weights, T_g 's, and Viscosities (η s) of Polyurethanes Used in This Study

Polymer	X	Y	M_n^a	M_w^a	M_w/M_n^a	T_g (°C) ^b	η (dL/g) ^c
1	H	H	4440	8137	1.83	128	0.11
2	H	CH ₃	3488	5585	1.60	120	0.10
3	CH ₃	CH ₃	3388	6239	1.84	124	0.09

^aDetermined by GPC with a poly(ethylene glycol)-calibrated column set.

^bDetermined from DSC measurements.

^cDetermined from η measurement with 1-methyl-2-pyrrolidone at 30°C.

Figure 2 shows the experimental setup used for the investigation of the photochemically induced birefringence behavior of the photoresponsive polyurethanes. The sample films were irradiated with an s-polarized Ar⁺ laser at 514.5 nm (American Laser Corp. (Fraser, MI), model 60c). Light from a xenon lamp, which was polarized at 45° with respect to the polarized direction of the writing light, was used as a probe light. Its wavelength was chosen to be 650 nm with a monochromator (Jasco SM-5, Tokyo, Japan). The induced alignment in the sample film was monitored by the measurement of the power of the light after an analyzer with a photodetector (Anritsu ML9001A and MA9411A, Tokyo, Japan), and the data were collected with a microcomputer. The birefringence (Δn) induced by the change in the alignment of the azobenzene moiety was estimated with the following equation:²

$$I/I_0 = \sin^2(\pi d \Delta n / \lambda) \quad (1)$$

where I is the transmitted light after the analyzer, I_0 is the intensity of the light passing through the pair of parallel polarizers, and λ represents the wavelength of the probe light.

RESULTS AND DISCUSSION

Before the investigation of the photochemically induced birefringence of polymers 1–3, we carried out UV–vis absorption spectral measurements on spin-coated films of these polymers (Fig. 3).

Polymers 1–3 exhibited maximum absorbances (λ_{\max} 's) at 460, 460, and 465 nm, respectively. The absorption bands around these λ_{\max} values could be assigned to the π – π^* transition of the azobenzene moieties, and it is well known that their positions are

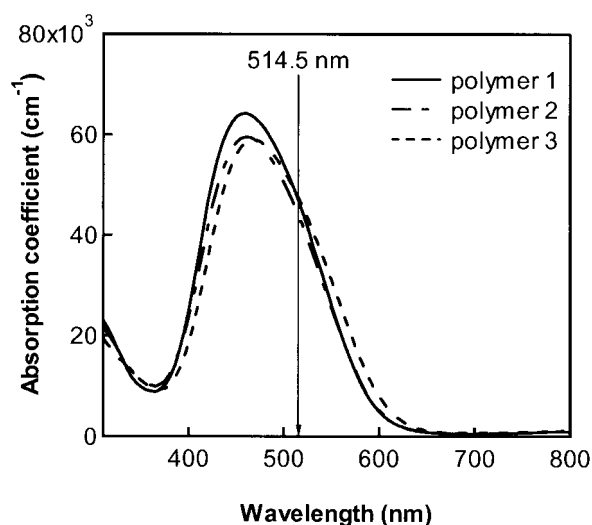


Figure 3 UV–vis absorption spectra of spin-coated films of polymers 1–3.

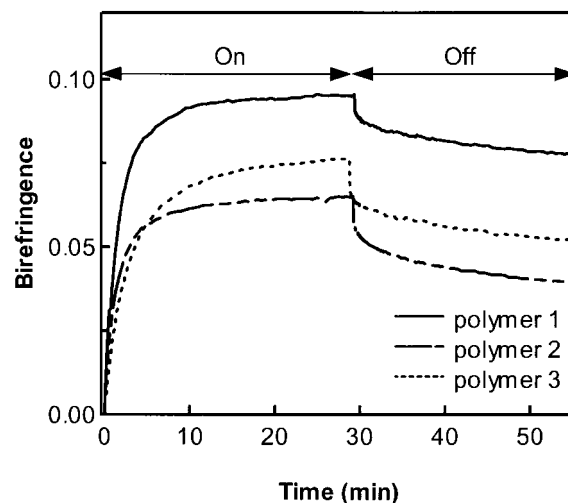


Figure 4 Typical behavior of the photochemically induced birefringence of polymers 1–3 at room temperature.

affected by the magnitude of the dipole of the chromophores.³⁴ In our series, no significant difference in λ_{\max} was observed, so it can be suggested that the introduction of methyl groups to 2- or 2,2'-positions of the azobenzene moieties scarcely affects the magnitude of their dipole moment. However, the absorption coefficient value at the wavelength of the irradiated light is an important factor with respect to the photochemically induced birefringence behavior because the efficiency of the photochemical isomerization of the photochromic molecules depends on the number of absorbed photons. We estimated the absorption coefficient value at 514.5 nm for polymers 1–3. The absorption coefficient showed nearly the same values: 5.73×10^4 , 5.35×10^4 , and 5.51×10^4 cm⁻¹, respectively. Consequently, the contribution from the absorption coefficient to the behavior of the photoinduced birefringence could be neglected in this study.

The photochemically induced birefringence behavior of the photoresponsive polyurethanes used in this study was explored at room temperature. Figure 4 shows the typical behavior of the photochemically induced birefringence with the pumping light turned on and off for polymers 1–3.

In polymer 1, before irradiation at 514.5 nm, no optical anisotropy was observed because of the homogeneously random alignment of the azobenzene moieties. The birefringence was induced immediately on photoirradiation at 514.5 nm (40 mW/cm²). This result was due to the change in the alignment of the azobenzene moieties resulting from their multiple trans–cis–trans isomerization cycles on photoirradiation. The photoinduced birefringence in amorphous polymers containing the azobenzene moiety is induced in two steps: the trans–cis isomerization of the azobenzene moieties due to photoselection excitation and the alignment of the azobenzene moieties through trans–cis–trans isomerization cycles (Fig. 5).

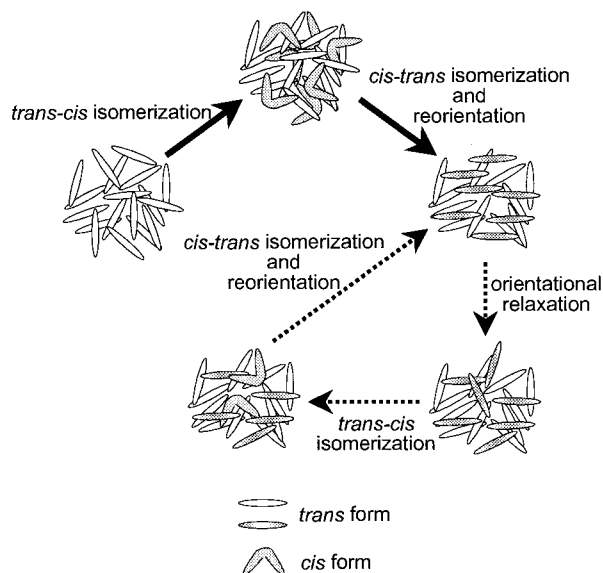


Figure 5 Schematic illustration for the mechanism of photochemically induced birefringence in an amorphous polymer.

In this sample, the saturated value of the induced birefringence was approximately 0.096, which is comparable to that achieved in the other amorphous polymer systems.^{15–22} The birefringence decreased gradually when photoirradiation was ceased. This was caused by a relaxation of the alignment of the azobenzene moieties. Moreover, the induced birefringence could be erased completely with heating above the T_g value of the polymers. It was confirmed that the UV-vis absorption spectra of the polymer films showed no angular dependence on the absorbance, and the absorbance recovered to the initial state before photoirradiation. Therefore, no degradation of the chromophore occurred under these experimental conditions. Similar behavior was also observed for polymers 2 and 3. The obtained saturated values of their birefringence (0.065 and 0.076, respectively), however, were smaller than that of polymer 1. Furthermore, it was confirmed that there are significant differences in the growth behaviors of the birefringence for these polymers.

At first, we evaluated the growth process of the birefringence in these polymers. We compared the slopes of the growth curves at time zero, which indicates the overall growth rate of the birefringence. As shown in Figure 4, the slope of polymer 1 is the highest, and polymer 3 shows the gentlest slope. This indicates that the introduction of a methyl group obstructs the growth of the birefringence. As mentioned previously, the growth process of the photoinduced birefringence is attributable to the change in the alignment through the multiple trans–cis–trans isomerization cycles of the azobenzene moiety. The polymers used in this study include the tertiary amine group of

the azobenzene moiety in their polymer backbones, so that cooperative motion between the azobenzene moiety and the polymer backbone will be required for the change in the alignment of the photochromic moiety. In polymers 1–3, however, M_n , M_w , T_g , and viscosity values, considered to be important factors in the dynamics of the polymer chain, are nearly the same. Therefore, the influence of the motion of the polymer backbones would be expected to make very little difference among these polymers. In this system, the main dissimilarity is the bulkiness of the close position of the azo group. The absorption coefficients of these polymers showed nearly the same values at the wavelength of 514.5 nm, as shown in Figure 2, which indicates the same absorption efficiency. Therefore, the difference in the efficiency of the trans–cis–trans isomerization cycle of the azobenzene moiety among the three polymers may be the main factor that accounts for the difference in the growth process of the birefringence. If the trans–cis–trans isomerization cycle of the azobenzene is performed efficiently, the change in alignment can be induced quickly, leading to a large growth rate of the birefringence. On the contrary, a lower efficiency of the isomerization cycle for the photochromic moieties would require more time for the induction of their reorientation, resulting in a smaller growth rate of the birefringence. Polymer 3 includes azobenzene moieties substituted on its 2- and 2'-positions by methyl groups. In the liquid phase, for which the introduction of the substituents to the azobenzene derivatives causes the no change in the shape of the absorption spectra, the isomerization behavior is not influenced by the introduction of the substituents.³⁴ However, in the condensed state, the introduction of such bulky substituents to the closely spaced positions to the azo group could inhibit the photochemical trans–cis isomerization and the cis–trans back-isomerization of the azobenzenes because the sweep volume of the photochromic moieties becomes large compared to the critical volume around them. In fact, there is a report in the literature that documents the reduction of the growth response of the optically induced birefringence due to the low efficiency of the isomerization cycle caused by the introduction of bulky substituents on the azobenzene moiety.¹⁶ Consequently, the small growth rate of the birefringence in polymer 3 is ascribed to a reduction of the efficiency of the trans–cis–trans isomerization cycle of the azobenzenes by the introduction of methyl groups to their 2- and 2'-positions.

We subsequently examined the importance of the saturated value of the birefringence on irradiation by linearly polarized light. As previously described, there is a large difference in the saturated values of the obtained birefringence in polymers 1–3. Similar results were reported by Natansohn et al.¹⁶ In their system, this phenomenon is apparently due to differences in

the effective refractive index that originate in the difference between the λ_{\max} and the wavelength of the probe light. However, the polymers used in this study exhibited nearly the same absorption coefficient and UV-vis absorption spectra; this suggests that there is little difference between their effective refractive indices. It is well known that azobenzene derivatives show an angular dependence of the absorbance because the $\pi-\pi^*$ transition moment is polarized along the long molecular axis.³⁵ When the azobenzene moieties align perpendicular to the electric field vector of the linearly polarized light, they hardly absorb the irradiated light. However, the orientational relaxation of these azobenzenes could, nevertheless, occur during photoirradiation, and it is suggested that the induction and relaxation of the alignment of the azobenzene moiety can take place simultaneously during the writing process. In such a situation, the birefringence could reach its saturated state when the amount of the azobenzene aligned per unit of time is equal to the amount of the azobenzene relaxed per unit of time, that is, an equilibrium state. Therefore, we suggest that the observed difference in the saturated values of the birefringence might be closely related to differences in the relaxation rate of the alignment of the azobenzene moieties. As mentioned previously, polymer **1** exhibited the largest saturated value in the birefringence among the three polymers. Therefore, we expect that the orientational relaxation rate of the azobenzene moiety will be the smallest. However, in polymer **2**, which showed the smallest saturated value of the birefringence, the largest rate of the orientational relaxation of the azobenzene moiety would be expected. To test our explanation, we performed an analysis of the dynamics of the decay process of the birefringence in polymers **1–3**. First, we compared the slope of the decay curve, which shows the decrease in the birefringence caused by thermal cis–trans isomerization and thermal rotational diffusion. An analysis of the slopes revealed that polymer **1** showed the slowest thermal decay and polymer **3** showed the fastest thermal decay. From the viewpoint of the thermal relaxation process, no explanation for the difference in the saturated value could be given. Only the behavior of isomerization under photoirradiation is expected to affect the saturated value. In the initial growth process of birefringence, polymer **2** showed a faster slope than polymer **3**. However, the slopes were reversed after about 5 min of irradiation. This indicates that the growth process is composed of more than two mechanisms. We considered again the effect of reorientation of the polymer backbone induced by the photoirradiation. Although the introduction of two methyl groups restrains the isomerization process, reducing the growth rate, the motion of the azobenzene moiety, including the two methyl groups, could easily induce the reorientation of the polymer backbone. As a result, polymer **3**

showed a higher saturated value of the birefringence than polymer **2**.

CONCLUSIONS

The photoinduced birefringence behavior of three types of photoresponsive polyurethanes containing slightly different and strong electron donor–acceptor azobenzene moieties was measured. These polyurethanes showed nearly the same M_n , M_w , T_g , and viscosity values. Moreover, the introduction of the methyl groups at the 2- or 2,2'-positions of the azobenzene moieties had little effect on the shape of their absorption spectra or on the absorption coefficient at the wavelength of irradiating light. For all the polymers, a birefringence could be induced on photoirradiation through the mechanism of multiple trans–cis–trans isomerization cycles. However, the growth process of the birefringence was different among the polymer samples. The polyurethane containing both ortho-position-substituted azobenzenes showed the slowest response. We believe this resulted from a lowering of the efficiency of the isomerization behavior of the azobenzene moiety resulting from a lack of critical volume. Furthermore, a large difference in the saturated value of the induced birefringence was observed in these polymers, and it was related to the reorientation behavior induced by the introduction of two methyl groups.

REFERENCES

1. Todorov, T.; Tomova, N.; Nikolova, L. *Opt Commun* 1983, 47, 123.
2. Todorov, T.; Nikolova, L.; Tomova, N. *Appl Opt* 1984, 23, 4309.
3. Gibbons, W. M.; Shannon, P. J.; Sun, S. T.; Swetlin, B. J. *Nature* 1991, 351, 49.
4. Fischer, T.; Läscher, L.; Stumpe, J.; Kostromin, S. *J Photochem Photobiol A* 1994, 80, 453.
5. (a) Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. *Makromol Chem Rapid Commun* 1987, 8, 59; (b) Eich, M.; Wendorff, J. H. *Makromol Chem Rapid Commun* 1987, 8, 457.
6. (a) Berg, R. H.; Hvilsted, S.; Ramanujam, P. S. *Nature* 1996, 383, 505; (b) Hvilsted, S.; Andruzzi, F.; Kulinna, C.; Siesler, H. W.; Ramanujam, P. S. *Macromolecules* 1995, 28, 2172; (c) Holme, N. C. R.; Ramanujam, P. S.; Hvilsted, S. *Opt Lett* 1996, 21, 902.
7. Andruzzi, L.; Altomare, A.; Ciardelli, F.; Solaro, R.; Hvilsted, S.; Ramanujam, P. S. *Macromolecules* 1999, 32, 448.
8. Zilker, S. J.; Bieringer, T.; Haarer, D.; Stein, R. S.; van Egmond, J. W.; Kostromine, S. G. *Adv Mater* 1998, 10, 855.
9. (a) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl Phys Lett* 1995, 66, 1166; (b) Kim, D. Y.; Li, L.; Jiang, X. L.; Shivshankar, V.; Kumar, J.; Tripathy, S. K. *Macromolecules* 1995, 28, 8835.
10. Ikeda, T.; Tsutsumi, O. *Science* 1995, 268, 1873.
11. (a) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* 1998, 31, 349; (b) Wu, Y.; Ikeda, T.; Zhang, Q. *Adv Mater* 1999, 11, 300.
12. (a) Hasegawa, M.; Yamamoto, T.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Adv Mater* 1999, 11, 675; (b) Yamamoto, T.; Hasegawa, M.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J Phys Chem B* 1999, 103, 9873.

13. Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl Phys Lett* 1986, 49, 248.
14. Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem Rev* 1994, 94, 31.
15. (a) Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. *Appl Phys Lett* 1992, 60, 4; (b) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* 1992, 25, 2268.
16. Natansohn, A.; Xie, S.; Rochon, P. *Macromolecules* 1992, 25, 5531.
17. Rochon, P.; Bissonnette, D.; Natansohn, A.; Xie, A. S. *Appl Opt* 1993, 32, 7277.
18. Natansohn, A.; Rochon, P.; Pérolet, M.; Audet, P.; Brown, D.; To, S. *Macromolecules* 1994, 27, 2580.
19. Brown, D.; Natansohn, A.; Rochon, P. *Macromolecules* 1995, 28, 6116.
20. Natansohn, A.; Rochon, P.; Ho, M. S.; Barrett, C. *Macromolecules* 1995, 28, 4179.
21. Ho, M. S.; Natansohn, A.; Rochon, P. *Macromolecules* 1995, 28, 6124.
22. Ho, M. S.; Natansohn, A.; Barrett, C.; Rochon, P. *Can J Chem* 1995, 73, 1773.
23. (a) Rochon, P.; Batalla, E.; Natansohn, A. *Appl Phys Lett* 1995, 66, 136; (b) Barrett, C.; Natansohn, A.; Rochon, P. *J Phys Chem* 1996, 100, 8836.
24. Sekkat, Z.; Dumont, M. *Synth Met* 1993, 54, 373.
25. Sekkat, Z.; Wood, J.; Knoll, W. *J Phys Chem* 1995, 99, 17226.
26. Sekkat, Z.; Dumont, M. *Mol Cryst Liq Cryst Technol Sect B* 1992, 2, 359.
27. Osman, A. E.; Dumont, M. *Proc SPIE* 1998, 3417, 36.
28. Blanche, P.-A.; Lemaire, P. C.; Maertens, C.; Dubois, P.; Jérôme, R. *J Opt Soc Am B* 2000, 17, 729.
29. Blanche, P.-A.; Lemaire, P. C.; Dumont, M.; Fischer, M. *Opt Lett* 1999, 24, 1349.
30. Tsuchimori, M.; Watanabe, O.; Ogata, S.; Okada, A. *Jpn J Appl Phys Part 1* 1997, 36, 5518.
31. Watanabe, O.; Tsuchimori, M.; Okada, A. *Polym Adv Technol* 1999, 10, 459.
32. (a) Watanabe, O.; Tsuchimori, M.; Okada, A.; Ito, H. *Jpn J Appl Phys Part 1* 1998, 37, 5588; (b) Tsuchimori, M.; Watanabe, O.; Ogata, S.; Okada, A. *Jpn J Appl Phys Part 2* 1996, 35, 444.
33. Alasfar, S.; Ishikawa, M.; Kawata, Y.; Egami, C.; Sugihara, O.; Okamoto, N.; Tsuchimori, M.; Watanabe, O. *Appl Opt* 1999, 38, 6201.
34. Rau, H. In *Photochromism: Molecules and Systems*; Dürr, H.; Laurent, H. B., Eds.; Elsevier: Amsterdam, 1990; Chapter 4.
35. Bisle, H.; Romer, M.; Rau, H. *Ber Bunsen-Ges Phys Chem* 1976, 80, 301.