Azo Polymers for Reversible Optical Storage. 7. The Effect of the Size of the Photochromic Groups

M. S. Ho and A. Natansohn*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

P. Rochon

Department of Physics, Royal Military College, Kingston, Ontario, Canada K7K 5L0

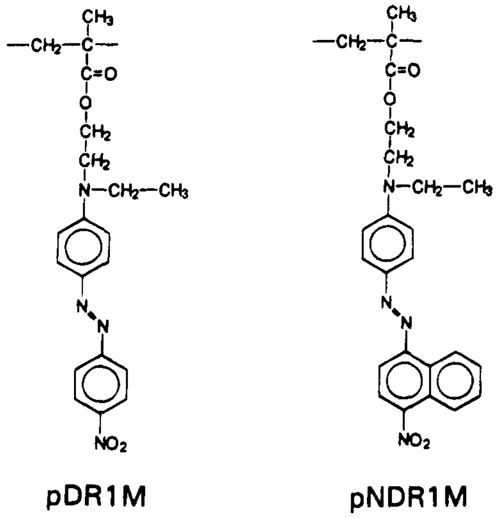
Received February 21, 1995; Revised Manuscript Received May 31, 1995®

ABSTRACT: Poly[(4-nitronaphthyl)[4-[[2-(methacryloyloxy)ethyl]ethylamino]phenyl]diazene] (pNDR1M) was prepared. The effect of the size of the azo moiety in the optical storage properties was studied. Both writing and relaxation processes can be described by biexponential functions. The bulkier pNDR1M exhibits a slower writing rate. However, there is no significant difference in the maximum birefringence achieved and in the relaxation rate when compared with the less bulky poly[(4-nitrophenyl)[4-[[2-(methacryloyoxy)ethyl]ethylamino]phenyl]diazene] (pDR1M).

In previous publications,[1−3] we have shown that amorphous polymers containing azobenzenes as side chains can be used as reversible optical storage media. Optical information can be written, read, erased, and rewritten on the same spot by a laser beam. The mechanism postulated for the writing is related to the trans−cis−trans isomerizations.[1] The photochemical excitation of the azobenzene group induces a trans−cis isomerization, and the cis−trans isomerization allows the cis configuration to go back to the trans configuration after some reorientation. By repetition of these trans−cis−trans isomerization and reorientation cycles, a sufficiently large portion of the initially homogeneous distribution of the azobenzene groups becomes aligned perpendicular to the polarization direction of the laser beam. This preferred orientation of the azobenzene groups can be observed by monitoring the birefringence of the polymer film.

The rate of achieving birefringence and the level of birefringence achieved depend on the type of the azo groups.[2,4] We are studying the relationship between the molecular structure of the azo polymer and the optical storage properties. Since a larger local free volume should be needed for the isomerization of molecules with a bulkier displacing group, the rates of photoisomerization in polymers should be significantly influenced by the size of the isomerizing chromophore. According to the proposed mechanism, the optical storage properties would be affected by the size of the azobenzene in the side group. This paper presents a comparison between poly[(4-nitrophenyl)[4-[[2-(methacryloyloxy)ethyl]ethylamino]phenyl]diazene] (pDR1M) and a polymer containing a bulkier phenylazonaphthalene moiety: poly[(4-nitronaphthyl)[4-[[2-(methacryloyloxy)ethyl]ethylamino]phenyl]diazene] (pNDR1M). The molecular structures of the repeating unit of the two polymers compared are given in Chart 1.

Chart 1



Experimental Section

The proton spectra were recorded on a Bruker AC-F 200 NMR spectrometer. UV absorption spectra were obtained from a Hewlett Packard 8452A diode array spectrophotometer. The molecular weight was obtained from a Waters Associates liquid chromatograph equipped with μ-styragel columns and a R401 differential refractometer. The glass transition temperature (T_g) was obtained from a Mettler TA 3000 thermal analysis system equipped with a TC10A TA processor and DSC30 head.

Monomers. (4-Nitrophenyl)[4-[[2-(methacryloyloxy)ethyl]ethylamino]phenyl]diazene (DR1M). (4-Nitrophenyl)[4-[[2-(methacryloyloxy)ethyl]ethylamino]phenyl]diazene was prepared by the procedure described below. A solution of Disperse Red 1 (Aldrich) (3.3 g, 0.010 mol) and triethylamine (1.5 mL) was dissolved in THF (50 mL). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (1.1 mL, 0.011 mol) in THF (10 mL) was added slowly to the above mixture. After the addition of methacryloyl chloride, the resultant mixture was stirred at room temperature overnight. The solvent was removed by rotary evaporation, and the residue was washed with a solution of sodium carbonate (1.0 g) in water (50 mL). The solid was filtered, washed with water, and air dried. The solid was recrystallized from ethanol. Yield: 2.8 g of purple crystals (80%). ^{1}H NMR ($CDCl_3$): δ 1.28 (3H), 1.95 (3H), 3.55 (2H), 3.75 (2H), 4.40 (2H), 5.58 (1H), 6.12 (1H), 6.80 (2H), 7.92 (4H), 8.34 (2H).

(4-Nitronaphthyl)[4-[[2-(methacryloyloxy)ethyl]ethylamino]phenyl]diazene (NDR1M). 4-Nitronaphthyl)[4-[[2-(methacryloyloxy)ethyl]ethylamino]phenyl]diazene was prepared by reacting (4-nitronaphthyl)[4-[[2-hydroxyethyl]ethylamino]phenyl]diazene with methacryloyl chloride. To obtain (4-nitronaphthyl)[4-[[2-hydroxyethyl]ethylamino]phe-

---

® Abstract published in *Advance ACS Abstracts,* August 1, 1995.

nyl]diazene, a solution of sodium nitrite (0.8 g, 0.011 mol) in 5 M hydrochloric acid (50 mL) was cooled to $\sim$0 °C in an ice bath. A solution of 1-amino-4-nitronaphthalene (1.8 g, 0.011 mole) in acetone (40 mL) was added slowly to the above sodium nitrite solution. The mixture was allowed to stir in an ice bath for 0.5 h. The mixture was then filtered and the filtrate was added to a solution of 2-(*N*-ethylanilino)ethanol (1.6 g, 0.010 mol) in glacial acetic acid (20 mL). After 20 min, the pH of the mixture was adjusted to $\sim$4 by adding aqueous sodium hydroxide. The mixture was allowed to stir in an ice bath for 1 h, and then it was neutralized by adding aqueous sodium hydroxide. The aqueous layer was discarded, and the black residual was dissolved in chloroform. The chloroform solution was washed with water and then dried over anhydrous sodium sulfate. The chloroform was removed by rotary evaporation. Yield: 2.6 g (70%) of (4-nitronaphthyl)[4-[[2-hydroxyethyl]ethylamino]phenyl]diazene. ^{1}H NMR ($CDCl_3$): δ 1.28 (3H), 1.75 (1H), 3.55 (2H), 3.60 (2H), 3.90 (2H), 6.84 (2H), 7.72 (3H), 7.96 (2H), 8.30 (1H), 8.68 (1H), 9.02 (1H).

A solution of (4-nitronaphthyl)[4-[[2-hydroxyethyl]ethylamino]phenyl]diazene (2.6 g, 0.007 mol) and triethylamine (1.0 mL) was dissolved in THF (50 mL). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (0.7 mL, 0.007 mol) in THF (10 mL) was added slowly to the above mixture. After the addition of methacryloyl chloride, the resultant mixture was stirred at room temperature overnight. The solvent was removed by rotovap, and the residue was washed with a solution of sodium carbonate (1.0 g) in water (50 mL). The product was extracted with chloroform, and the chloroform solution was washed with water and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography over silica gel and eluted with dichloromethane. Further recrystallization in ethanol gave 1.8 g (60%) of (4-nitronaphthyl0[4-[[2-(methacryloyloxy)ethyl]ethylamino]phenyl]diazene. ^{1}H NMR ($CDCl_3$): δ 1.28 (3H), 1.94 (3H), 3.55 (2H), 3.74 (2H), 4.40 (2H), 5.58 (1H), 6.12 (1H), 6.84 (2H), 7.72 (3H), 7.96 (2H), 8.30 (1H), 8.68 (1H), 9.02 (1H).

Polymers. The polymerizations for both monomers were carried out in dry toluene with 10% weight 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. The monomer was allowed to polymerize under argon at 60 °C for 2 days. The polymerization was stopped by pouring the reaction mixture into methanol. The polymers were redissolved in THF and precipitated again in methanol and finally dried under vacuum. The yields were 50% and 56% for pNDR1M and pDR1M, respectively. The GPC indicated an equivalent molecular weight of 3400 and 9700 for pNDR1M and pDR1M, respectively. From DSC, the glass transition temperatures were found to be 116 °C for both polymers.

Polymer Films and Optical Studies. Thin films of both polymers were obtained by dissolving the polymers in THF and spin-coating onto clean glass slides. The films were allowed to dry and subsequently heated above the T_g of the polymers. Relatively homogeneous thin films from 100 to 300 nm thickness were obtained by this procedure. The thickness was measured by interferometry. The procedures for the measurement of the optically induced birefringence have been described previously.[1]

Results and Discussion

The pDR1M and pNDR1M polymer films exhibit maximum absorbances (λ_{max}) at 458 and 488 nm, respectively. The occurrence of λ_{max} at longer wavelengths for pNDR1M suggests that the phenylazonaphthalene moiety has a larger dipole moment. A writing laser beam with a wavelength of 514 nm (0.7 W/cm^2) was used to induce birefringence on the polymer films at room temperature. Similar to previously reported azo polymer systems, both polymer films can be "written" onto by a linearly polarized laser beam and then "erased" by a circular polarized laser beam. The writing curves for the two polymer films are presented in Figure 1. As shown in Figure 1, the saturation values of the optically induced birefringence are very similar for both polymers although their λ_{max} differ by 30 nm. The phenylazonaphthalene moiety could in principle increase the conformational rigidity of the macromolecule, so as to magnify the dichroic effect. However, the result suggests that the replacement of phenyl by a naphthyl ring in the azo polymer does not appear to provide any improvement of the induced dichroism. This result is similar to a recent report that there is no remarkable improvement in the chiroptical properties of optically active azo copolymers when the phenyl ring is replaced by a naphthyl ring in the side chain azo moiety.[5]

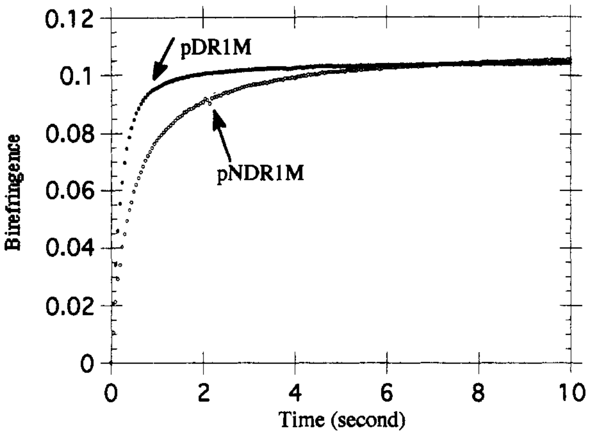


Figure 1. Photoinduced birefringence curves for pDR1M and pNDR1M.

Despite the fact that pNDR1M has a larger absorptivity at 514 nm (3.6 × 10^4 cm^{-1} for pDR1M and 5.1 × 10^4 cm^{-1} for pNDR1M), the time to achieve the saturation value for the pNDR1M is much longer than that of pDR1M. The growth of the birefringence can be quite well described by a biexponential equation:

$$y = A(1 - \exp(-k_a t)) + B(1 - \exp(-k_b t)) \qquad (1)$$

The growth of the birefringence of the polymers together with the fitting curves are shown in Figure 2. The fitted parameters obtained are summarized in Table 1. It appears that the writing process involves an initial "fast" response mode and a "slow" response mode. The "fast" and "slow" characteristic rate constants are an approximation for the multiplicity of writing rates. The parameter A_n in Table 1 represents the weighted contribution of the fast growth component with rate constant k_a. The magnitude of k_a would depend on the quantum yield, the trans–cis–trans isomerization rates, and the local mobility of the azo moiety. The local mobility is controlled by the size of the azo moiety, the free volume around the azo moiety, and the strength of the coupling interaction between the azo moiety and the polymer backbone. The parameter B_n in Table 1 represents the weighted contribution of the slow growth component with rate constant k_b. The magnitude of k_b would depend on the coupling interaction between the azo moiety and the polymer segments and the mobility of the polymer segments. Although the mobility of the polymer segments is fairly restricted in the glassy state, there are studies suggesting that conformational changes of the polymer segments occur during the photoisomerization even in the glassy state.[6-8] We believe that not only the chromophores undergo

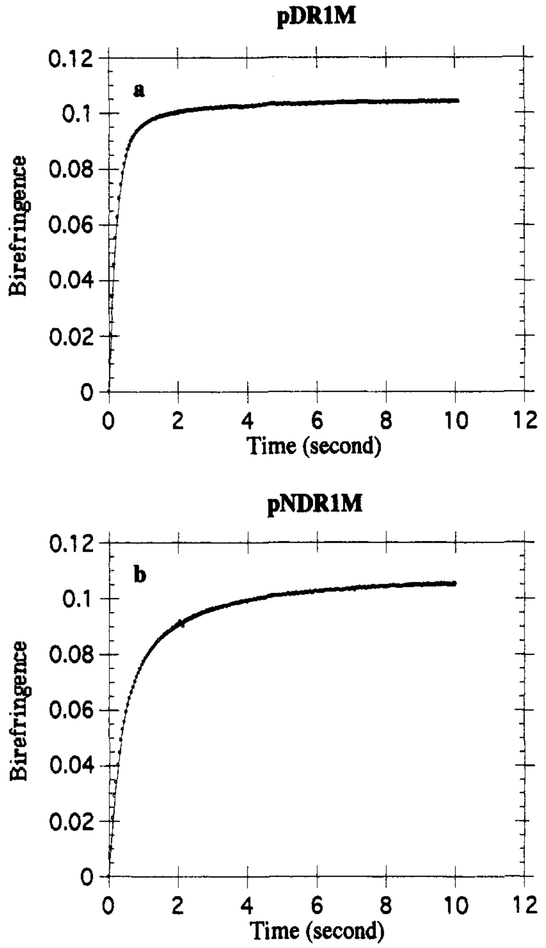


Figure 2. (a) Photoinduced birefringence curve for pDR1M (solid circle). The solid line is a fit to a biexponential function (eq 1). (b) Photoinduced birefringence curve for pNDR1M (open circle). The solid line is a fit to a biexponential function (eq 1).

Table 1. Parameters Obtained by Fitting the Birefringence Growth Curves in Figure 2 to Eq 1

	pNDR1M	pDR1M
10^2A	6.67 ± 0.06	9.15 ± 0.02
10^2B	3.83 ± 0.06	1.24 ± 0.02
k_a (s^{-1})	2.96 ± 0.04	4.45 ± 0.02
k_b (s^{-1})	0.48 ± 0.01	0.58 ± 0.01
A_n[a]	0.635	0.881
B_n[a]	0.365	0.119

[a] $A_n = A/(A + B)$. $B_n = B/(A + B)$.

reorientational motion but the polymer segments also rearrange during the writing process. In fact, it has been observed that if the polymer is semicrystalline, there is a 3-fold increase of the induced birefringence. However, it takes much longer time (tens of seconds) to achieve saturation because whole crystalline domains are oriented in the preferred direction with the azo moieties.[8]

As mentioned previously, the photoinduced birefringence in the polymer film results from a reorientation of the azo moieties after the trans–cis–trans isomerization. Since the trans–cis–trans isomerization cycle requires space, enough free volume (a critical volume) must be available around the azo molecules.[9] Because the critical volume for photoisomerization becomes larger with increasing sweep volume of the azo residue,[10] it would be expected that the larger the sweep volume of the azo molecule, the slower will be the "fast" response mode. Table 2 shows the sweep volume for isomerization of azobenzene with the phenyl and naphthyl rings. In addition, it has been observed that the quantum yield for the photoisomerization decreases when bulkier substituents are introduced on the azobenzene.[11] In our case, the naphthyl ring in pNDR1M is much bulkier than the phenyl ring in pDR1M. Therefore, the smaller k_a for the pNDR1M in comparison to pDR1M can be explained in terms of an increase in critical volume and a decrease in quantum yield for the isomerization. In fact, by replacing a hydrogen with a chlorine atom in the azo moiety of an azo polymer, a similar effect has also been observed.[2] On the other hand, k_b for both pDR1M and pNDR1M is quite similar. Both polymers have the same polymer backbone and T_g, and the naphthyl ring in pNDR1M is far away from the backbone. Therefore, it is not surprising that the coupling interaction between the azo moiety and the polymer segments and the mobiliy of the polymer segments are similar in both polymers. For both polymers, the weighting factors A_n and B_n indicate that the "fast" response mode is more important than the "slow" response mode. However, the "slow" response mode is more important in pNDR1M than in pDR1M.

Table 2. Sweep Volume for Isomerization (nm^3)[a]

mode	phenyl	1-naphthyl
inversion	0.12	0.16
rotation	0.25	0.44

[a] Data taken from ref 11.

Qualitatively, the relaxation of the birefringence on removal of the laser beam can also be analyzed by two different steps: an initial fast decay and a slow decay. The same relaxation pattern is well-known for the cis–trans thermal isomerization of azo polymers in the glassy state.[12–17] Again, a biexponential function (eq 2) gives a good fit to the birefringence decay curves (Figure 3).

$$y = C\exp(-k_c t) + D\exp(-k_d t) + E \qquad (2)$$

The fitted parameters obtained are summarized in Table 3. Although the detailed relaxation mechanisms are not known, it is believed that the thermal cis–trans isomerization and thermally activated dipole reorientation contribute to the relaxation process. In addition, it was suggested that illumination may cause a local increase of free volume around the azo group which contributes to the faster decay of dipole orientation after photoinduced poling.[18]

The data show there are two modes for the relaxation process, a "fast" mode and a "slow" mode which are represented by the terms "$C\exp(-k_c t)$" and "$D\exp(-k_d t)$", respectively. The "fast" decay can be attributed to the fast component of the thermal cis–trans isomerization and the dipole reorientation. The "slow" decay is attributed to the slow component of the thermal cis–trans isomerization and, possibly, some motion involving the polymer matrix. In contrast to the writing behaviors, there is no significant difference in the birefringence relaxation rates between pNDR1M and pDR1M.

Among the weighting factors C_n, D_n, and E_n involved in the decay of birefringence, E_n does not depend on time. Thus, E_n represents the fraction of induced birefringence conserved in the polymer film. It is very interesting to note that both pDR1M and pNDR1M conserve about 84% of the maximum birefringence after relaxation. In addition, C_n and D_n are less significant than parameter E_n. For pDR1M, C_n and D_n seem to be of equal importance to the relaxation process. On the

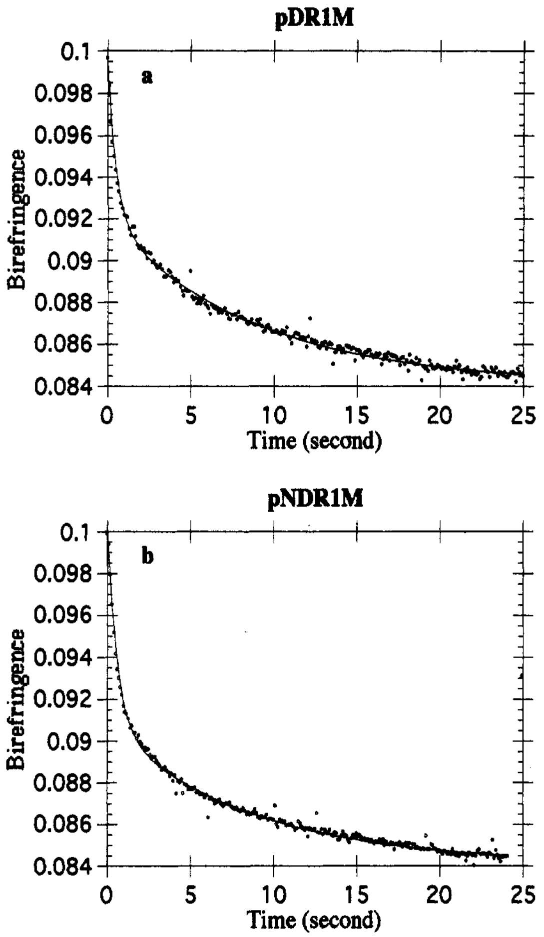


Figure 3. (a) Decay of birefringence after the writing laser was turned off for pDR1M (solid circle). The solid line is a fit to a biexponential function (eq 2). (b) Decay of birefringence after the writing laser was turned off for pNDR1M (open circle). The solid line is a fit to a biexponential function (eq 2).

Table 3. Parameters Obtained by Fitting the Birefringence Decay Curves in Figure 3 to Eq 2

	pNDR1M	pDR1M
10^2C	0.95 ± 0.02	0.75 ± 0.02
10^2D	0.67 ± 0.01	0.78 ± 0.01
10^2E	8.41 ± 0.01	8.41 ± 0.01
k_c (s^{-1})	1.70 ± 0.06	1.90 ± 0.09
k_d (s^{-1})	0.12 ± 0.01	0.11 ± 0.01
C_n[a]	0.095	0.075
D_n[a]	0.067	0.078
E_n[a]	0.838	0.846

[a] $C_n = C/(C + D + E)$. $D_n = D/(C + D + E)$. $E_n = E/(C + D + E)$.

other hand, the "fast" decay process is somewhat more important than the "slow" decay process for pNDR1M. This is quite different from the writing behavior, where the "fast" process had much more weight than the slow one. Obviously, the driving force during writing is the energy provided by the laser beam, and this is absent during relaxation. Thus, thermal cis–trans isomerization and overall motions involving the polymer chain have relatively equal importance in relaxation.

Since the slow component in both the writing and the relaxation processes is related to the overall motions of the polymer matrix, the effect of laser illumination can be observed by comparing the magnitude of k_b and k_d. For both polymers, k_b is much larger than k_d. It indicates that the energy provided by the laser beam can enhance the mobility of the polymer matrix. The enhanced mobility of the polymer matrix is probably induced by the chromophores which undergo photoinduced isomerization cycles and reorientations.

It is important to note that the rate of achieving birefringence will depend on the laser intensity and on the polymer absorptivity at the laser wavelength. Thus, different laser intensities will generate different rate constants in eq 1. In eq 2, relaxation through the thermal process will obviously depend on the difference between the operating temperature and glass transition temperature. All parameters will be affected when the operating temperature is changed, thus only polymer films with similar T_g's and absorptivities at the laser wavelength could be compared quantitatively. Therefore, in principle, eq 1 and 2 could offer a quantitative comparison for polymer films with similar T_g's and absorptivities at the laser wavelength and irradiated with the same laser intensity. Nonetheless, for polymers with different physical properties, the parameters from eq 1 and 2 could be used as a guideline for searching ideal polymer systems for practical applications.

Conclusion

We found that both the writing and the relaxation processes can be described by an initial "fast" response mode and a "slow" response mode. The biexponential functions give good fits to the writing and relaxation curves. The polymer pNDR1M, which has a bulkier azo group, exhibits a slower writing rate. However, there is no significant difference in the maxmium birefringence achieved and in the relaxation rate when compared with pDR1M.

Acknowledgment. Funding from the Office of Naval Research, NSERC Canada, and the Department of Defense Canada is gratefully acknowledged.

References and Notes

(1) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* **1992**, *25*, 2268.
(2) Natansohn, A.; Xie, S.; Rochon, P. *Macromolecules* **1992**, *25*, 5531.
(3) Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. *Appl. Phys. Lett.* **1992**, *60*, 4.
(4) Ho, M. S.; Natansohn, A.; Rochon, P. *Can. J. Chem.*, in press.
(5) Angiolini, L.; Caretti, D.; Carlini, C. *J. Polym. Sci., Polym. Chem.* **1994**, *32*, 1159.
(6) Wiesner, U.; Anotonietti, M.; Boeffel, C.; Spiess, H. W. *Makromol. Chem.* **1990**, *191*, 2133.
(7) Loucif-Saibi, R.; Nakatani, K.; Delaire, J. A.; Dumont, M.; Sekkat, Z. *Chem. Mater.* **1993**, *5*, 229.
(8) Natansohn, A.; Rochon, P. Pezolet M.; Audet, P.; Brown, D.; To, S. *Macromolecules* **1994**, *27*, 2580.
(9) Mita, I.; Horie, K.; Hirao, K. *Macromolecules* **1989**, *22*, 558.
(10) Naito, T.; Horie, K.; Mita, I. *Macromolecules* **1991**, *24*, 2907.
(11) Rau, H. In *Photochemistry and Photophysics*; Rebek, J. K., Ed.; CRC Press, Inc.: Boca Ruton, FL, 1990; Vol. 2, p 119.
(12) Tabak, D.; Morawetz, H. *Macromolecules* **1970**, *3*, 403.
(13) Eisenbach, C. D. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 287.
(14) Paik, C. S.; Morawetz, H. *Macromolecules* **1972**, *5*, 171.
(15) Lamarre, L.; Sung, C. S. P. *Macromolecules* **1983**, *16*, 1729.
(16) Morishima, Y.; Tsuji, M.; Kamachi, M. *Macromolecules* **1992**, *25*, 4406.
(17) Beltrame, P. L.; Seves, A.; Marcandall, B. *J. Appl. Polym. Sci.* **1993**, *49*, 2235.
(18) Bauer-Gogonea, S.; Bauer, S.; Wirges, W.; Gerhard-Multhaupt, R. *J. Appl. Phys.* **1994**, *76*, 2627.

MA950180A