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Azo polymers for reversible optical storage. 8. The effect of polarity of the azobenzene groups

Mei-Sing Ho, A. Natansohn, C. Barrett, and P. Rochon

Abstract: Poly[4′-[[(2-methacryloyloxy)ethyl]ethylamino]azobenzene] (pMAEA) was prepared. Its reversible optical storage properties were studied and compared with the properties of previously reported poly[4-(2-methacryloyloxy)ethylazobenzene] (pMEA) and poly[4-nitrophenyl-4′-[[2-(methacryloyloxy)ethyl]ethylamino]phenyldiazene] (pDR1M). The effect of the dipole moment of the azobenzene moiety on the optical storage properties was studied by comparing the photochemically induced birefringence "writing" and "relaxation" behaviors. The writing and relaxation rates are both in the order pDR1M > pMAEA > pMEA. In addition, pDR1M, which contains donor/acceptor substituents in the azobenzene side chain, exhibits the highest saturation level of optically induced birefringence. The fraction of birefringence conserved after relaxation is lowest for pMEA, which has no donor/acceptor substituents in the azobenzene side chain, and highest for pDR1M.

Key words: polymers, azobenzene type, birefringence, photochemically induced orientation, reversible optical storage.

Résumé : On a preparé le poly[4′-[[(2-méthacryloyloxy)éthyl]éthylamino]azobenzène] (pMAEA). On a étudié ses propriétés d'emmagasinage optique réversible et on les a comparées avec celles des poly[4-(2-méthacryloyloxy)éthylazobenzène] (pMEA) et poly[4-nitrophényl-4′-[[2-(méthacryloyloxy)éthyl]éthylamino]phényldiazène] (pDR1M). On a étudié l'effet du moment dipolaire de la portion azobenzène sur les propriétés d'emmagasinage optique en comparant les comportements à l'«écriture» et à la «relaxation» de la biréfringence photochimiquement induite. Les vitesses dans les modes écriture et relaxation sont dans chaque cas dans l'ordre pDR1M > pMAEA > pMEA. De plus, le pDR1M, qui contient des substituants donneur/accepteur dans la chaîne latérale, présente le niveau de saturation de biréfringence optiquement induite le plus élevé. La fraction de la biréfringence qui est conservée après relaxation est le plus élevé avec le pDR1M et le plus faible avec le pMEA qui ne porte pas de substituants donneur/accepteur dans la chaîne latérale de l'azobenzène.

Mots clés : polymères, type azobenzène, biréfringence, orientation photochimiquement induite, emmagasinage optique réversible.

[Traduit par la rédaction]

Introduction

Azo polymers are attracting much attention because of their potential use in various optical applications (1). In previous publications, we have demonstrated that stable birefringence can be optically induced in amorphous polymer thin films (2–7). The mechanism postulated for optically induced birefringence is related to the *trans–cis–trans* isomerization of the azobenzene group. A series of *trans–cis–trans* isomerization cycles is accompanied by the movement of the rigid azo groups and eventually creates an excess of azo groups oriented perpendicular to the laser polarization direction. This dichroism produces a measurable birefringence. Circularly polarized light restores the initial disordered state of the azo groups. According to Rau (8), azo compounds can be divided into three classes: azobenzene type, aminoazobenzene type, and pseudo-stibene type. Azobenzenes with electron donor and electron acceptor substituents (pseudo-stilbene type) and aminoazobenzene-type molecules isomerize from the *cis* configuration back to the *trans* configuration very quickly at room temperature. However, the thermal *cis–trans* isomerization in azobenzene-type molecules is relatively slow, and it is even possible to isolate the *cis* isomer.

We are studying various aspects of the mechanism for the optically induced supramolecular organization and structure–properties relationship of the polymers. However, our previous studies have only focused on azo polymers with the pseudo-stilbenes (2–6) and azobenzene (7) type side chain. To have a better understanding of the mechanism and the requirements for achieving optically induced supramolecular orientation, it is important to explore the optical properties of polymers with the aminoazobenzene-type side chain. This paper presents the synthesis of an azo polymer that contains an

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This paper is dedicated to Professor J.E. (Jim) Guillet in recognition of his contributions to Canadian chemistry.

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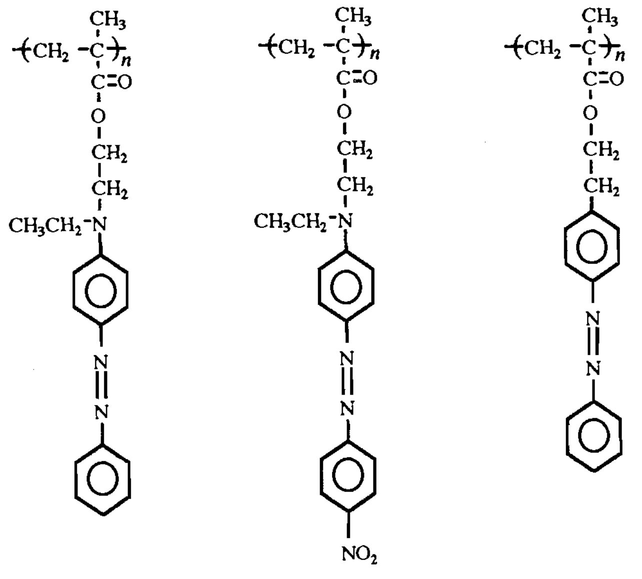
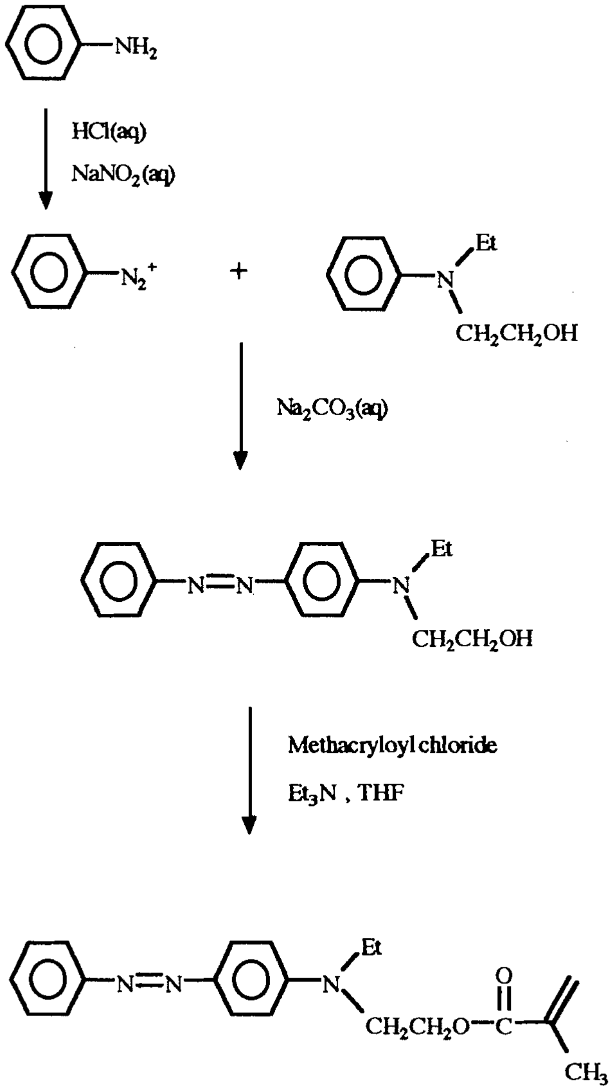
Chart 1.



pMAEA pDR1M pMEA

aminoazobenzene-type group in the side chain. In addition, its optical properties are compared with two structurally similar azo polymers, pMEA (7) and pDR1M (9). The molecular structures of the three polymers compared are presented in Chart 1.

Scheme 1.



Experimental

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 with a Mettler TA 3000 thermal analysis system equipped with a TC10A TA processor and a DSC30 head.

Monomer

4′-[[(2-Methacryloyloxy)ethyl]ethylamino]azobenzene (MAEA)

The monomer was prepared according to the synthetic scheme shown in Scheme 1. 4′-[[(2-Methacryloyloxy)ethyl]-ethylamino]azobenzene was obtained by reacting the corresponding alcohol with methacryloyl chloride. The 4′-[2-(hydroxy)ethyl)ethylamino]azobenzene was prepared by coupling the diazonium salt of aniline with 2-(*N*-ethylanilino)ethanol and the procedure is as follows.

Aniline (2.4 g, 0.025 mol) was dissolved in a solution of concentrated HCl (10 mL) in water (50 mL). The mixture was cooled in an ice bath until the temperature was below 4°C. Then a solution containing sodium nitrite (1.9 g, 0.027 mol) in water (20 mL) was added slowly to the aniline solution. The mixture was allowed to stir in the ice bath for 15 min. The resultant solution, which contained the diazonium salt, was added to a solution of 2-(*N*-ethylanilino)ethanol (4.2 g, 0.025 mol) in glacial acetic acid (10 mL) and water (20 mL). The mixture was stirred for 5 min in the ice bath and aqueous sodium carbonate solution was added to adjust the pH to ~6. The solid was filtered and air dried. The solid was recrystallized from ethanol–water mixture (3/2 by volume). Yield 4.5 g of 4′-[2-(hydroxy)ethyl)ethylamino]azobenzene (68%): mp 119–120°C. ^{1}H NMR(CDCL$_3$), δ: 1.24(3H), 1.76(1H), 3.50(2H), 3.60(2H), 3.88(2H), 6.80(2H), 7.50(3H), 7.88(4H). Anal. calcd. for $C_{16}H_{19}N_3O$: C 71.35, H 7.11, N 15.60; found: C 71.53, H 7.29, N 15.58.

A solution of 4′-[2-(hydroxy)ethyl)ethylamino]azobenzene (5.4 g, 0.020 mol) and triethylamine (3.0 mL) was dissolved in THF (80 mL). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (2.3 mL, 0.022 mol) in THF (20 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 (1.6 g) in water (100 mL). The product was extracted with diethyl ether and the solution was washed with water and dried over anhydrous sodium sulphate. The solvent was removed by rotary evaporation and the residue was purified by column chromatography

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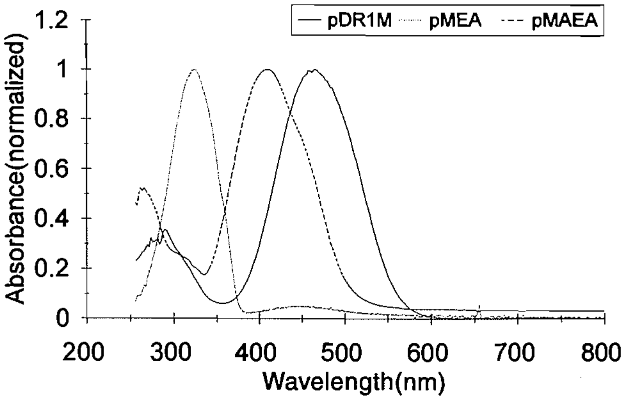


Fig. 1. UV–vis spectra of pMEA, pDR1M, and pMAEA polymer films.

over silica gel and eluented with chloroform. Yield 5.0 g (74%) of 4′-[[(2-methacryloyloxy)ethyl]ethylamino]azobenzene as a red viscous liquid. ^{1}H NMR(CDCl$_3$), δ: 1.24(3H), 1.95(3H), 3.55(2H), 3.72(2H), 4.38(2H), 5.60(1H), 6.12(1H), 6.80(2H), 7.50(3H), 7.88(4H). Anal. calcd. for $C_{20}H_{23}N_3O_2$: C 71.19, H 6.87, N 12.45; found: C 70.76, H 6.97, N 12.14.

Polymer

The polymerization of MAEA was carried out in dry toluene with 1% weight 2,2′-azobisisobutyronitrile (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 polymer was redissolved in THF, precipitated again in methanol, and finally dried under vacuum. The yield was 60% and the polymer had a weight-average molecular weight of 41 000 (relative to polystyrene). From the DSC, the glass transition temperature was found to be 104°C for pMAEA. The preparations of pMEA (7) and pDR1M (9) have been reported previously.

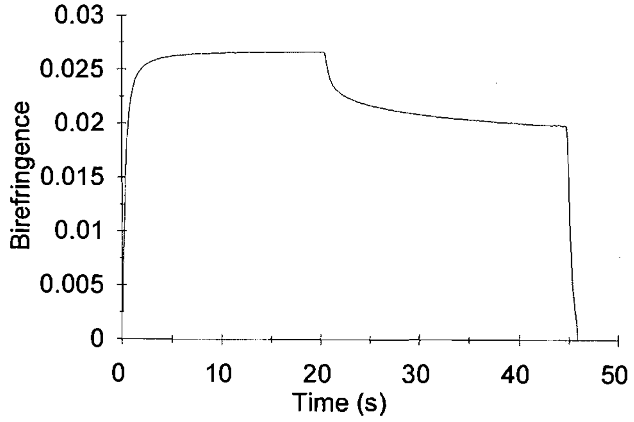
Polymer films and optical studies

Thin films of the polymers were obtained by dissolving the polymers in THF and spin-coating onto clean glass slides. The films were allowed to dry and were subsequently heated above the T_g of the polymers. Relatively homogeneous thin films from 100 to 400 nm thickness were obtained by this procedure. Film thickness was determined by interferometry. Detailed procedures for the measurement of the optically induced birefringence (2–6) and thermal *cis–trans* isomerization rate (10) have been described previously.

Results and discussion

The UV–vis spectra for pMAEA, pDR1M, and pMEA films are shown in Fig. 1. The maximum absorbances (λ_{max}) are 410, 458, and 324 nm for pMAEA, pDR1M, and pMEA, respectively. The UV–vis spectrum of pMEA exhibits a high-intensity band in the UV region and the low-intensity band in the visible region corresponds to the absorption band of the cis isomer. These bands are characteristic for the “azobenzene” type in Rau’s classification (8). The UV–vis spectra of pMAEA and pDR1M exhibit high-intensity bands in the visible region, which is characteristic for the “aminoazobenzene” and “pseudo-stilbene” types (8). In addition, the λ_{max} of the polymers suggests that the dipole moments of the *trans* isomers are in the order pDR1M > pMAEA > pMEA. The absorptivity values for pMEA, pMAEA, and pDR1M at 514 nm are 5.8×10^2 cm^{-1}, 3.5×10^3 cm^{-1} and 3.6×10^4 cm^{-1} respectively.

Fig. 2. Write–erase profile of optically induced and erased birefringence of pMAEA with laser beam at 488 nm. Time = 0 s: linearly polarized laser ON; time = 20 s: laser OFF; time = 45 s: circularly polarized laser ON.



For the sake of consistency, a writing laser beam with a wavelength of 514 nm (0.7 W/cm^2) was used to induce birefringence in all the polymer films. Figure 2 shows a typical sequence of inducing and erasing birefringence for pMAEA. Birefringence is induced to a saturated level by a linearly polarized laser beam, and relaxation occurs when the laser beam is turned off at 20 s. As the circularly polarized laser beam is turned on at 45 s, the induced birefringence is “erased.” Both pMEA (7) and pDR1M (9) exhibit similar write–erase profiles. The saturation levels of birefringence for pMEA, pMAEA, and pDR1M are 0.012, 0.026, and 0.103, respectively. This result suggests that the saturation level of birefringence follows the order of strength of the dipole moment of the azo group in the polymer. However, it has been observed that a polymer with nitrophenylazocarbazole in the side chain[2] exhibits a saturation level of birefringence as high as 0.09, although its λ_{max} (428 nm) is quite similar to pMAEA. This suggests that not only the dipole moment of the side group but also the presence of the nitro group may be important to achieve high induced birefringence. Since the maximum obtainable birefringence should depend on the interaction between the oriented dipoles (11), the presence of a lateral dipole can stabilize the local orientational ordering induced by the polarized laser beam. In fact, the presence of a terminal nitro group in liquid crystals was found to enhance the layered smectic phase (12).

The growth and relaxation of the optically induced birefringence can be quite well described by the biexponential functions [1] and [2], respectively. In fact, eq. [1] and [2] were found to give good fits to the growth and relaxation of the optically induced birefringence in other polymer systems (9).[2] To study the structural effect on the optical properties, data from the growth and relaxation of the optically induced birefringence were analyzed by eqs. [1] and [2], respectively. The fitting parameters obtained are summarized in Table 1.

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[2] M.S. Ho, J. Paterson, C. Barrett, A. Natansohn, and P. Rochon. To be published.

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Table 1. Parameters obtained by fitting the birefringence growth curves and decay curves to eqs. [1] and [2], respectively. Experiments were performed at room temperature.

Parameter	pMEA	pMAEA	pDR1M
k_a (s^{-1})	1.45 ± 0.01	3.10 ± 0.01	4.45 ± 0.02
k_b (s^{-1})	0.26 ± 0.01	0.54 ± 0.01	0.58 ± 0.01
$A \times (10^3)$	11.3 ± 0.1	22.3 ± 0.1	91.5 ± 0.2
$B \times (10^3)$	1.18 ± 0.07	4.20 ± 0.07	12.4 ± 0.2
A_n[a]	0.905	0.841	0.881
B_n[b]	0.095	0.159	0.119
k_c (s^{-1})	0.70 ± 0.01	1.68 ± 0.03	1.90 ± 0.09
k_d (s^{-1})	0.037 ± 0.001	0.095 ± 0.002	0.113 ± 0.004
$C \times 10^3$	2.35 ± 0.02	3.70 ± 0.03	7.53 ± 0.18
$D \times 10^3$	1.86 ± 0.01	3.46 ± 0.02	7.85 ± 0.08
$E \times 10^3$	8.41 ± 0.01	19.6 ± 0.1	84.1 ± 0.1
C_n[b]	0.186	0.138	0.08
D_n[b]	0.147	0.130	0.08
E_n[b]	0.667	0.732	0.84
α (cm^{-1})[c]	5.8×10^2	3.5×10^3	3.6×10^4
k_i (s^{-1})[d]	$(1.9 \times 10^{-4}) \pm (3 \times 10^{-5})$	0.53 ± 0.03	0.22 ± 0.01

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

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

[c] Absorptivity at 514 nm.

[d] Thermal *cis–trans* isomerization rate.

$$[1] \quad y = A(1 - \exp(-k_a t)) + B(1 - \exp(-k_b t))$$

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

The writing process involves an initial "fast" response mode and a "slow" response mode. The fast process is associated with the *trans–cis–trans* isomerization rates, with quantum yields, and with the local mobility of the azo group. Therefore, the fast process is controlled by the size of the azo group, the free volume around it, and the strength of the coupling interaction between the azo group and the polymer backbone. The slow process should be associated with the coupling interaction between the azo group and the polymer segments and with the mobility of the polymer segments. The parameter A in eq. [1] represents the contribution of the fast growth component with rate constant k_a. The parameter B represents the contribution of the slow growth component with rate constant k_b. Similarly, the relaxation process can be described by 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, in eq. [2]. In addition, the parameter E represents the induced birefringence conserved after relaxation.

Growth of the optically induced birefringence

Since k_a and k_b in Table 1 represent the rate constants for the fast and slow response modes, it is clear that pMEA has a slower writing response to the writing laser beam than pMAEA and pDR1M. For all three polymers, the parameter A indicates that the fast response mode contribution, which is related to the isomerization and reorientation of the chromophores, is the major component of the optically induced birefringence. The probability of an optical transition from *trans*-azobenzene to *cis*-azobenzene is proportional to $|\mu \cdot \boldsymbol{E}|^2$, where μ is the transition dipole moment and $\boldsymbol{E}$ is the electric field of the laser beam (13). Since the optically induced birefringence is created from the *trans–cis–trans* isomerization and reorientation of the azo moieties, it is expected that the rate of inducing birefringence will depend on the isomerization rate. For the same electric field, azo moieties with larger dipole moments would have a faster *trans–cis* isomerization rate and hence a faster rate of inducing birefringence. In addition, *trans–cis* isomerization rates also depend on the energy absorbed by the polymer film at the irradiation wavelength. The absorptivity of pMEA films at 514 nm is much lower than that of pDR1M and pMAEA, and most of the energy is absorbed by the *cis* isomers. Therefore, the *trans–cis* isomerization rate will be much lower in pMEA than in pDR1M and pMAEA. In spite of the low absorption at 514 nm, using a laser at this wavelength can photochemically activate the *cis–trans* isomerization, which otherwise would be very slow thermally (14) (see also Table 1). Therefore, pMEA can still give a reasonably fast response under these experimental conditions. Although the *trans–cis* and *cis–trans* isomerizations are both photochemically activated at the irradiating wavelength, a slower writing response for pMAEA than for pDR1M is observed. This discrepancy probably comes from the fact that pDR1M has a higher absorptivity and a larger dipole moment than pMAEA. As well as the rate of isomerization, the rate of inducing birefringence should also depend on the molecular associations among the chromophores. The molecular associations should be, in principle, more pronounced for polymers with stronger polar groups. For pDR1M, the donor/acceptor arrangement provides a large dipole, and the intra-chain and inter-chain interactions among these dipoles can create a local ordering that contributes to the observed induced birefringence.

Since it is proposed that the slow component in the writing process is related to the overall motion of the polymer matrix,

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Table 2. The weight-average molecular weight (M_w), polydispersity index (M_w/M_n), and glass transition temperatures (T_g) of the polymers investigated.

Polymer	M_w	M_w/M_n	T_g (°C)
pMEA	70 000	2.2	80
pMAEA	41 000	2.2	104
pDR1M	9 000	1.8	116

its magnitude should be affected by the molecular weight and glass transition temperature of the polymer sample. It is expected that the higher the molecular weight and the glass transition temperature of a polymer, the more difficult such motions are. Among the three polymers, pMEA exhibits the lowest glass transition temperature and highest molecular weight (Table 2). Although k_b is not solely determined by the molecular weight, it appears that the high molecular weight of pMEA could be the reason for it having the smallest k_b among the three polymers studied. In spite of having the highest glass transition temperature, pDR1M exhibits the largest k_b. This result suggests that the low molecular weight of pDR1M would facilitate the mobility of the polymer matrix.

Relaxation of the induced birefringence

As shown in Table 1, the relaxation rates (k_c and k_d) also follow the order pDR1M > pMAEA > pMEA. Although the thermal *cis–trans* isomerization is expected to be involved in the relaxation processes, the relaxation rates are much faster than the thermal *cis–trans* isomerization rate for pMEA ($k_i = 1.9 \times 10^{-4}$ s^{-1}) (14). Therefore, the contribution of thermal *cis–trans* isomerization to the relaxation processes should be insignificant for pMEA; in this case the dipole reorientation and the relaxation of the polymer segments would be the major constituents in the relaxation processes. The situation is very different for pDR1M and pMAEA, since both polymers exhibit fast thermal *cis–trans* isomerization rates (Table 1), which would have a significant effect on the observed relaxation rates. In addition to the contribution from thermal *cis–trans* isomerization, one should also consider the effect of molecular association during the dipole reorientation. The effect of molecular association should be more pronounced for the azo group with a stronger dipole. Therefore, the effect of molecular association might account for the difference between the relaxation rates (k_c and k_d) of pMAEA and pDR1M. Similar to the writing process, the slow component in the relaxation process is also related to the overall mobility of the polymer matrix. As pointed out in the previous section, the overall mobility of the polymer matrix would be affected by the glass transition temperature and molecular weight of the polymer. The higher the molecular weight and glass transition temperature of a polymer, the more difficult such motions are. As shown in Table 1, pMEA, which exhibits the lowest glass transition temperature and highest molecular weight, has the smallest k_d among the three polymers. On the other hand, pDR1M, which exhibits the highest glass transition temperature and lowest molecular weight, has the largest k_d. This result agrees with the previous suggestion that the low molecular weight of pDR1M facilitates an increased mobility of the polymer matrix.

The parameter E in eq. [2] is time independent, thus it represents the birefringence conserved in the polymer film after relaxation. It is interesting to note that the fraction of induced birefringence remaining after relaxation is different for every polymer. The fractions of birefringence remaining after relaxation are 0.67, 0.73, and 0.84 for pMEA, pMAEA, and pDR1M, respectively. This result agrees with the suggestion that dipolar interactions are important in stabilizing the local ordering, as discussed in previous section. In addition, the fraction of birefringence remaining increases with the increase in glass transition temperature of the polymer. This observation is reasonable because the orientational ordering conserved in the polymer will depend on the difference between the operating temperature and the glass transition temperature.

Conclusion

The saturated levels of birefringence were found to increase with the increase in dipole moment of the azo moiety in the azo polymers. In addition, the fraction of birefringence conserved after relaxation also follows the same trend as the dipole moment and glass transition temperature. The writing and relaxation behaviors were found to be related to the dipole moment of the azo moiety, the glass transition temperature, and the molecular weight of the polymer. From a practical point of view, the azo moiety with donor/acceptor arrangement (pseudo-stilbene-type azobenzene) gives the best optical properties. The pseudo-stilbene-type azobenzene offers the advantages of fast *trans–cis–trans* isomerization and strong dipolar interactions, which are important for the optically induced ordering and stability.

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