Azo Polymers for Reversible Optical Storage. 10. Cooperative Motion of Polar Side Groups in Amorphous Polymers

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ABSTRACT: 4-Nitrophenyl 4-[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]oxy]benzoate (BEM) was synthesized and copolymerized with 4′-[[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]ethyl]amino]-4-nitroazobenzene (DR1M) in dioxane at 60 °C. BEM and DR1M copolymerize in a random fashion with reactivity ratios $r_{\mathrm{DR1M}} = 0.82$ and $r_{\mathrm{BEM}} = 1.03$. The copolymers are amorphous. Interactions between the azo and the BEM side groups produce a shift of absorption maxima in the electronic spectra. Birefringence can be photoinduced and photoerased on films of all copolymers. The photoinduced birefringence per azo chromophore is very high in copolymers with low azo contents, about 4 times that of poly(DR1M). A cooperative motion of BEM groups with the azo groups is postulated as the reason for the additional birefringence. To our knowledge this is the first example of cooperative motion in amorphous polymers. The growth and relaxation of the birefringence are fitted by biexponential equations and "writing" rate constants are calculated for two processes, one is assigned to the fast motion of side groups and the other to the slow motion of the main chain. The fast "writing" rate increases with the DR1M content while the slow "writing" rate is almost constant. From the relaxation of the birefringence, about 85% of it is maintained in copolymers with high BEM contents. The maximum "writing" efficiency obtained for poly(DR1M-*co*-BEM) is 5×10^{-6} cm^3/J (at about 50 mol % DR1M) which is higher than that of poly(DR1M).

Introduction

Azo-containing amorphous polymers are being studied as suitable materials for reversible optical storage.[1] The photochemically induced trans−cis−trans isomerization of the azobenzene groups within the polymer can generate a local orientation of the azobenzene groups when the polymer film is irradiated with a linearly polarized laser beam.[2] This resulting birefringence has long term stability, but can be eliminated by irradiation with a circularly polarized laser and then introduced again by a linearly polarized laser. Ideal materials for this should possess a suitably large induced birefringence, high writing−erasing rates, and long term stability of the induced birefringence.

While most of the studies in the literature deal with liquid crystalline polymers, some amorphous polymers have also been reported as suitable for inducing orientation, including polyacrylate- and polymethacrylate-bound Disperse Red 1,[3] Disperse Red 13,[4] copolymers and blends of poly(methyl methacrylate) (poly(MMA)) with poly[4′-[[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]ethyl]amino]-4-nitroazobenzene] (poly(DR1M)) or poly[4′-[[[2-[(1-oxo-2-propenyl)oxy]ethyl]ethyl]amino]-4-nitroazobenzene] (poly(DR1A)),[5] poly(L-glutamate)-bound dialkylazobenzene,[6] polyacrylate- and polymethacrylate-bound (dimethylamino)azobenzene,[7] poly(dimethylsiloxane)-bound (allyloxy)azobenzene,[8] poly(MMA) doped with *p*-(dimethylamino)azobenzene,[9] poly[4-[2-(methacryloyloxy)ethyl]azobenzene] (poly(MEA)),[1] poly[(4-nitronaphthyl)[4-[[[2-(methacryloyloxy)ethyl]ethyl]amino]phenyl]diazene] (poly(NDR1M)),[10] poly[4′-[[[2-(methacryloyloxy)ethyl]ethyl]amino]azobenzene] (poly(MAEA)),[11] and poly[(4-nitrophenyl)[*N*-[2-(methacryloyloxy)ethyl]carbazol-3-yl]diazene].[12] It has been shown that the photoinduced birefringence is related to the structure of the azo chromophore, the type of the polymer backbone, and the interaction between azo dipoles. In a previous study[5] done in our laboratory a dipolar interaction between neighboring azo groups was found in poly(DR1A-*co*-MMA) and poly(DR1M-*co*-MMA), and it has an effect on the level of photoinduced birefringence. The local electric field of neighboring dipoles raises or lowers the absorption energy of an azo group. Parallel dipoles decrease the absorption energy, antiparallel dipoles increase the absorption energy, and hence shifts of absorption maxima to higher energy in the electronic spectra of poly(DR1A-*co*-MMA) and poly(DR1M-*co*-MMA) with increasing azo contents suggest that the dipoles prefer to align in an antiparallel fashion. This state lowers the mobility of azo groups and, therefore, the induced birefringence value. This reduced mobility occurs preferentially in poly(DR1M) or poly(DR1A) and the high azo content copolymers. The antiparallel pairing is not prevalent in the lower azo content copolymers since the azo dipoles are isolated by MMA units, so that the induced birefringence per dipole becomes higher.[5]

For all amorphous polymers studied up to now, the induced birefringence is limited to about 0.1, but much larger birefringence levels can be achieved (up to 0.2−0.3) for some semicrystalline polymers[13,14] with comparable azo contents. The increase in birefringence is attributed to cooperative motion of some photoinactive groups present and to the formation of semicrystalline domains. Examples of cooperative motion have also been reported in side chain liquid crystalline copolymers.[15−17] Spiess and co-workers[16,17] studied the photoinduced orientation in a liquid crystalline copolymer of similar azobenzene and phenyl benzoate monomers (Chart 1, copolymer I) and found that under continuous irradiation with polarized light, a coupled orientation of both azobenzene and phenyl benzoate moieties takes place both above and below the T_g. This orientation is strongly dependent on the azo concentration and temperature. The side chains can be easily oriented when the azo content is up to 50 mol %, even at temperatures below T_g. Low azo content samples

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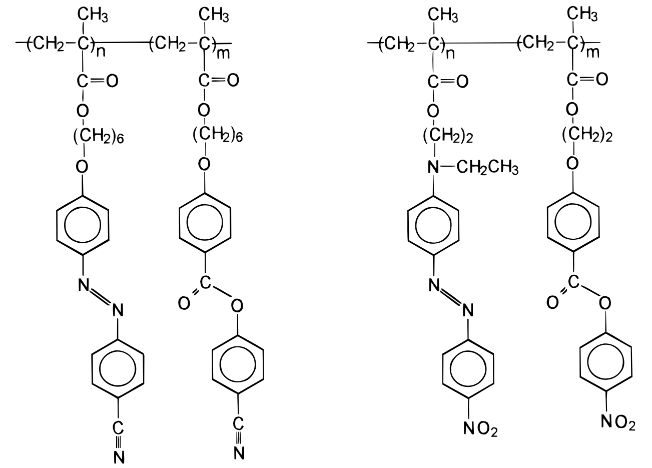
Chart 1



Copolymer I

Copolymer II [p(DR1M-co-BEM)]

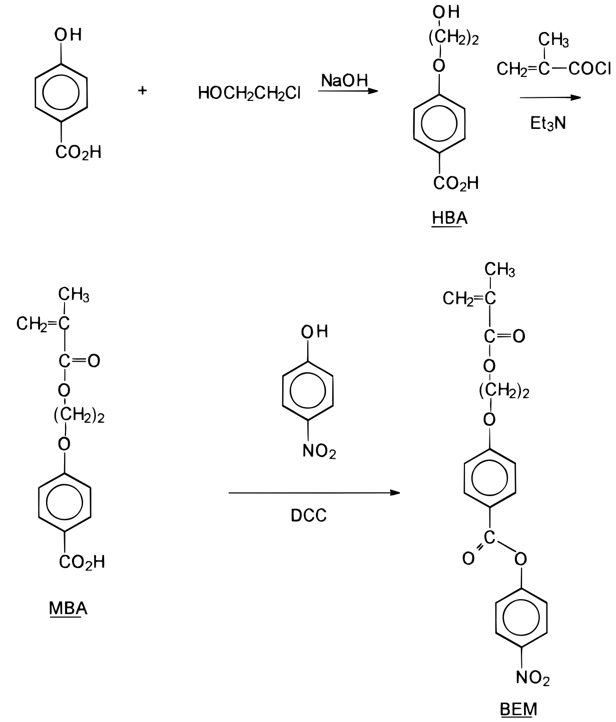
show a very slow and small orientation, however, suggesting that more energy is needed to align the side groups when the azo moieties are surrounded by the nonphotoactive phenyl benzoate groups. Stumpe et al.[15] reported a similar study on a liquid crystalline methacrylate copolymer with 14 mol % azobenzene side chains. They too found that laser-induced orientation of the azobenzene groups strongly affects the orientation of neighboring benzoate groups, suggesting a cooperative motion process between photoactive and nonphotoactive mesogens.

Since the high level of birefringence achieved in semicrystalline or liquid crystalline polymers is often at the expense of slower rates and incomplete erasure,[13] it becomes important to explore whether this kind of motion exists in amorphous polymers and how it affects the induced birefringence. In fact, orientation performed below T_g in liquid crystalline polymers strongly suggests the existence of cooperative motion in amorphous polymers as well.[16,17] Studies of amorphous copolymers of DR1M with a monomer containing much less polar azobenzene side groups, poly(DR1M-*co*-MEA),[18] did not show any enhancement in the birefringence level, indicating no cooperative motion of the two structural units. This suggested that dipolar interaction is probably more important than a possible steric cooperative motion. As part of our investigation of the steric and polar factors affecting cooperative motions, amorphous azo copolymers with a polar nonphotoactive group in the side chain are reported in this study. It will be demonstrated that there is a strong interacton between the photoactive and nonphotoactive rigid groups in the amorphous copolymers of 4-nitrophenyl 4-[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]oxy]benzoate (BEM) and DR1M (poly(DR1M-*co*-BEM)) and that high levels of birefringence inducible in high BEM content films are a strong indication of cooperative motion between the two types of side groups. This cooperative motion of polar groups in copolymers bearing azobenzene groups and substituted phenyl benzoate groups enhances the photoinduced per azo chromophore birefringence in comparison with poly(DR1M).

Experimental Section

This investigation was performed with poly(DR1M-*co*-BEM). The structures are detailed in Chart 1 (copolymer II). The synthetic routes for BEM and its copolymerization with DR1M are outlined in Scheme 1 where HBA and MBA were synthesized using a procedure similar to that in the literature.[19]

Scheme 1



Starting Materials. Disperse Red 1, 4-hydroxybenzoic acid, 2-chloroethanol, 4-nitrophenol, and dicyclohexylcarbodiimide all from Aldrich were used as purchased. Methacryloyl chloride (Fluka), triethylamine (Aldrich), and 1,4-dioxane (Aldrich) were distilled before use.

Synthesis. 4′-[[[2-(Methacryloyloxy)ethyl]ethyl]amino]-4-nitroazobenzene (DR1M) was synthesized by a procedure similar to the one described previously.[3] It was recrystallized from ethanol/acetone (100/15, v/v), yield 67%, mp 76.5−78.5 °C.

4-(2-Hydroxyethoxy)benzoic Acid (HBA). A solution of 138 g of 4-hydroxybenzoic acid and 150 g of potassium hydroxide in a mixture of 150 mL of water and 350 mL of ethanol was heated to 80 °C with stirring. Added to this solution was 74 mL of 2-chloroethanol in 40 mL of ethanol dropwise in about 2 h. The solution was refluxed while stirring for 15 h. The solution was then concentrated by rotaevaporation to approximately 100 mL, and the residue was dissolved in 1 L of water. The solution was washed with ether and then made strongly acidic with HCl. The white precipitate was collected and dried. Colorless needles (138 g) were obtained after recrystallization from ethanol, yield 76%, mp 174−176 °C. ^{1}H-NMR [dimethyl sulfoxide (DMSO)-d_6, δ in ppm]: 12.6 (broad, 1 H, −COOH), 7.9 (d, 2 aromatic H, ortho to −COOH), 7.0 (d, 2 aromatic H, ortho to O), 4.9 (broad, 1H, −OH), 4.2 (t, 2H, $-CH_2OPh-$), 3.7 (broad, 2H, $-CH_2-$, ortho to −OH).

4-[2-(Methacryloyloxy)ethoxy]benzoic Acid (MBA). HBA (21 g) and 40 mL of triethylamine were dissolved in 200 mL of THF in a flask placed in an ice bath. Added to this solution dropwise was 10.5 mL of methacryloyl chloride in 20 mL of THF in about 2 h. The solution was allowed to reach room temperature after stirring in the ice bath for 1 h and then stirred for another 12 h at room temperature. The solid formed was filtered out, and the solvent was evaporated by rotary evaporator. The residue was dissolved in about 200 mL of water and was acidified by adding concentrated hydrogen chloride solution to pH < 2. The precipitate was collected and recrystallized from a mixture of water and ethanol (4:3, v/v) to yield 19.4 g (67%) of colorless needle crystals, mp 120−122 °C. ^{1}H-NMR (DMSO-d_6, δ in ppm): 12.5 (broad, 1 H, −COOH), 8.1 (d, 2 aromatic H, ortho to −COOH), 7.0 (d, 2 aromatic H, ortho to O), 6.15 (s, 1 H, $H_2C{=}C$), 5.6 (s, 1 H, $H_2C{=}C$), 4.55 (t, 2 H, $-COOCH_2-$), 4.3 (s, 2 H, $-CH_2OPh-$), 1.95 (s, 3 H, $-CH_3$).

4-Nitrophenyl 4-[2-(Methacryloyloxy)ethyl]benzoate (BEM). MBA (6.4 g), 3.1 g of 4-nitrophenol, 22 mL of dicyclohexylcarbobiimide (DCC) dichloromethane solution (1 mol/L), and 0.3 g of 4-(dimethylamino)pyridine (DMAP) were dissolved in 50 mL of dry dichloromethane, and then the solution was stirred at room temperature for 20 h. The solid formed was filtered out and washed twice with dichloromethane. The filtrate and the washing were combined, washed with 3 × 100 mL water, and then dried under anhydrous sodium sulfate. The crude product obtained by evaporating the solvent was passed through a silica gel column (chloroform as eluent). The first fraction was collected and recrystallized from 2-propanol to yield 7.0 g (86%) of colorless needle crystals, mp 98−99 °C. ^{1}H-NMR ($CDCl_3$, δ in ppm) 8.30 (d, 2 aromatic H, ortho to $-NO_2$), 8.13 (d, 2 aromatic H, ortho to −COOPh−), 7.38 (d, 2 aromatic H, metal to $-NO_2$), 7.02 (d, 2 aromatic H, meta to −COOPh−), 6.15 (s, 1 H, $H_2C{=}C$), 5.60 (s, 1 H, $H_2C{=}C$), 4.54 (t, 2 H, $-COOCH_2-$), 4.32 (t, 2 H, $-CH_2OPh-$), 1.94 (s, 3 H, $-CH_2$).

Polymerization Procedure. The polymerization of DR1M and BEM and their copolymerization were carried out in dioxane at 60 °C initiated with AIBN (5−10% of the total mass of the monomers) for various reaction times. A typical experiment was as follows: 1 g of DR1M, 1 g of BEM, and 0.2 g of AIBN were dissolved in 12 mL of dioxane in an ampule; then the solution was degassed by bubbling nitrogen for 15 min, and the ampule was sealed in vacuum. The ampule was placed in an oil bath set at 60 °C. After 30 min the solution was poured into 150 mL of methanol. The precipitate was collected, dissolved in a mixture of dimethyl sulfoxide (DMSO) and dioxane (1/1, v/v), and then reprecipitated twice from methanol. The red solid was dried in a vacuum oven at 100 °C for 20 h. Copolymer (0.23 g) was obtained, conversion 11.5%. A ^{1}H-NMR spectrum is shown in Figure 1.

Characterization and Optical Testing. To prepare the thin films, the polymer was dissolved in hot DMSO and the hot solution deposited onto a glass slide on a hot plate at 90−110 °C. The solvent evaporated slowly, and a film formed at that temperature. The film was then dried under vacuum at 100 °C for 48 h to eliminate the solvent, as determined by FTIR spectroscopy.

The procedure for reversibly storing information with a laser beam on a polymer film has been previously described.[3] Writing and erasing were performed at room temperature using an argon laser (514 nm) of 5 mW on a spot 2 mm in diameter. The film densities were measured as described previously.[5]

Thermal transitions were measured at a second heating scan on a Mettler TA-30 DSC instrument equipped with a TA-3000 processor at a scan rate of 20 °C/min, and electronic spectra were recorded on a Shimadzu spectrometer (as a film or in DMSO/dioxane solution). Molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with polystyrene standard using a Waters Associates liquid chromatography equipped with a Model R401 differential refractometer and Model 440 absorbance detector. THF was used as the eluent. The ^{1}H-NMR spectra were obtained on a Bruker AC-F 200 NMR spectrometer in chloroform-*d* or DMSO-d_6 at room temperature or 90 °C.

Results and Discussion

Synthesis of Monomers and Copolymers. DCC was used to keep preparation conditions of BEM milder than those with thionyl chloride reported in the literature for a similar monomer containing 4-cyanophenyl benzoate.[19] A higher yield (near 90%) was obtained, as compared to 38% with the acid chloride route. It is important to maintain neutral conditions when recrystallization of BEM from 2-propanol is performed, as the monomer is very sensitive to both acid and base and hydrolyzes easily.

The homopolymerization of BEM and its copolymerization with DR1M were carried out in dioxane at 60 °C initiated with AIBN. The polymerization rates were quite high with 5% AIBN, and a conversion of 37% was obtained in 40 min for copolymerization with a 49/51 DR1M/BEM feed and 10% AIBN. Much higher conversions (~95%) can be reached in about 20 h.

Table 1. Polymerization of DR1M with BEM in Dioxane at 60 °C and 5 wt % AIBN

copolymer	initial feed F(DR1M)[a]	time (h)	composition f(DR1M)[b]	conversion (%)	T_g (°C)
0	0	37	0	~95	104
1	0.097	0.25	0.116	13.3	107
2	0.195	0.25	0.227	9.7	108
3	0.294	0.5	0.325	10.0	111
4	0.393	0.5	0.410	11.5	113
5	0.492	0.5	0.516	11.6	116
6	0.593	0.5	0.610	11.2	117
7	0.694	1	0.707	8.4	120
8	0.795	0.25	0.809	8.4	125
9	0.897	0.3	0.903	7.8	127
10[c]	1	48	1	~90	129

[a] *F*(DR1M) = fraction of monomer DR1M in the initial feed. [b] *f*(DR1M) = fraction of DR1M structural unit in the copolymer. [c] 10 wt% AIBN was used.

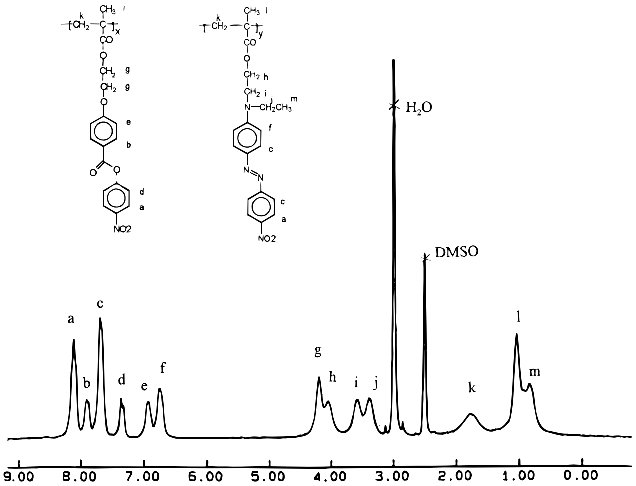


Figure 1. ^{1}H-NMR spectrum of poly(DR1M-*co*-BEM) (copolymer 5) in DMSO-d_6 at 90 °C.

Copolymerizations and Copolymer Characterization. The results of polymerization are summarized in Table 1. The copolymer compositions were obtained from ^{1}H-NMR spectra, an example is shown in Figure 1 for a typical copolymer sample of poly(DR1M-*co*-BEM) (sample 5 in Table 1). The assignments of the peaks were made by comparison with poly(DR1M) and poly(BEM), and the copolymer composition can be readily calculated from the ratio of integrated peak areas in both aromatic and aliphatic regions. The results are listed in Table 1.

Reactivity ratios for the low conversion copolymerizations were estimated by the Kelen−Tudos method.[20] The reactivity ratios obtained for poly(DR1M-*co*-BEM) are $r_{DR1M} = 1.03$ and $r_{BEM} = 0.82$. As is expected for methacrylates having similar structures, these two ratios are similar and near unity, showing no strong preference for either monomer.

The copolymers were not completely soluble in THF even at its boiling point but dissolved easily in dioxane/DMSO (1/1, v/v). The copolymers with DR1M content over 30 mol % were insoluble in DMSO at room temperature but soluble at 90 °C. This solubility behavior is caused by the different solubilities of the two structural units. The BEM homopolymer is quite soluble in DMSO but insoluble in THF and in dioxane,

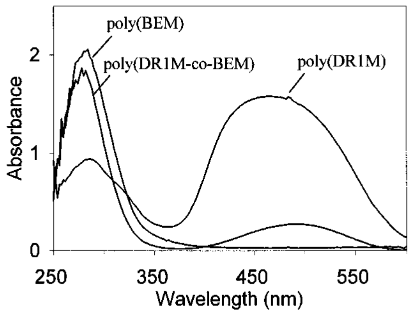


Figure 2. Electronic spectra of poly(DR1M), poly(BEM), and copolymer 5 films.

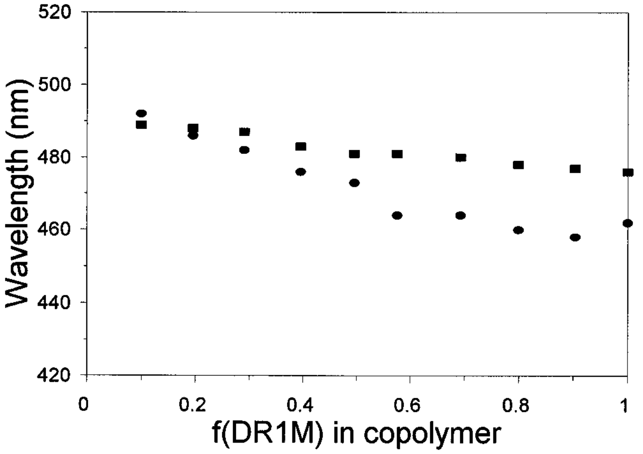


Figure 3. Absorption maxima of poly(DR1M-*co*-BEM) in a mixture of DMSO/dioxane (■) and in film (●) as a function of composition.

while the homopolymer of DR1M is soluble in THF but insoluble in DMSO at room temperature. All copolymers are amorphous, as determined by DSC and polarized microscopy. The glass transition temperatures decreased slightly with increasing BEM content (Table 1).

Absorption Spectra. The electronic spectra of films of poly(DR1M), poly(BEM), and copolymer **5** are shown in Figure 2. The visible absorption maximum shifts to longer wavelengths (red shift) as the BEM content in the copolymer increases, and this is observed both in films and in DMSO/dixoane solutions (Figure 3). The total shift in λ_{max} between films of poly(DR1M) and poly(DR1M-*co*-BEM) containing 11.6 mol % DR1M units is about 35 nm, which is greater than that found in poly(DR1A-*co*-MMA) (about 22 nm).[5] The total shift in λ_{max} between the films is also greater than that in DMSO/dioxane solutions. This large shift is probably due to two effects. The first is the association of DR1M groups with polar solvents or polar BEM groups (behaving like a solvent). The absorbance maxima of an azo dye similar to DR1M has been studied in different solvents by Whitten and co-workers.[21] They found that the absorption maxima of 4-nitro-4′-(*N*,*N*-diethylamino)azobenzene shifted from 451 nm in heptane to 512 nm in DMSO due to solvatochromic effects. A review on the solvatochromic dyes has been published recently by Reichardt.[22] DR1M and poly(DR1M) absorption maxima also shift to longer wavelengths in more polar solvents, as shown in Table 2. Differences between DR1M and poly(DR1M) absorption maxima arise from the second effect which must be considered, that of the dipole interaction of DR1M dipoles in poly(DR1M), as reported previously.[5]

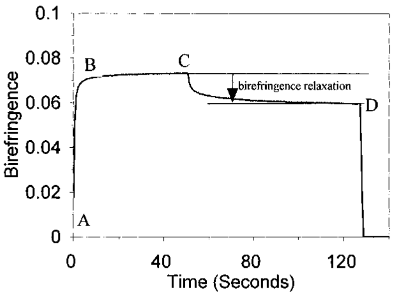


Figure 4. Inducing and erasing birefringence on a film of copolymer 5.

Table 2. UV–Vis Absorption Maxima of DR1M and Poly(DR1M) in Different Solvents at Room Temperature

	λ_{max} (nm)	
solvents	DR1M	poly(DR1M)
DMSO	498	483
DMSO/dioxane (1/1, v/v)	488	477
hexane	442	
(in film)		462

The shift of absorption maxima in films is larger than that in solution, because most azo dipoles in solution are surrounded by solvent instead of other dipoles. The solvation in solution causes a shift of maxima to longer wavelengths and at the same time reduces the interaction between dipoles. The blue shift caused by dipole interaction is then less in solution than in films. The mixture of the two homopolymers in DMSO/dioxane solution shows no absorption maxima shift. This suggests that the blue shift must be a consequence of intramolecular interactions of the dipoles only. Since the BEM group is strongly polar with a dipole moment of 7.0 Debye (calculated with PC model software), it acts as a strong polar “solvent” when associating with DR1M groups in the copolymer. The absorption maximum of poly(DR1M-*co*-BEM) films then shifts in a fashion similar to that in the polar solvent DMSO. Unlike BEM groups, the MMA groups in the poly(DR1M-*co*-MMA) film were not polar enough to induce the same shift,[5] as observed in poly(DR1M-*co*-BEM). This also indicates that the association between DR1M and BEM groups is stronger than that between the DR1M dipoles.

Reversible Optical Storage. A typical writing–erasing curve of optically induced and subsequently eliminated birefringence for a poly(DR1M-*co*-BEM) sample (copolymer 5) is presented in Figure 4. The linearly polarized laser beam is turned on at point A, and the birefringence is rapidly induced and then reaches a maximum level at point B. The writing beam is turned off at point C, and the birefringence relaxes to a stable level at point D. The induced birefringence is completely eliminated when a circularly polarized light is turned on at point D, and the film is ready to be rewritten in the same manner.

The maximum induced birefringence in a series of poly(DR1M-*co*-BEM) films is plotted vs DR1M weight fraction in Figure 5. The birefringence increases with the azo concentration up to about 40%, then it becomes almost constant at about the same value as poly(DR1M). The levels of birefringence are greater in these copolymers than those achievable in the poly(DR1M-*co*-MMA) series.[5] The increase in birefringence with azo content for the MMA copolymers is not linear[5] but is clearly less than in the poly(DR1M-*co*-BEM) which contains polar groups (BEM). For example, the birefringence of the copolymer films at a DR1M weight fraction of 0.4 was

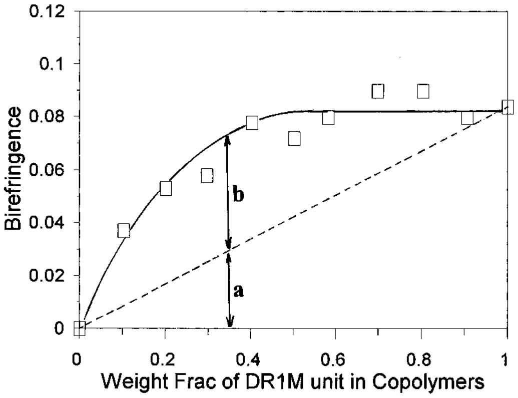


Figure 5. Maximum induced birefringence for poly(DR1M-*co*-BEM). The dashed line represents a hypothetical poly(DR1M)-*blend*-poly(BEM) where the induced birefringence would be proportional to the azo content.

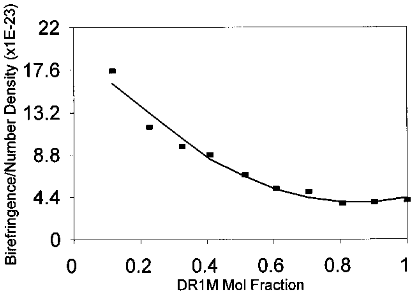


Figure 6. Birefringence per azo chromophore in copolymers as a function of composition (squares) and the triad fitting curve (solid line) using eq 2.

about 0.05 for poly(DR1M-*co*-MMA) and is about 0.08 for poly(DR1M-*co*-BEM).

The most useful comparison between poly(DR1M-*co*-BEM) and poly(DR1M) can be made by calculating birefringence levels per azo unit. The film densities were measured at room temperature using a previously described method,[5] and the azo chromophore number density was calculated from the film density and the azo weight fraction in the copolymers as follows:

$$\mathrm{ND} = DF_{\mathrm{w}}/(AM_{\mathrm{DR1M}}) \qquad (1)$$

Here ND is the number density of the DR1M chromophore, D is the film density, F_{w} is the weight fraction of DR1M in the copolymer, M_{DR1M} is the molecular weight of the DR1M structural unit, and A is Avogadro's number. The average contribution to the orientation per azo chromophore is obtained by dividing the maximum birefringence by the azo number density.

Figure 6 shows this birefringence contribution per azo chromophore in the copolymers as a function of copolymer composition. A very high birefringence per azo unit is found for high BEM content copolymers, about 4 times that of poly(DR1M). This can be interpreted in two ways. Either the azo groups in low azo content copolymer films can produce 4 times the orientation per azo groups in comparison to those in the DR1M homopolymer, or in addition to the enhanced birefringence for isolated azo groups,[5] the BEM groups are contributing to the orientation as well, in sympathetic neighboring alignment. This large difference in the birefringence per azo group, coupled with evidence of strong interactions between DR1M and BEM groups from the electronic spectra strongly suggest that, as in the liquid crystalline copolymers, cooperative motion takes place in these amorphous polymer films.

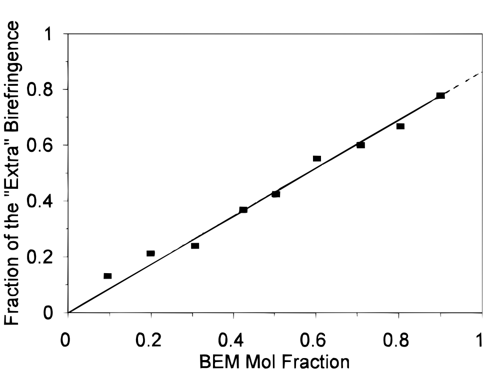


Figure 7. Fraction of the "extra" birefringence (defined in the text) as a function of copolymer composition.

The best way to estimate the effect of the BEM side groups in poly(DR1M-*co*-BEM) would be to compare the behaviors of DR1M–BEM random copolymers and their blends. Unfortunately, the two homopolymers are incompatible and thus optical measurements are not possible on blends. As reported previously, there is no significant interaction between the two components in poly(DR1A)-*blend*-poly(MMA) and the photoinduced birefringence for the blends is proportional to the azo content.[5] As mentioned in the previous section, there was no dipole interaction found between poly(DR1M) and poly(BEM) in solution since the electronic spectrum of their mixture did not show any shift, but the spectra of copolymer solutions did. Similarly, it is reasonable to predict that the photoinduced birefringence for a hypothetical blend of poly(DR1M) and poly(BEM) is also proportional to its azo content (shown as the dashed line in Figure 5). Consequently, the extent of the sympathetic alignment of BEM mesogens mentioned above can be then estimated by calculating this "extra" or non azo contribution to the induced birefringence. Assuming that the contribution of DR1M groups to the birefringence in copolymers is the same as in a hypothetical poly(DR1M)/poly(BEM) blend with the same azo content, shown as the quantity "a" in Figure 5, the extra birefringence can be obtained by subtracting the DR1M contribution from the total birefringence, shown as the quantity "b". The fraction of the extra birefringence can be then calculated by dividing b by the total birefringence ($a + b$) and is plotted as a function of the molar fraction of BEM in Figure 7. It is very clear that the "extra" birefringence increases linearly with the BEM content. This indicates that most of the increase of birefringence in comparison with the hypothetical poly(DR1M)-*blend*-poly(BEM) is related directly to the presence of the BEM groups. The BEM groups associate with the DR1M group in the orientation process. Furthermore, a poly(BEM) would give a hypothetical birefringence of 80% of the total obtainable level. That is to say the contribution of DR1M to the birefringence will be only about 20% when the BEM content of copolymer is close to 100%. This means that the maximum contribution of the "inert" BEM group to the birefringence can reach 4 times that of DR1M in the copolymer. This is an extremely large effect on the photoinduced birefringence.

To confirm the effect of the neighboring group, sequence distribution effects on birefringence in poly(DR1M-*co*-BEM) are discussed. Assuming the first order Markov statistics to be valid, the fractions of DR1M-centered triads (DDD, DDB, BDB) (B = BEM unit, D = DR1M unit) can be calculated, and the least squares fit of the following equation can be determined:

$$\Delta n_{\mathrm{p}} = af_{\mathrm{BDB}} + bf_{\mathrm{BDD}} + cf_{\mathrm{DDD}} \qquad (2)$$

Here Δn_{p} is the birefringence per DR1M unit, f_{BDB}, f_{BDD}, and f_{DDD} are the normalized triad fractions of each azo-centered triad, and a, b, and c are fit coefficients representing the relative contribution to birefringence of the central azo group in each triad. The fitted curve is shown in Figure 6 and the corresponding parameters are $a = 20$, $b = 0.94$, and $c = 4.3$ (all $\times 10^{-23}$) with the correlation coefficient of 0.96. The greatest contribution to the birefringence in these copolymer films is clearly from BDB triads, i.e. azo groups with two BEM neighbors. It contributes to the induced order in BEM copolymer films about 4 and 20 times more than DDD and BDD triads do, respectively, showing that there is a greater extra birefringence contribution when there are more non-azo groups available to align sympathetically. It has been shown that in MMA copolymer films, as well, the greatest contribution to birefringence is from MDM (two methacrylate neighbor azo-centered triads), but to a lesser extent ($a = 10.1 \times 10^{-23}$ for the MMA copolymer,[5] $a = 20 \times 10^{-23}$ for the BEM copolymer for eq 2), and this was attributed to the possibility of moving the azo dipole easier in the MDM triad, due to the lack of intramolecular dipolar interactions.[5] This kind of effect of the MMA unit is not available in the BEM system, since the BEM unit is also a dipole with the dipole moment similar to that of DR1M.

One of the strongest arguments for proof of cooperative motion should come from studies of dichroic ratios of FTIR absorbances specific to BEM in "written" sample. Recording the infrared spectra of a written film with the infrared radiation polarized parallel ($A_{\|}$) and perpendicular ($A_{\perp}$) to the writing direction allows one to follow the orientation of the BEM group in the copolymer film. The dichroic ratio $A_{\|}/A_{\perp}$ monitors the degree of photoinduced orientation for DR1M and BEM groups, respectively. These studies are in progress in M. Pézolet's laboratory at Laval University.

The growth and relaxation of the induced birefringence (points A to C and points C to D, respectively, in Figure 4) can be described by the following biexponential equations, respectively:[10]

$$\Delta n = A[1 - \exp(-k_{\mathrm{a}}t)] + B[1 - \exp(-k_{b}t)] \qquad (3)$$

$$\Delta n = C\exp(-k_{\mathrm{c}}t) + D\exp(-k_{\mathrm{d}}t) + E \qquad (4)$$

Here Δn is the birefringence, t is time, $A-E$ are coefficients, and k_{a}, k_{b}, k_{c}, and k_{d} are rate constants for various processes during writing or relaxation. The sum of A and B represents the maximum induced birefringence, and the value of $(C + D)/(C + D + E)$ represents the fraction of birefringence which disappears after the light is turned off. The fitted parameters are summarized in Table 3.

Table 3. Biexponential Fitted Parameters for Eqs 3 and 4

copoly-mers	A_{n}[a]	B_{n}[a]	k_{a} (s^{-1})	k_{b} (s^{-1})	C_{n}[b]	D_{n}[b]	E_{n}[b]	k_{c} (s^{-1})	k_{d} (s^{-1})
1	0.68	0.32	0.78	0.09	0.08	0.05	0.87	0.83	0.05
2	0.87	0.13	1.27	0.10	0.10	0.06	0.84	0.66	0.03
3	0.94	0.06	1.51	0.23	0.13	0.08	0.80	0.70	0.05
4	0.92	0.08	1.25	0.12	0.11	0.06	0.84	0.75	0.04
5	0.93	0.07	1.70	0.11	0.12	0.07	0.81	0.76	0.05
6	0.93	0.07	1.97	0.15	0.10	0.07	0.83	0.73	0.04
7	0.93	0.07	1.97	0.15	0.11	0.07	0.82	0.71	0.04
8	0.90	0.10	1.88	0.17	0.10	0.14	0.76	0.62	0.02
9	0.95	0.05	1.99	0.12	0.15	0.08	0.77	0.67	0.04
10	0.95	0.05	1.97	0.05	0.13	0.08	0.80	0.67	0.05

[a] A_{n} and B_{n}: normalized A and B (e.g. $A_{\mathrm{n}} = A/(A + B)$). [b] C_{n}, D_{n}, and E_{n}: normalized C, D, and E (e.g. $C_{\mathrm{n}} = C/(C + D + E)$).

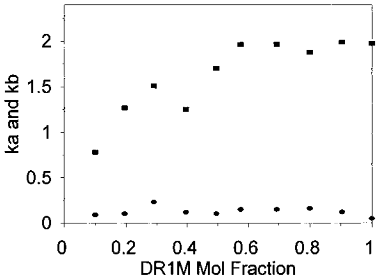


Figure 8. Writing rate constant k_{a} (■) and k_{b} (●) as functions of copolymer composition.

With these parameters, the biexponential equations indicate that two kinds of processes are involved during writing and during relaxation, one fast and the other slow. The fast process is associated with the movement of the side groups DR1M and BEM. It is related to the isomerization processes, the structure of the side group, and its interaction with the other groups. The slow process is mainly associated with the motion of the polymer chain.[10] The writing rate constants k_{a} and k_{b} are plotted as a function of DR1M content in Figure 8. The rate of the slow process (k_{b}) is fairly constant over the whole range of compositions, while the rate of the fast process (k_{a}) increases with the DR1M content, leveling off at about midrange concentrations. In addition to increased levels of alignment, high BEM content films also provide a different environment for the alignment process. A slower rate is observed with increased content of the BEM groups, as expected if cooperative motion is indeed the source of the enhanced birefringence. In films with low BEM content the main contributor to birefringence is the isomerization process; hence the writing rate is faster. BEM groups move because neighboring DR1M groups are changing their orientation. Since the spacer between the rigid group and the main chain is very short, one can assume that main chain motions increase with the increase of BEM group motion. This is confirmed by data in Table 3 which show that A_{n} decreases with decreasing the DR1M fraction, meaning that the slow motion becomes more important for high BEM content copolymers.

Because of the retardation of the writing rate with cooperative motion, a decrease in efficiency of the process is noted for high BEM content copolymers. The efficiency is defined as the birefringence achieved per unit of absorbed energy and can be calculated as follows:[1]

$$\mathrm{Eff} = \Delta n/(Pt) \qquad (5)$$

Here Δn is 95% of the maximum birefringence, P is the laser power density inside the material, and t is the time required to reach 95% of the maximum level (since it is difficult to point out the exact time to reach the maximum birefringence). In a plot of efficiency vs DR1M content (Figure 9), a maximum efficiency is obtained at the midrange compositions of about 40−60 mol % BEM. This is because the BEM group has two opposite effects on the induced birefringence, enhancing the birefringence level and decreasing the orientation rates. As mentioned above, the writing rate constant k_{a} decreases and the contribution of BEM to the birefringence level increases with increasing BEM content. At low BEM concentrations both effects are less impor-

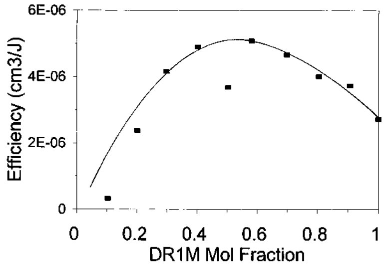


Figure 9. Writing efficiency on poly(DR1M-*co*-BEM) films as a function of copolymer composition. Line drawn to guide the eye.

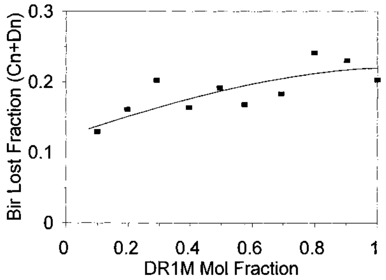


Figure 10. Fraction of birefringence lost by relaxation as a function of composition. Line drawn to guide the eye.

tant. There is little opportunity for enhancement of the birefringence, as there are fewer “neighbors” available for cooperative motion, and an efficiency near that of poly(DR1M) is observed. At high BEM concentrations, there is the opportunity for cooperative enhancement of the birefringence, but the associated decrease in writing rate drives the efficiency down. The maximum efficiency at midrange BEM concentrations can be regarded as enhanced due to the cooperative motion from BEM groups, but in low enough content that they can be sympathetically aligned without a significant decrease in the alignment rate.

In addition to enhanced birefringence levels, the incorporation of BEM groups appears as well to increase the level of the stable birefringence after relaxation. The fraction of birefringence lost, $(C + D)/(C + D + E)$ is plotted vs DR1M content in Figure 10. This loss is smaller for high BEM content. The solid state dynamics of the relaxation process is not well understood, but it is believed that there are at least two separate relaxation processes. One is a relatively fast relaxation through cis−trans thermal isomerization as the written area returns to photochemical equilibrium from the photostationary state[23] and the order is decreased, and the other is a longer term orientational relaxation to relieve the strains induced by the alignment process. This second process should be governed by the size, shape, and interaction energies of the oriented groups, which are similar for both BEM and DR1M. The thermal isomerization from the less stable cis form of the azobenzene units, however, is specific to DR1M. In high BEM content films this contribution to the relaxation would be reduced, and the result is a greater portion of stable birefringence, as observed. Another important parameter would be the glass transition temperature (T_g), but the effect of T_g is not large enough in this copolymer series. As shown in Table 1, the T_g of the copolymers is lower at higher BEM concentrations. Generally, the lower T_g should decrease the stability of the induced birefringence, but this does not happen in this case probably because the T_g of all copolymers varies only in a relatively small range.

Conclusions

A new monomer BEM was synthesized and copolymerized with DR1M in various compositions. Large shifts of λ_{max} in the electronic spectra between high and low BEM content copolymers indicate a strong interaction between the two different polar side groups. Irradiation with polarized light to induce birefringence showed high levels of birefringence per azo unit for the high BEM content copolymers. The enhanced birefringence is attributed to a sympathetic alignment of the BEM groups by the DR1M groups, which suggests a cooperative motion in these amorphous copolymer thin films. To our knowledge this is the first report of cooperative motion in an amorphous polymer. Both the writing and relaxation processes can be fitted by biexponential equations. The writing rate constants increase with the azo content. The efficiency increases with azo content, reaches a maximum at about 40−60 mol % azo groups, and then decreases slightly toward the poly(DR1M) level.

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