

Molecular Addressing? Selective Photoinduced Cooperative Motion of Polar Ester Groups in Copolymers Containing Azobenzene Groups

Almeria Natansohn,^{*,†} Paul Rochon,[‡] Xiansheng Meng,^{†,||} Christopher Barrett,[†] Thierry Buffeteau,^{§,⊥} Sacha Bonenfant,[§] and Michel Pérozet[§]

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

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

Département de chimie, Université Laval, Cité Universitaire, Québec, G1K 7P4, Canada,

Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6, Canada, Laboratoire de Spectroscopie Moléculaire et Cristalline, Université de Bordeaux I, 33405 Talence, France

Received August 22, 1997; Revised Manuscript Received December 13, 1997

ABSTRACT: Amorphous copolymers with rigid azobenzene and ester side groups form films in which birefringence can be induced using linearly polarized light. When both the azobenzene and the ester groups are polar, cooperative motion occurs and high levels of birefringence can be achieved at relatively low azobenzene content. With less polar ester groups, this cooperative motion is significantly reduced, suggesting that the effect is not dictated by steric factors (as is the case in liquid crystalline copolymers), but by electric interaction between the side group dipoles. The differences in cooperative motion of two copolymer systems: poly{4'-[(2-(methacryloyloxy)ethyl)ethylamino]-4-nitroazobenzene (DR1M)-*co*-4-nitrophenyl 4-[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]oxy]benzoate (BEM)} (a polar azo/polar ester pair), and poly{DR1M-*co*-4-phenyl 4-[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]oxy]benzoate (NBEM)} (a polar azo/less polar ester) have been investigated using birefringence measurements and time dependent infrared spectroscopy. Thus, the "molecular addressing" concept introduced by Anderle and Wendorff for liquid crystalline copolymers is real. Kinetic analysis using time-dependent infrared spectroscopy clearly shows that the azobenzene groups move first and are followed by the ester groups, which move to a much greater degree when they have similar polarity (BEM with DR1M).

Introduction

It is well-known that azobenzene groups bound or dissolved in an amorphous or liquid crystalline polymer film can be oriented in a preferred direction using polarized laser light. The photoinduced orientation is very stable for long times. Orientation can be achieved even close to T_g in amorphous polymers, but it is not stable, due to a significant degree of motion in the film at these temperatures, which restores disorder. On the other hand, in liquid crystalline polymer films, the photoinduced orientation is stable above T_g , because of the thermodynamic tendency to form ordered domains, and is lost only at the clearing temperature. In amorphous polymers, the photoinduced orientation can be optically destroyed using circularly polarized light. These phenomena are based on the photoinduced isomerization and the associated motion of the azobenzene groups. This area of research has been extremely active for about 12 years, and quite a few groups have brought different contributions to it. One of the most interesting findings in our laboratory is the cooperative motion of ester groups activated by the motion of the azobenzene groups in amorphous copolymers. This has been demonstrated by analyzing the photoinduced birefringence (which is a bulk phenomenon)¹ and also by investigating various motions at the molecular level using infrared difference spectroscopy.² The copolymers studied contained 4-nitrophenyl 4-[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]oxy]benzoate (BEM) as the ester structural

unit and 4'-[(2-(methacryloyloxy)ethyl)ethylamino]-4-nitroazobenzene (DR1M) as the azobenzene structural unit.

Indirect proof that such a cooperative motion may exist also came from the study of DR1M copolymers with the "inert" comonomer methyl methacrylate.³ The most intriguing reports, however, were published in 1991 and covered two pairs of liquid crystalline copolymers. Using IR spectroscopy, Anderle et al.⁴ showed that above T_g , in the liquid crystalline state, cooperative motion is dominant and both azobenzene and ester groups orient perpendicular to the laser polarization, while below T_g , in the glassy state, only azobenzene groups are "addressed" by the light; the ester groups maintain their original orientation. The authors called this phenomenon "molecular addressing". Their results were almost immediately contradicted by Stumpe et al.,⁵ in a qualitative manner, and by Wiesner et al.,^{6,7} who demonstrated using infrared spectroscopy that the ester groups move (albeit to a lesser degree) even below T_g . Chart 1 illustrates the chemical structures of the "molecular addressing" controversy.

The key question with respect to the cooperative motion in the amorphous phase is what is its driving force. The rigid groups may move in concert due to their similar shape, which is the usual explanation for cooperative motion in the liquid crystalline state, or they may be affected by the neighboring groups' electric fields, as the dipoles are being moved by the polarized light. It is believed that in an amorphous film the azobenzene dipoles are mainly oriented antiparallel to each other,³ thus creating a compensating "electric field" in the film; when one of the azobenzene groups isomerizes and moves, the electric field in the film may force it to fall in a position similar to its initial one, so that

[†] Queen's University.

[‡] Royal Military College.

[§] Université Laval.

^{||} Carleton University.

[⊥] Université de Bordeaux I.

Chart 1

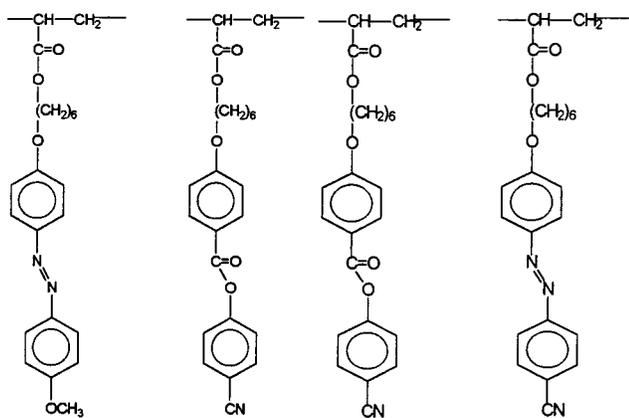
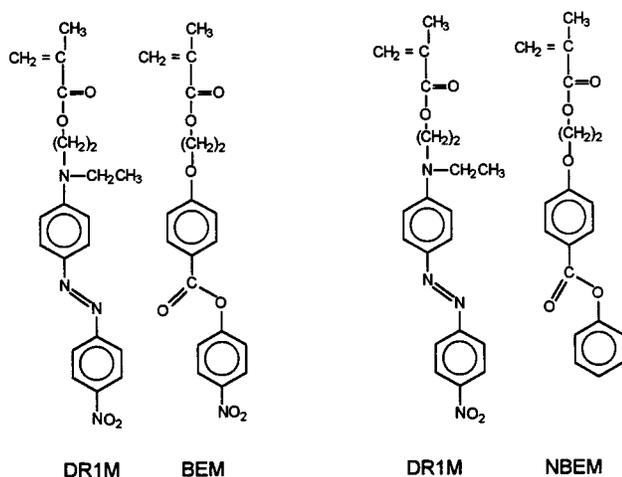
Molecular addressing⁴Motion above and below T_g ^{6, 7}

Chart 2



DR1M

BEM

DR1M

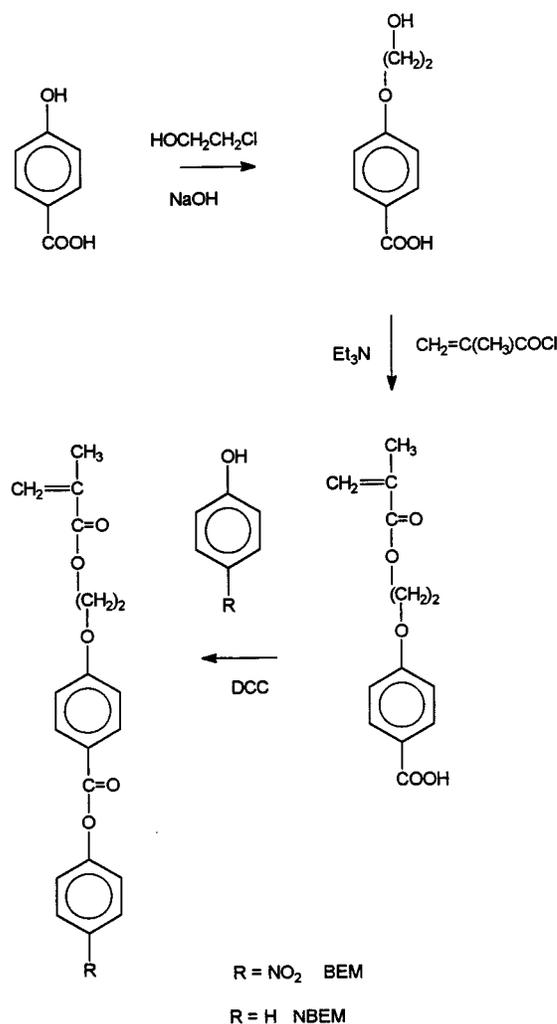
NBEM

the disturbance of the equilibrium is minimal. Thus, it should be more difficult to induce orientation for materials containing a high dipole concentration, and it should also be more difficult for these materials to "lose" orientation by relaxation after the light has been turned off. To answer this question, the obvious strategy is to investigate pairs of polar azo/polar ester copolymers (such as poly(DR1M-*co*-BEM)) in comparison with polar azo/nonpolar ester copolymers. This paper presents the synthesis of 4-phenyl 4-[[2-[2-(2-methyl-1-oxo-2-propenyl)oxy]ethyl]oxy]benzoate (NBEM), its copolymerization with DR1M, and a study of the photo-induced orientation in poly(DR1M-*co*-NBEM) in comparison with poly(DR1M-*co*-BEM). The structures of the two monomer pairs are shown in Chart 2.

Experimental Section

Polymer Synthesis and Characterization. DR1M, BEM, and NBEM were synthesized as previously described¹ and by a slightly modified method. The synthetic route for the monomers BEM and NBEM is shown in Scheme 1. NBEM was obtained as an oil with 84% yield. ¹H NMR (acetone-*d*₆): 8.15 ppm (d, 2 aromatic H, ortho to -COOPh-), 7.40 ppm (t, 2 aromatic H, on the phenol ring, meta to -OCOPh-), 7.2–7.3 ppm (m, 3 aromatic H, on the phenol ring, 2 ortho to and 1 para to -OCOPh-), 7.14 ppm (d, 2 aromatic H, meta to -COOPh-), 6.05 ppm (s, 1H, $H_2C=C(CH_3)CO_2^-$, trans to -CH₃), 5.62 ppm (s, 1H, $H_2C=C(CH_3)CO_2^-$, cis to -CH₃), 4.52 ppm (t, 2 H, -COOCH₂-), 4.42 ppm (t, 2 H, -CH₂Oph-), 1.94 ppm (s, 3 H, -CH₃).

Scheme 1

R = NO₂ BEM

R = H NBEM

The polymerization of DR1M, BEM, and NBEM and their copolymerizations were carried out in dioxane or toluene at 60 °C initiated with AIBN. The polymers obtained were purified by reprecipitation twice from methanol.

Film Preparation and Optical Measurements. Thermal transitions were measured on a Mettler TA-30 DSC instrument equipped with a TA-3000 processor at a scan rate of 20 °C/min. The ¹H NMR spectra were obtained on a Bruker AC-F 200 NMR spectrometer in deuterioacetone or deuterio-dimethyl sulfoxide solution. The density of the films was measured at 23 °C as described previously.³ Films for birefringence measurements were prepared by spin-coating from THF solution onto glass substrates and dried in a vacuum at 100 °C for 20 h. The film thickness was in the 100–200 nm range as measured by interferometry. The procedure for reversibly inducing birefringence with a laser beam on the polymer film was described previously.¹ "Writing" and "erasing" were performed using an argon laser (514 nm) of 6 mW intensity on a spot of 2 mm in diameter, at room temperature.

To prepare films for infrared measurements, the copolymers were dissolved in hot dimethyl sulfoxide and the solutions deposited onto hot (100 °C) calcium fluoride disks. The films were heated at 100 °C in a vacuum oven for about 40 h in order to remove any trace of solvent. The thickness of all films was similar, as designed to produce comparable absorbances in the infrared spectra.

Infrared linear dichroic (IRLD) spectra obtained by polarization modulation (PM) were recorded at room temperature with a Bomem Michelson MB-100 spectrophotometer using the optical setup and the two channel electronic processing previously described.⁸ The films were irradiated in situ in the

Table 1. Copolymer Samples, Compositions, and Glass Transition Temperatures

poly(DR1M-co-BEM)		poly(DR1M-co-NBEM)	
mol % azo	T_g (°C)	mol % azo	T_g (°C)
100	129		
90.3	127	87	112
80.9	125		
70.7	120	64.3	105
61	117		
51.6	116	44	104
41	113	33.8	
32.5	111		
22.7	108	16.3	92
11.6	107	8.2	90
		3.5	87
0	104	0	88

spectrometer using a polarized frequency-doubled Nd:YAG laser (532 nm) with an irradiance at the sample of about 10 mW/cm². Spectra were recorded during approximately 1 h for both the orientation (laser on) and the relaxation (laser off) periods, with a spectral resolution of 4 cm⁻¹ and an acquisition time of 52 s per spectrum. By using a proper calibration procedure,⁹ PM-IRLD spectra were converted quantitatively to the dichroic difference spectra $\Delta A = A_{\parallel} - A_{\perp}$, where A_{\parallel} and A_{\perp} are the absorbances with the infrared radiation polarized parallel and perpendicular to the laser polarization, respectively.

Results and Discussion

Table 1 summarizes the azo content and the glass transition temperatures of all copolymer samples analyzed here. Molecular weights of equivalent polystyrene samples (as determined by GPC) were between 10 000 and 15 000 with no particular dependence on composition noted. The dipole moments for the three structural units were calculated using PCModel and the values found are about 7 D for both DR1M and BEM and only about 0.95 D for NBEM.

Photoinduced Birefringence. Measuring photoinduced birefringence offers a bulk probe for various motions occurring in the sample. For the system poly(DR1M-co-BEM), the birefringence induced by exposure to polarized light was high even at fairly low azo content, and it has been shown that the excess birefringence could be directly correlated with the amount of BEM structural unit present in the copolymer.¹ Figure 1 shows the levels of photoinduced birefringence for the two copolymer series. It seems apparent that the saturated birefringence of poly(DR1M-co-NBEM) increases approximately linearly with the azo content, suggesting that the contribution of the NBEM groups to the overall orientation is negligible. This is in obvious contrast with the poly(DR1M-co-BEM) system, where samples with much lower azo content produce levels of birefringence comparable with poly(DR1M).

The "excess" birefringence in the poly(DR1M-co-BEM) copolymers has been correlated to the amount of BEM groups present in each sample and extrapolated to a "virtual" poly(BEM), showing that such a homopolymer would contribute up to 80% of the birefringence obtained in poly(DR1M).¹ This means that the maximum contribution of a BEM group to the orientation could reach 45% of the overall orientation. If the same calculation is attempted on poly(DR1M-co-NBEM), there would be zero contribution from the NBEM groups, suggesting that they are completely inert to light and that only the azo groups generate the orientation and the birefringence. One must exercise caution when such calcu-

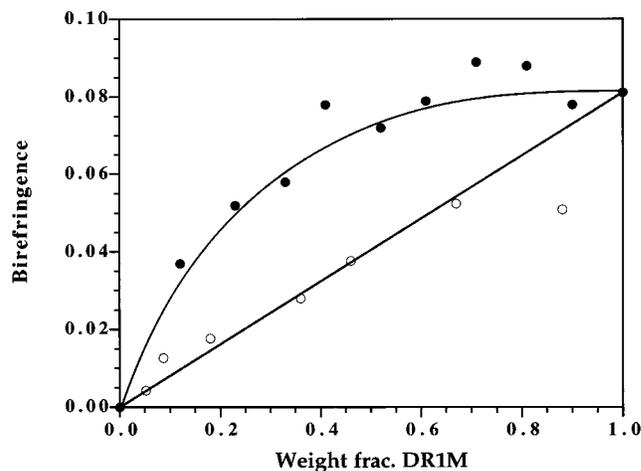


Figure 1. Saturated levels of photoinduced birefringence in poly(DR1M-co-BEM) (full circles) and in poly(DR1M-co-NBEM) (empty circles) as a function of DR1M weight fraction in the copolymer.

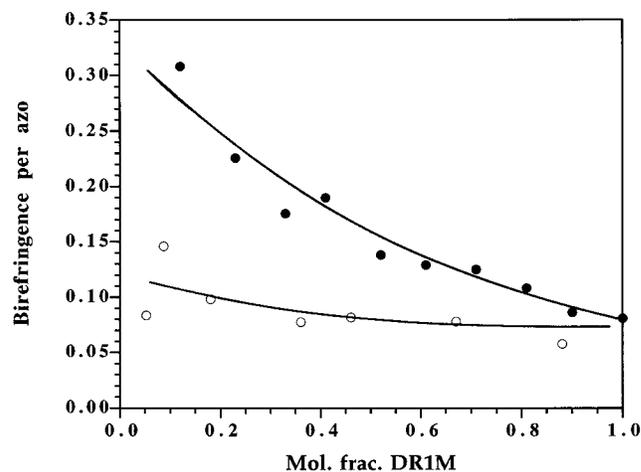


Figure 2. Photoinduced birefringence per azo unit for the two copolymer series: full circles, poly(DR1M-co-BEM); empty circles; poly(DR1M-co-NBEM).

tions are made, because of the assumption that the "normal" dependence of the birefringence on the azo weight fraction should be linear, since this is not necessarily true. There are differences in the glass transition temperatures of the two series of copolymers, which are small differences that may have an influence on the overall birefringence levels.

Figure 2 shows the birefringence calculated per azo structural unit. As in previous reports,³ isolated azo groups appear to contribute more to the birefringence than azo groups having azo neighbors. This has been previously interpreted based on the assumption that isolated azo groups have more freedom to move, while azo groups with azo neighbors will be hindered by the presence of neighboring dipoles. The same interpretation may be valid for the poly(DR1M-co-NBEM) copolymers, while the big deviation of the poly(DR1M-co-BEM) birefringence can be assigned to the "extra" contribution of the BEM units.

The best test for the actual contribution of the DR1M, BEM, and NBEM groups to the orientation process is the in situ analysis of the photoorientation by difference infrared spectroscopy.

Time Dependent Infrared Spectroscopy. To determine the actual contribution of DR1M, BEM, and

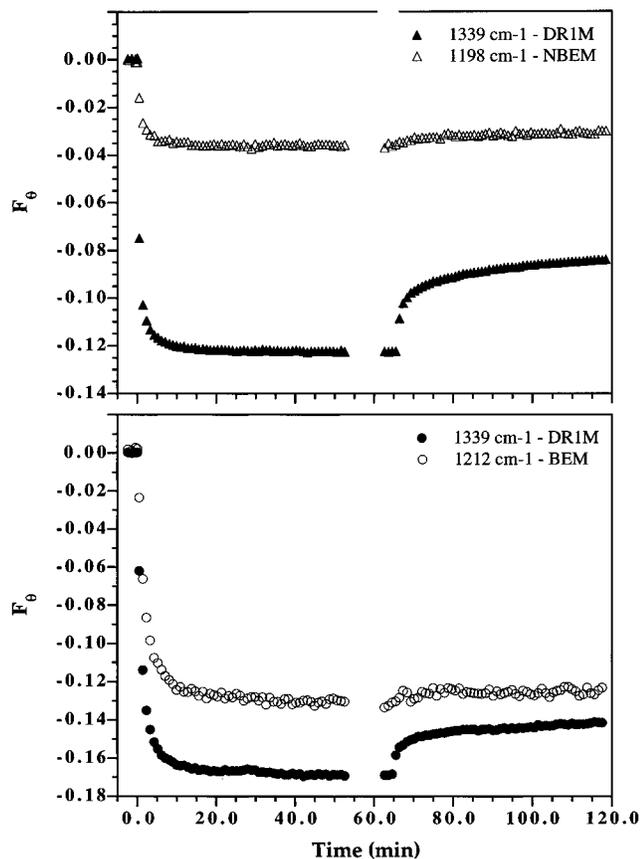


Figure 3. Time dependence of the orientation function F_θ for $\nu_s(\text{NO}_2)$ band (DR1M groups) and $\nu_a(\text{C-O-C})$ bands (BEM and NBEM groups) for poly(DR1M-*co*-NBEM) with 44 mol % azo groups (top) and for poly(DR1M-*co*-BEM) with 52 mol % azo groups (bottom).

NBEM side groups to the orientation process, we have used polarization-modulation time-dependent infrared spectroscopy. With this technique it is possible to record highly accurate dichroic difference spectra, ΔA , as a function of time during both the orientation and the relaxation processes. The orientation function, F_θ , for a uniaxial orientation distribution, can be calculated by normalizing the area of a specific band in the dichroic difference spectrum by the surface area of the corresponding band in the unpolarized absorbance spectrum recorded before sample irradiation:

$$F_\theta = \Delta A / 3A_0$$

To follow independently the orientation function of the active and inert side chains in the copolymers, we have used the 1339 cm^{-1} band, due to the symmetric stretching vibration of the NO_2 group ($\nu_s(\text{NO}_2)$) of the DR1M side group, and the bands at 1212 and 1198 cm^{-1} , due to the C-O-C antisymmetric stretching vibration of the BEM and NBEM groups, respectively.

Figure 3 shows the time dependence of the orientation function, F_θ , for the absorption bands associated with the DR1M, BEM, and NBEM groups in poly(DR1M-*co*-BEM) and poly(DR1M-*co*-NBEM) copolymers containing about 50 mol % azo groups. At time zero, the films are amorphous and all azo and ester groups are randomly distributed in all directions; hence, the orientation function is zero. When the linearly polarized laser light is turned on, the orientation function becomes negative for all observed bands, showing that the rigid side

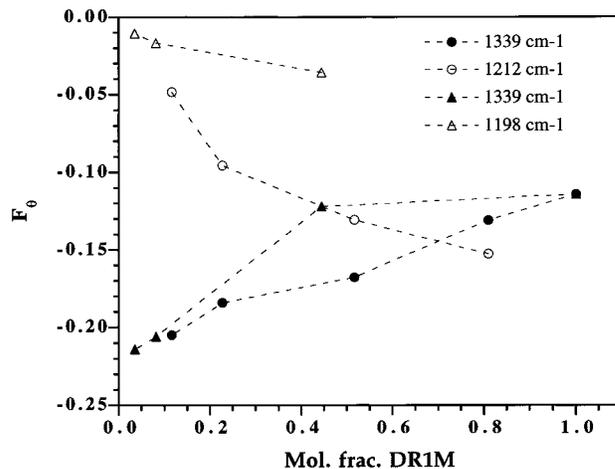


Figure 4. Orientation function of $\nu_s(\text{NO}_2)$ and $\nu_a(\text{C-O-C})$ vibrations as a function of copolymer composition (circles, poly(DR1M-*co*-BEM), full, the azo groups, and open, the ester groups; triangles, poly(DR1M-*co*-NBEM), full, the azo groups, and open, the ester groups).

groups start moving toward a direction perpendicular to the polarization. The orientation increases for the first few minutes, then it reaches a plateau and remains constant until the "writing" laser is turned off. At this point, the system relaxes to some extent, as shown by the reduction in the orientation function, but the initial randomness is not achieved under these conditions.

Figure 3 shows clearly that the azo groups achieve a much higher alignment than the ester groups for the poly(DR1M-*co*-NBEM) copolymer. On the other hand, for the poly(DR1M-*co*-BEM) copolymer, the difference of the orientation between the azo and polar ester groups is drastically reduced and the orientation of the polar ester groups is about three times higher than that of the nonpolar ester groups. Therefore, the polar ester group is involved in the cooperative motion to an extent almost equal to the azo structural units, while the nonpolar ester groups move somewhat, but they do not reach even one-third of the orientation level achieved by the azo structural units of the same copolymer. It is interesting to note that the orientation of the azo groups in poly(DR1M-*co*-BEM) is significantly higher than the orientation of the azo groups in poly(DR1M-*co*-NBEM) (F_θ is about -0.17 and -0.12 in the photostationary state, respectively). The film thicknesses of the two samples are comparable (as measured by the infrared absorbances), and the orientation function is calculated as normalized to the absorbance. Thus, it appears that the orientation of azo groups is also enhanced by the presence of a dipolar environment; i.e., cooperative motion occurs for all polar side groups, as we have previously observed in the copolymers of DR1M with methyl methacrylate.³

Figure 4 shows the effect of the copolymer composition on the orientation function of the DR1M, BEM, and NBEM groups. The azobenzene groups are more oriented when they are relatively isolated in the copolymer (at low content). As the azobenzene content in the copolymer increases, the orientation of the azobenzene groups decreases, and it appears to decrease more in its copolymer with the nonpolar ester group. The differences between the two copolymer series do not appear to be very significant. The azobenzene groups are the least oriented in the homopolymer (pDR1M). In contrast, the ester groups' orientations increase with the

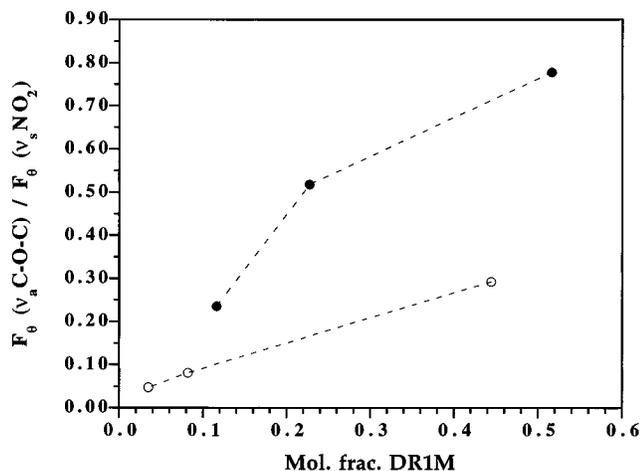


Figure 5. Normalized orientation functions $\nu_a(\text{C-O-C})/\nu_s(\text{NO}_2)$ as a function of copolymer composition: full symbols for poly(DR1M-co-BEM); open symbols for poly(DR1M-co-NBEM).

azobenzene content, and there is a significant difference in orientation between the two copolymer series. In poly(DR1M-co-BEM), the polar ester groups may achieve a better orientation than the azobenzene groups at 81 mol % DR1M units in the copolymer. In the poly(DR1M-co-NBEM) series, the maximum orientation function achieved by the nonpolar ester groups is only about 30% of the orientation of the azobenzene groups. Higher orientation may be achieved at higher azo content in the copolymer, but the overall trend clearly shows that there is a significant difference between polar and nonpolar ester groups in their cooperative motion.

A better way to visualize this difference in orientation is to normalize the orientation function of the asymmetric stretching vibration $\nu_a(\text{C-O-C})$ of the ester group to the symmetric stretching vibration of the NO_2 group of DR1M. This normalized orientation function indicates the extent of participation of the ester group to the overall orientation and is represented as a function of DR1M fraction in Figure 5. The full circles in Figure 5 are normalized orientation functions for poly(DR1M-co-BEM) and show—as was previously reported using bulk orientation (birefringence)¹—that the BEM groups may achieve orientations up to 80% of the level of the DR1M groups at very low BEM contents. There is some contribution from the NBEM groups as well (empty circles in Figure 5), and the trend is similar to that found in poly(DR1M-co-BEM); i.e., the NBEM groups orient more at high DR1M content in the copolymer. However, the level of contribution of the NBEM groups is well below half the level achievable with BEM groups.

Kinetics of Cooperative Motion. It is clear that the ester groups, both the polar ones and to some extent the nonpolar ones, are being moved by the isomerizing azobenzene groups in films well below their glass transition temperature. Since polarized infrared spectroscopy offers a molecular probe for the motions of the azobenzene and ester groups, it is interesting to investigate how the two motions (the driving azobenzene group and the cooperative ester group) relate to each other. Biexponential equations can be used to fit the growth and relaxation of the photoinduced orientation both in bulk¹⁰ and in a separate manner for each infrared band.⁸ It is important to note that different laser powers are being used to photoinduce orientation

Table 2. Kinetic Data for the Photoinduced Birefringence

mol % azo	growth				relax				
	k_a (s^{-1})	k_b (s^{-1})	A_n	B_n	k_c (s^{-1})	k_d (s^{-1})	C_n	D_n	E_n
Poly(DR1M-co-BEM)									
100	1.97	0.05	0.95	0.05	0.68	0.04	0.12	0.08	0.80
90.3	1.99	0.12	0.95	0.05	0.67	0.03	0.15	0.08	0.77
80.9	1.88	0.17	0.90	0.10	0.62	0.02	0.10	0.14	0.76
70.7	1.97	0.15	0.93	0.07	0.71	0.04	0.11	0.07	0.82
61	1.97	0.15	0.93	0.07	0.73	0.04	0.10	0.07	0.83
51.6	1.70	0.11	0.93	0.07	0.76	0.05	0.12	0.07	0.81
41	1.25	0.12	0.92	0.08	0.75	0.04	0.11	0.06	0.84
32.5	1.51	0.23	0.94	0.06	0.70	0.05	0.13	0.08	0.80
22.7	1.27	0.10	0.87	0.13	0.66	0.03	0.10	0.06	0.84
11.6	0.78	0.09	0.68	0.32	0.83	0.05	0.08	0.05	0.87
Poly(DR1M-co-NBEM)									
87	2.54	0.19	0.85	0.15	0.47	0.05	0.12	0.11	0.77
64.3	2.23	0.16	0.92	0.08	0.96	0.07	0.10	0.13	0.77
44	2.89	0.25	0.84	0.16	1.07	0.07	0.11	0.15	0.74
33.8	1.79	0.14	0.91	0.09	1.03	0.07	0.15	0.16	0.69
16.3	2.38	0.19	0.83	0.17	1.06	0.07	0.15	0.16	0.69
8.2	1.02	0.15	0.70	0.30	0.37	0.27	0.15	0.12	0.73
3.5	2.85	0.10	0.35	0.65	1.40	0.17	0.11	0.20	0.69

in order to measure birefringence and infrared difference spectra; thus, the kinetic parameters found cannot be compared between the two processes. The only acceptable comparison is between the preexponential factors which describe the relative weight of each process. The two biexponential equations used are

$$\Delta n \text{ or } F_\theta = A(1 - \exp(-k_a t)) + B(1 - \exp(-k_b t))$$

for photoinduced orientation and

$$\Delta n \text{ or } F_\theta = C \exp(-k_c t) + D \exp(-k_d t) + E$$

for orientation relaxation. It is convenient to normalize the preexponential parameters; thus, A_n is defined as $A/(A+B)$, and C_n is defined as $C/(C+D+E)$, etc. E_n is the fraction of birefringence conserved for very long times.

Table 2 summarizes the bulk kinetic data obtained by measuring photoinduced birefringence and its relaxation. With respect to photoinducing birefringence, the rate constant of the fast process is almost independent of composition for the polar-nonpolar pair, but it increases with increasing azo content for the polar-polar pair, reaching its highest values at a similar level with the polar-nonpolar pair. This would suggest that the BEM groups are involved in the fast process, and they slow the motion of the DR1M groups due to cooperative motion. Since there is little cooperative motion of the NBEM groups, their effect on the rate constants is negligible. The slow process rate constants are almost the same for all samples. These motions can be analyzed separately for each type of groups using the PM infrared results. Figure 6 shows the individual fast rate constant of orientation of DR1M in the copolymers. As can be seen, the motion of DR1M increases with azo content for the polar-polar copolymer, but it always is slower than in the polar-nonpolar copolymer. The azo groups are much freer to move because they do not interact with the nonpolar ester groups (fast rate constants are more than double until at least 50 mol % azo content). The fast rate constant for the ester groups also increases with the azo content, but the motion of the ester groups lags behind that of the azo group, which

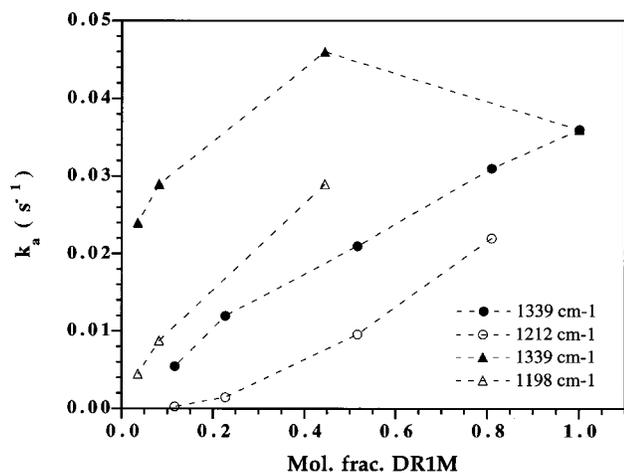


Figure 6. Fast rate constants determined by infrared spectroscopy for photoinduced orientation of the azo and ester groups as a function of copolymer composition (circles, poly(DR1M-*co*-BEM), full, the azo groups, and open, the ester groups; triangles, poly(DR1M-*co*-NBEM), full, the azo groups, and open, the ester groups).

is not surprising because the rate constant for the orientation of the inactive side groups is dictated by that of the DR1M side groups (see Figure 6).

The relative contribution of the fast process of inducing bulk birefringence, A_n , (Table 2) is smaller at low azo content, but reaches about 90% when the azo content is about 30% in the copolymer and remains constant after that. The two copolymer systems behave in a similar manner with respect to A_n and B_n .

Regarding the bulk birefringence relaxation (Table 2), the data show less distinct trends, but it can be seen that the rate constant of the fast process for poly(DR1M-*co*-BEM) is independent of the composition, while in poly(DR1M-*co*-NBEM) the rate constant steadily decreases as the azo content increases, reaching the level of poly(DR1M-*co*-BEM) and poly(DR1M). This can be explained in terms of cooperative motion, since at low azo content there should be less interference from the ester groups in poly(DR1M-*co*-NBEM). As the azo content increases, cooperative motion between azo groups become dominant and may be slowing down the relaxation process, making the birefringence more stable. For the polar-polar copolymer, there is the same dipolar interaction between the groups for all compositions, because of the azo-azo and azo-ester interactions.

The most interesting parameter in Table 2 is E_n , because it reflects the long term stability of the birefringence. It slightly decreases for poly(DR1M-*co*-BEM) and slightly increases for poly(DR1M-*co*-NBEM) with the azo content in the copolymers. The increase in stability for the polar-nonpolar pair as the polarity of the copolymer increases can be explained as above, but why copolymers composed mostly of polar ester groups maintain their orientation better than those with mostly polar azo groups is not so obvious. Figure 7 shows the E_n values obtained from the infrared spectra for the three kinds of groups in the two types of copolymers. First, it is clear that the ester groups maintain more of their orientation at long term than the azo groups. Second, the polar-polar copolymers are always more stable than the corresponding polar-nonpolar pairs, for both the ester and the azo groups. The stability seems to decrease slightly for each component at higher azo

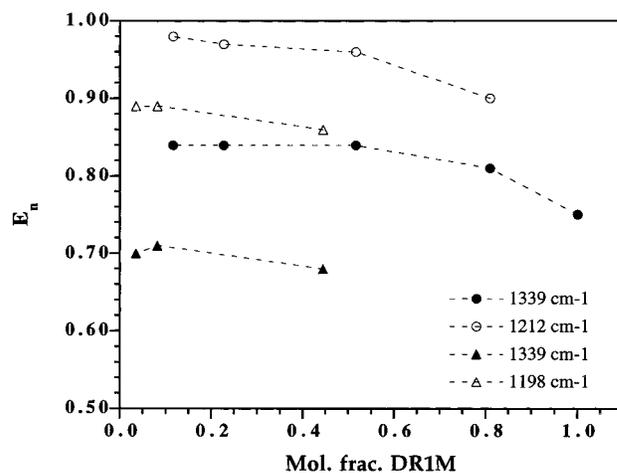


Figure 7. Values of E_n determined by infrared spectroscopy of the azo and ester groups as a function of copolymer composition (circles, poly(DR1M-*co*-BEM), full, the azo groups, and open, the ester groups; triangles, poly(DR1M-*co*-NBEM), full, the azo groups, and open, the ester groups).

content. These data can be related to the fact that most of the orientation is probably destroyed by the thermal *cis*-*trans* isomerization of the azobenzene groups which happen to be in the *cis* state when the light is turned off. This randomizes the orientation and obviously affects the azobenzene groups more than the ester groups; it is also more important at higher azobenzene contents. The higher stability of the polar ester groups may be explained by the electric field effect in the film; i.e., it would be easier to move a nonpolar ester group out of its oriented state since that would perturb the electric field less than moving a polar ester group.

Discussion

All the data shown here demonstrate the existence of cooperative motion to a great degree in the poly(DR1M-*co*-BEM) system and to a much lesser degree in poly(DR1M-*co*-NBEM), indicating that the polarity of the system is the driving factor for the cooperative motion of the ester groups with the azobenzene groups below the glass transition temperature of the film. In this context it is interesting to analyze again the data published in 1991 regarding cooperative motion in liquid crystalline azo copolymers below T_g , i.e., in their amorphous state. Anderle et al.⁴ used a nonpolar azobenzene structural unit (calculated dipole moment = 0.04 D) and a polar ester (calculated dipole moment = 5.35 D). Below T_g , moving the azobenzene groups through isomerization cycles would not affect the electric field of the film much, because of the relatively nonpolar nature of the azo groups. Consequently, the ester groups will not really move in concert, thus "molecular addressing" could be achieved. Above T_g , the dominant factor had to be steric, since the films were liquid crystalline. On the other hand, Wiesner et al.^{6,7} used a polar azobenzene (calculated dipole moment = 4.4 D) and a polar ester (5.35 D) comonomer pair. Below T_g there had to be considerable cooperative motion, as was demonstrated in our system; thus, in this particular case, no "molecular addressing" was possible. Nevertheless, both reports were "right", the small detail was the polarity of the comonomers, which at that time was not understood as a decisive factor.

Conclusions

The analysis, in comparison, of these two copolymer series elucidates the existence of a cooperative motion in purely amorphous systems. The previously studied liquid crystalline copolymers in their amorphous state (below T_g) also showed cooperative motion, but its interpretation was based on principles of liquid crystal chemistry; i.e., it was believed that this cooperative motion is due to the similar shape of the rigid groups. However, even in the previous literature, cooperative motion was evidenced in the amorphous state only when the rigid groups were polar. Our research, including various pairs of amorphous copolymers, containing combinations of polar and nonpolar rigid groups, indicates that the polarity of the groups involved is the major factor in this cooperative motion below T_g . The cooperative motion probably appears due to changes in the overall electric field of the randomly distributed dipoles when they realign through trans-cis-trans isomerizations perpendicular to the light polarization.

Acknowledgment. This research is funded by the Office of Naval Research, the NSERC, Canada, and the Department of Defence, Canada. M.P. thanks FCAR

Quebec for funding, T.B. thanks the NATO committee for a fellowship and A.N. thanks the Canada Council for a Killam Research Fellowship.

References and Notes

- (1) Meng, X.; Natansohn, A.; Barrett, C.; Rochon, P. *Macromolecules* **1996**, *29*, 946.
 - (2) Buffeteau, T.; Natansohn, A.; Rochon, P.; Pérolet, M. *Macromolecules* **1996**, *29*, 8783.
 - (3) Brown, D.; Natansohn, A.; Rochon, P. *Macromolecules* **1995**, *28*, 6116.
 - (4) Anderle, K.; Birenheide, R.; Werner, M. J. A.; Wendorff, J. H. *Liq. Cryst.* **1991**, *9*, 691.
 - (5) Stumpe, J.; Muller, L.; Kreysig, D.; Hauck, G.; Koswig, H. D.; Ruhmann, R.; Rubner, J. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 81.
 - (6) Wiesner, U.; Reynolds, N.; Boeffel, C.; Spiess, H. *Makromol. Chem.* **1991**, *12*, 457.
 - (7) Wiesner, U.; Reynolds, N.; Boeffel, C.; Spiess, H. W. *Liq. Cryst.* **1992**, *11*, 251.
 - (8) Buffeteau, T.; Pérolet, M. *Appl. Spectrosc.* **1996**, *50*, 948.
 - (9) Buffeteau, T.; Desbat, B.; Pérolet, M.; Turlet, J. M. *J. Chim. Phys.* **1993**, *90*, 1467.
 - (10) Ho, M. S.; Natansohn, A.; Rochon, P. *Macromolecules* **1995**, *28*, 6124.
- MA9712716