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Study of Cooperative Side Group Motions in Amorphous Polymers by Time Dependent Infrared Spectroscopy

Thierry Buffeteau,[†,‡] **Almeria Natansohn,**[§] **Paul Rochon,**[||] **and Michel Pézolet***[,‡]

Centre de Recherche en Sciences et Ingénierie des Macromolécules, Département de Chimie, Université Laval, Québec, Canada, G1K 7P4, Department of Chemistry, Queen's University, Kingston, Ontario, Canada, K7L 3N6, and Department of Physics, Royal Military College, Kingston, Ontario, Canada K7K 5L0

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ABSTRACT: Amorphous copolymers of 4′-[(2-(methacryloyloxy)ethyl)ethylamino]-4-nitroazobenzene (DR1M) and 4-nitrophenyl 4-[2-(methacryloyloxy)ethyl]benzoate (BEM) have been studied by time dependent polarization modulation infrared spectroscopy. Bands due to several chemical groups of the copolymers have been analyzed in order to follow simultaneously the time dependence of the photoactive (DR1M) and inert (BEM) groups during the orientation (linearly polarized laser on) and relaxation (laser off) periods. The results show clearly the cooperative orientation of the BEM groups with the azobenzene side chains. The level of orientation and the rate constants of the two types of structural units have been determined for different copolymer compositions by fitting the orientation and relaxation curves with biexponential functions. The fast "writing" rate constant of DR1M increases linearly with the DR1M content while the slow "writing" rate constant is almost constant. The orientation kinetic of BEM groups is rather described by a monoexponential function and is mainly governed by that of photoactive side chains at high DR1M content. During the relaxation process, the fast and slow rate constants of DR1M groups are fairly constant over the whole range of copolymer composition while the degree of orientation of BEM groups is almost completely maintained.

Introduction

Amorphous high-T_g polymers, containing azobenzene groups can undergo optically induced reversible molecular orientation. When such polymer films are addressed with linearly polarized light, the azobenzene groups orient perpendicularly to the polarization direction while circularly polarized light restores the random distribution of orientation of the azobenzene side chains.[1] The phenomenon (photochemically induced *trans*−*cis*−*trans* isomerization of the azobenzene groups) is now very well-understood. It has initially been described on a polymer doped with an azobenzene derivative,[2] and extensive studies were performed on liquid crystalline polymers, especially for holographic storage applications.[3]

There are some structural factors which influence the degree of ordering and the rate of achieving this order in amorphous polymer films. One of these factors is the nature of the neighbor of the azobenzene unit. For copolymers containing azobenzene and methyl methacrylate structural units, it appears that azobenzene groups tend to move in concert with each other.[4] If one translates the photoinduced orientation into birefringence, measurements of birefringence reveal that its level and the rate of achieving it are strongly dependent on the distribution of the azobenzene units in the main chain. This is not a composition effect, since blends containing exactly the same amount of azobenzene units show a linear dependence of birefringence on azo content. However, birefringence values are an indirect proof for cooperative motion. Direct observation of the motion of the azobenzene groups can be achieved by using time dependent polarization modulation infrared spectroscopy.[5] For the system described above, results clearly indicate different motions of azobenzene groups depending on their next neighbor.[6]

Copolymers containing azobenzene and "inert" groups of similar shapes and polarities, such as substituted phenyl benzoates, are ideal systems to investigate the cooperative motion, because—in principle—one can investigate separately the motions of the two types of groups. A few studies of liquid crystalline polymers containing azobenzene and phenyl benzoate substituents have been performed using forced Rayleigh scattering,[7] solid-state ^{13}C-NMR,[8] and polarized infrared spectroscopy.[9−11] In these cases, where the azobenzene groups constitute the mesogens, cooperative motion is intrinsic to the system. Its cause is the thermodynamic tendency to organize due to a minimum conformational energy when the rod-shaped entities are aligned. It is surprising, however, to encounter the same type of cooperative motion in purely amorphous polymers, where there is no thermodynamic tendency of alignment. In fact, Anderle et al.[10] suggested that the phenyl benzoate groups could be moved only in the liquid crystalline phase, and that below the glass transition temperature (T_g) of the film (in the amorphous phase) only the azobenzene groups can be moved. This was, however, shown not to be true; the phenyl benzoate groups do move in concert even below T_g.[9]

In order to study systematically the cooperative motion of phenyl benzoate groups in their copolymers containing azobenzene units, a series of copolymers of the general formula shown in Scheme 1 [poly(DR1M-*co*-BEM)] has been synthesized and investigated with respect to the photoinduced birefringence.[12] These copolymers are completely amorphous, since the spacer between the rod-shaped group and the main chain is short and does not allow the decoupled motion necessary to create a liquid crystalline phase. The contribution

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* Author to whom correspondence should be sent.

[†] Permanent address: Laboratoire de Spectroscopie Moléculaire et Cristalline, Université de Bordeaux I, 33405 Talence, France.

[‡] Université Laval.

[§] Queen's University.

[||] Royal Military College.

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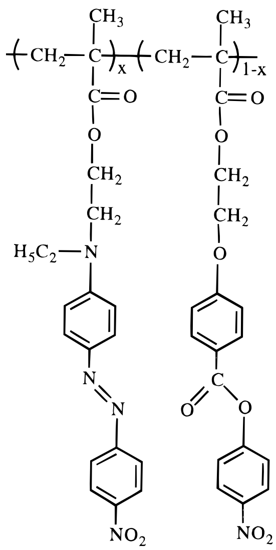
Scheme 1



of the phenyl benzoate units (BEM) to the photoinduced birefringence is very significant, calculated to a maximum of 80% of the contribution of the azobenzene groups (DR1M).

Poly(DR1M-*co*-BEM) samples have been investigated by time dependent polarization modulation infrared spectroscopy, and the results are presented in this paper. Bands due to several chemical groups of the copolymers have been analyzed in order to follow simultaneously the time dependence of the photoactive (DR1M) and the nonphotoactive (BEM) groups during the orientation (linearly polarized laser on) and relaxation (laser off) processes. A quantitative analysis of the orientation and relaxation kinetics by biexponential functions has allowed us to extract the level of orientation and the rate constants of the DR1M and BEM groups as a function of the copolymer composition. The results obtained in this paper reveal a strong interaction between the photoactive and the nonphotoactive groups and are interpreted as clear evidence for the cooperative motion of DR1M and BEM groups in these amorphous materials.

Experimental Section

Materials. The synthesis of 4′-[(2-(methacryloyloxy)ethyl)-ethylamino]-4-nitroazobenzene (DR1M) and 4-nitrophenyl 4-[2-(methacryloyloxy)ethyl]benzoate (BEM) and their copolymerization have been described elsewhere.[1,12] Random copolymers of poly(DR1M-co-BEM) with DR1M mole fractions (x) of 0.12, 0.23, 0.52, 0.81, and 1.0 have been investigated. To prepare thin films, the copolymers were dissolved in hot dimethyl sulfoxide and the solutions were 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 remaining solvent.

Experimental Setup. Infrared linear dichroism (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.[5] The optical anisotropy in the copolymer films was induced *in situ* in the spectrophotometer using a polarized frequency-doubled Nd:YAG laser (532 nm) with an irradiance at the sample of about 10mW/cm^2. The angle between the laser and infrared beams was 20°. PM-IRLD spectra of copolymer films were collected during the orientation (laser on) and the relaxation (laser off) periods. The total acquisition time for the orientation and relaxation kinetics was about 1 h. In order to get spectra with signal-to-noise ratio high enough to obtain kinetic curves with low data dispersion, 50 scans were collected for each spectrum at a resolution of 4 cm^{-1}. By using a proper calibration procedure,[13] PM-IRLD spectrum can be related quantitatively to the dichroic difference spectrum $\Delta A = A_{\parallel} - A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the absorbances with the infrared radiation polarized parallel and perpendicular to the laser polarization, respectively.

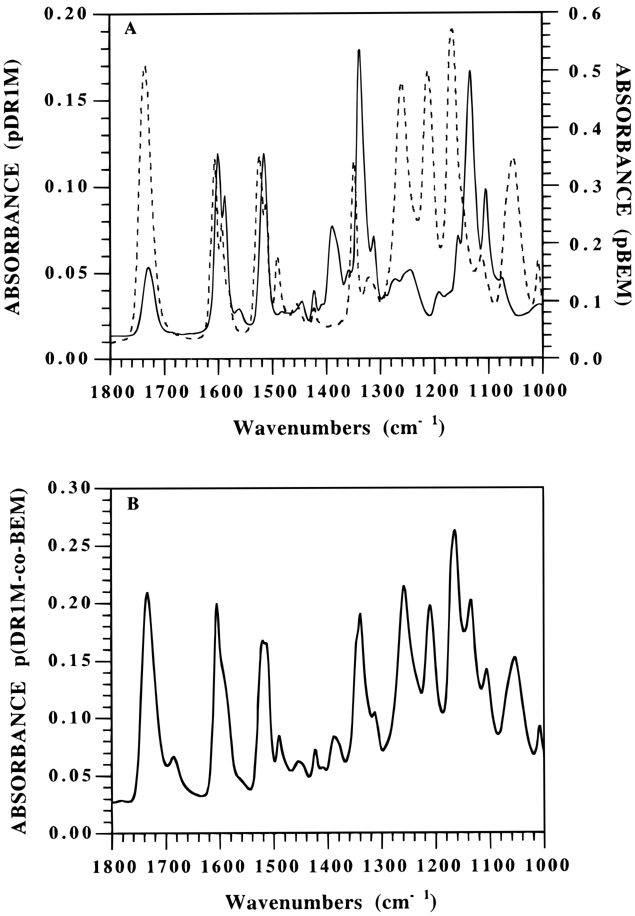


Figure 1. (A) Unpolarized infrared spectra of the poly(DR1M) (solid line) and poly(BEM) (dashed line) films recorded before irradiation. (B) Unpolarized absorbance spectrum of a poly-(DR1M-*co*-BEM) film with a DR1M mole fraction of 0.23 recorded before irradiation.

Results and Discussion

Infrared Spectra. The infrared spectra in the 1000−1800 cm^{-1} region of poly(BEM) and poly(DR1M) homopolymers recorded before irradiation are presented in Figure 1A. The assignment and the structural origin of characteristic absorption bands in these spectra are summarized in Table 1. The infrared spectra of the poly(BEM) and poly(DR1M) homopolymers exhibit some bands characteristic of either the phenyl benzoate or the azobenzene units. For example, the bands due to the C−O−C asymmetric stretching vibration, ν_a(C−O−C), of the C−O−Ar and Ar−CO−O−Ar′ functional groups of poly(BEM) occur at 1260, 1212, and 1166 cm^{-1}, whereas the band due to the N=N stretching vibration of poly(DR1M) is located at 1388 cm^{-1}. Bands due to the symmetric ν_s, and asymmetric, ν_a, stretching vibrations of the NO_2 group as well as the bands due to the ν_{8a}- and ν_{8b}(C=C) stretching vibrations of the para-substituted phenyl rings are present in the two spectra, but their frequencies are shifted because of the different environment of these groups in the pDR1M and pBEM homopolymers. The $\nu_s(NO_2)$ band for poly(DR1M) and

Table 1. Assignment, Frequency, and Structural Origin of the Major Bands in the Infrared Spectra of Poly(DR1M) and Poly(BEM) Homopolymers

assignment[a]	frequency (cm^{-1})	structural origin
$\nu(C{=}O)$	1736	pBEM
	1729	pDR1M
$\nu(C{=}C)_{Ar}$ (ν_{8a})	1607	pBEM
	1601	pDR1M
$\nu(C{=}C)_{Ar}$ (ν_{8b})	1594	pBEM
	1588	pDR1M
$\nu_a(NO_2)$	1524	pBEM
	1516	pDR1M
$\nu(C{=}C)_{Ar}$ (ν_{19a})	1512	pBEM + pDR1M
$\nu(C{=}C)_{Ar}$ (?)	1491	pBEM
$\delta(CH_2)$	1460−1440	pBEM + pDR1M
$\nu(C{=}C)_{Ar}$ (ν_{19b})	1424	pBEM + pDR1M
$\nu(N{=}N)$	1388	pDR1M
$\nu_s(NO_2)$	1348	pBEM
	1338	pDR1M
$\nu_a(C{-}O{-}Ar)$	1260	pBEM
$\nu_a(C{-}O{-}C)$	1212	pBEM
Ar−CO−O−Ar′	1166	
	1156	
$\nu(C{=}C)_{Ar}$	1133	pDR1M
	1105	
$\nu_s(C{-}O{-}Ar)$	1055	pBEM

[a] a = asymmetric, s = symmetric, Ar = aromatic).

poly(BEM) occurs at 1338 and 1348 cm^{-1}, respectively, whereas the ν_{8a}- and ν_{8b}(C=C) bands occur at 1601 and 1588 cm^{-1} for poly(DR1M) and at 1607 and 1594 cm^{-1} for poly(BEM), respectively.

The infrared spectrum in the 1000−1800 cm^{-1} region of poly(DR1M-*co*-BEM) with DR1M mole fraction of 0.23 before irradiation is presented in Figure 1B. All bands given in Table 1 appear in this spectrum with relative intensities depending on the copolymer composition. As can be seen, the bands due to the ν(N=N) and ν_a(C−O−C) vibrations associated with DR1M and BEM groups, respectively, are well-resolved and can thus be use to probe independently the orientation of the two structural units of the copolymers. On the other hand, the bands due to the ν_s and ν_a vibrations of the NO_2 group and those associated with the ν_{8a}- and ν_{8b}(C=C) stretching vibrations of the para-substituted phenyl rings of the DR1M and BEM groups overlap in the spectrum of the copolymers. Therefore, it was necessary to decompose these bands in order to separate the contribution of the photoactive and nonphotoactive groups in the infrared spectra of the copolymers. The integrated intensity of each component was evaluated using a least-squares fitting procedure with the minimum number of components. The frequency and the bandwith of each component were obtained from the spectra of the homopolymers and were not allowed to vary. Therefore, only the intensity of each component was adjusted.

Time Dependence of the Orientation and Relaxation Processes. The time dependent behavior of dichroic difference spectra of poly(DR1M-*co*-BEM) with a DR1M mole fraction of 0.52 during the orientation (laser on) and relaxation (laser off) periods are presented in Figure 2. For clarity, the scale of the ΔA axis has been inverted. When the polarized writing laser is turned on, the intensity of the bands observed in the dichroic difference spectra increases for approximately 15 min and then remains constant. As seen in this figure, most bands observed in the difference spectrum are negative and come from both the azobenzene or the phenyl benzoate side chains. Since the vibrations associated with these bands have their transition dipole moment essentially parallel to the long axis of the azobenzene or phenyl benzoate groups, the dichroic difference spectra clearly demonstrate that the irradiation of the copolymer produces a preferred orientation of the DR1M and BEM groups perpendicular to the writing polarization direction. As the BEM groups are not involved in the photoisomerization process, their orientation has to come from a cooperative motion of the BEM and DR1M groups, thus proving unambiguously that the photoactive and nonphotoactive side chains move in concert when the copolymer is irradiated. This result is in agreement with previous studies on liquid crystalline polymers containing azobenzene and phenyl benzoate groups.[9,11] When the writing laser is turned off, the intensity of some bands decreases slightly for the first few minutes, showing that the induced optical anisotropy is not completely preserved.

In order to allow the quantitative comparison of the time dependent behavior of different bands associated with the DR1M and BEM groups, the orientation function, F_θ, for a uniaxial orientation distribution was calculated by normalizing the area of each band in the dichroic difference spectrum, ΔA, by the integrated absorbance of the corresponding band in the unpolarized spectrum recorded before sample irradiation, A_0: $F_\theta = \Delta A/3A_0$. In this case the orientation function is associated with the orientation of the transition dipole moment of a given vibration. The limiting values of F_θ are 1.0 or −0.5, if the transition moments are perfectly oriented parallel or perpendicular to the polarization direction of the writing laser, respectively, or equal to zero for random orientation.

In Figure 3, values of F_θ for several vibrations of the DR1M and BEM groups and for different DR1M mole ratios ($x = 0.12$, 0.23, 0.52, and 0.81) are represented as a function of time for the irradiation period and after turning off the writing laser. The bands located at 1601, 1388, and 1338 cm^{-1} have been selected to follow the time dependence of the orientation of the DR1M groups, whereas the orientation of the BEM groups has been measured from the bands located at 1607, 1348, and 1212 cm^{-1}. For a copolymer of given composition, the time dependent behavior of F_θ for the DR1M bands is quite similar, but the limiting value of the orientation function is not the same for the three bands, since the direction of the transition dipole moment of each vibration with respect to the azobenzene molecular axis is different. At low DR1M mole fractions, the maximum degree of light-induced orientation of the DR1M groups is higher, but it is reached more slowly. During the relaxation period, the absolute value of the orientation function decreases slightly due to both thermal relaxation and angular reorientatio of the azobenzene groups. The degree of orientation of BEM bands increases as the mole fraction of DR1M groups increases, except for the band at 1607 cm^{-1} associated with ν_{8a}(C=C) stretching vibrations of the para-substituted phenyl rings. The loss of orientation during the relaxation period is very weak for all bands associated with the BEM groups.

Fit of the Orientation and Relaxation Curves. It has recently been shown from birefringence measurements that it is possible to fit very well the orientation and relaxation curves of poly(DR1M) homopolymers[14] and of poly(DR1A-*co*-MMA)[4] and poly(DR1M-*co*-BEM)[12] copolymers using the following biexponential functions

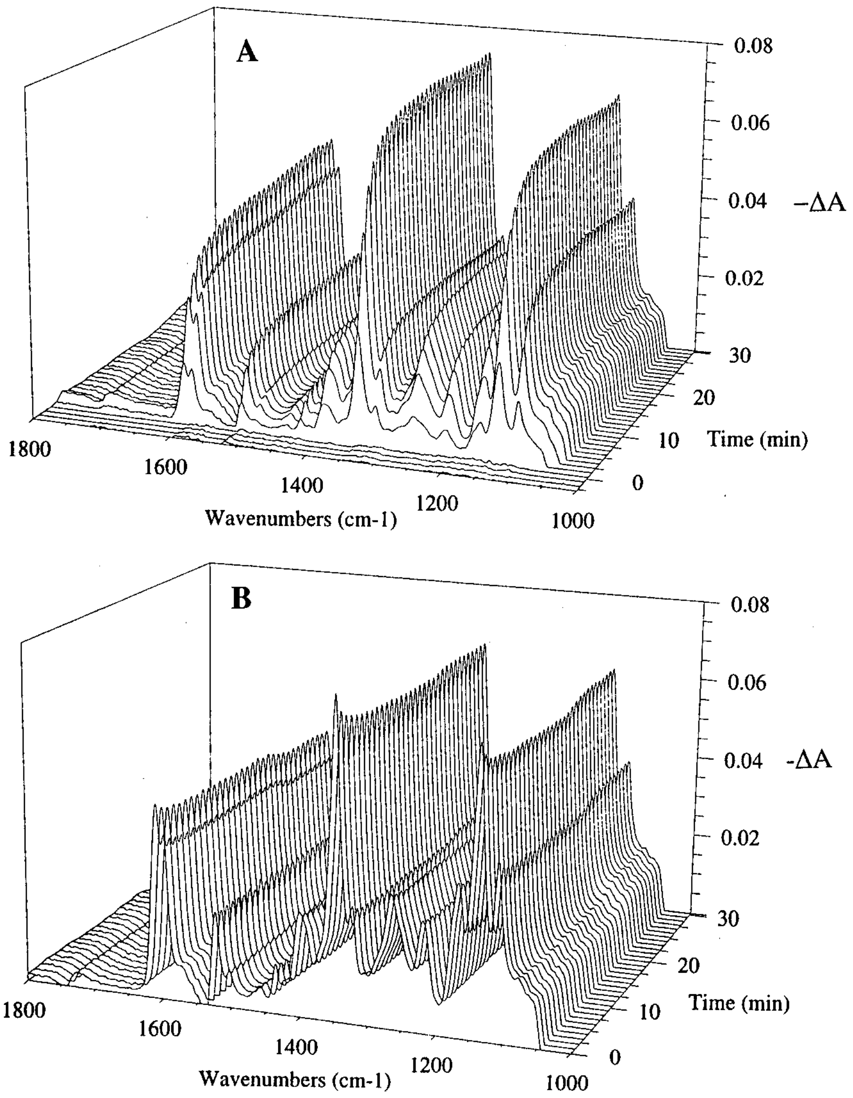


Figure 2. Time dependence of the dichroic difference spectra for optically induced (A) orientation and (B) relaxation processes of a poly(DR1M-*co*-BEM) film with a DR1M mole fraction of 0.23.

for the orientation or relaxation processes, respectively:

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

$$F_\theta(t) = C \exp(-k_c t) + D \exp(-k_d t) + E \quad (2)$$

In these equations k_a and k_b are the fast and slow orientation rate constants while k_c and k_d are the fast and slow relaxation rate constants. The constants A, B, C, and D are contributions to F_θ of the different exponential response modes, and E is F_θ at infinite time. It has been suggested from the analysis of the birefringence results that, for the orientation process, the "fast" response mode is associated with dipole reorientations through *trans*–*cis*–*trans* isomerization. The "fast" decay for the relaxation process has been attributed to thermal *cis*–*trans* isomerization and dipole reorientation as the written polymer returns to photochemical equilibrium from the photostationary state. On the other hand, the "slow" component of both the orientation and relaxation processes is associated with the dipole reorientations involving motions of the main chain of the polymer.[4,12,14]

More recently, Buffeteau and Pézolet[5] have also shown that the orientation and relaxation curves of poly(DR1A) obtained by time-dependent polarization modulation infrared spectroscopy are also well fitted using the same biexponential functions. However, by using infrared bands due to several chemical groups of the homopolymer, it has been shown that the azobenzene groups and the main chain of the polymer display the same kinetics behavior. Although the maximum induced orientation of the polymer chain is much smaller than that of the photoactive side chains, the kinetics of orientation of the two parts of the polymer, and in particular the values of their rate constants, are nearly the same. These results show clearly that the "slow" and "fast" response modes are not separately associated with the main chain and the side chains of the polymer, respectively. Moreover, theoretical models of the *trans*–*cis*–*trans* photoisomerization cycle also suggest that at least two exponentials are necessary to describe adequately the orientation and relaxation processes.[14,15] Therefore, it is very likely that the "fast" and "slow" response modes observed by infrared spectroscopy are both associated with the *trans*–*cis*–*trans* photoisomerization.

In order to extract more quantitative information from the results of Figure 3, the writing curves for vibrations associated with the DR1M and BEM groups were fitted with eq 1. The parameters obtained for the writing curves of poly(DR1M-*co*-BEM) with a DR1M

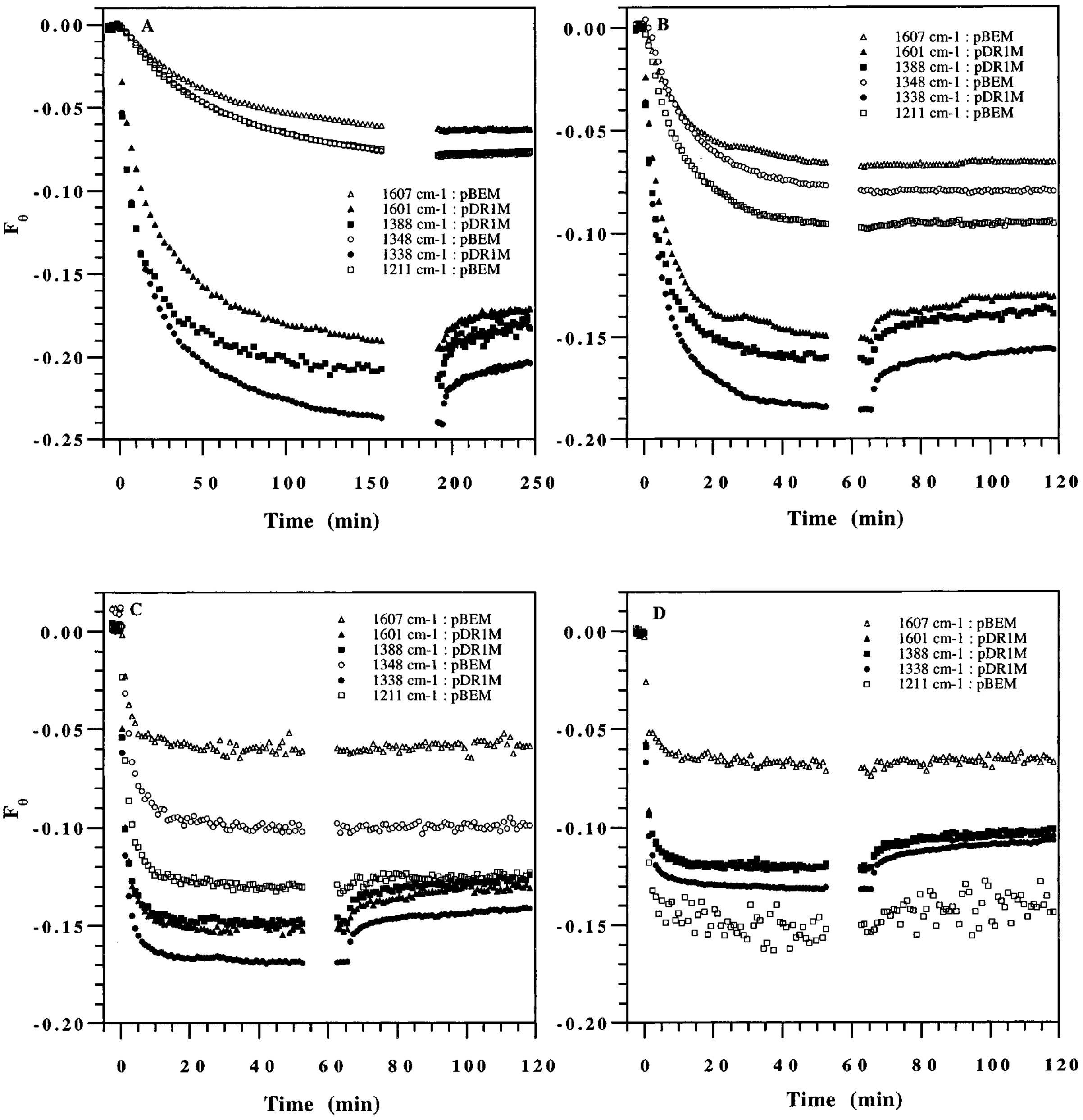


Figure 3. Time dependence of the orientation function F_θ for several vibrations of DR1M and BEM groups and for different DR1M mole ratios: (A) $x = 0.12$, (B) $x = 0.23$, (C) $x = 0.52$, and (D) $x = 0.81$. The writing laser was turned on at $t = 0$ for all samples and it was turned off at $t = 190$ min (A) or $t = 65$ min (B, C, D). In panel D, the behavior of the 1338 cm^{-1} band of the BEM group is not shown because of the very low intensity of this band.

Table 2. Parameters Obtained for the Orientation Process of Poly(DR1M-*co*-BEM) with a DR1M Mole Fraction of 0.51 by Fitting with Eq 1 the Time Dependence of F_θ for Several Vibrations of the BEM and DR1M Groups[a]

assignment		A_n	k_a (s^{-1})	B_n	k_b (s^{-1})	$A + B$	R^*
ν(C=C) 1607 cm^{-1}	BEM	0.86 ± 0.13	0.0074 ± 0.0015	0.14 ± 0.13	0.0013 ± 0.0008	−0.0602 ± 0.0157	0.975
ν_s(NO$_2$) 1348 cm^{-1}	BEM	0.81 ± 0.05	0.0062 ± 0.0006	0.19 ± 0.05	0.0015 ± 0.0008	−0.1000 ± 0.0094	0.990
ν_a(C−O−C) 1212 cm^{-1}	BEM	0.84 ± 0.03	0.0096 ± 0.0004	0.16 ± 0.03	0.0016 ± 0.0003	−0.1304 ± 0.0070	0.998
ν(C=C) 1601 cm^{-1}	DR1M	0.71 ± 0.04	0.0019 ± 0.001	0.29 ± 0.04	0.0037 ± 0.0004	−0.1513 ± 0.0106	0.999
ν(N=N) 1388 cm^{-1}	DR1M	0.71 ± 0.03	0.022 ± 0.001	0.29 ± 0.03	0.0039 ± 0.0003	−0.1481 ± 0.0086	0.999
ν_s(NO$_2$) 1338 cm^{-1}	DR1M	0.74 ± 0.02	0.021 ± 0.001	0.26 ± 0.02	0.0038 ±0.0002	−0.1676 ± 0.0065	0.999

[a] R^* is the correlation coefficient. A_n and B_n are normalized values of A and B (e.g., $A_n = A/(A + B)$).

mole fraction of 0.51 are given as a typical example in Table 2. As can be seen, for a given side chain, the k_a and k_b rate constants are approximately the same for all studied vibrations. However, the values of the rate constants associated to BEM groups are smaller than those obtained for DR1M groups, showing that the

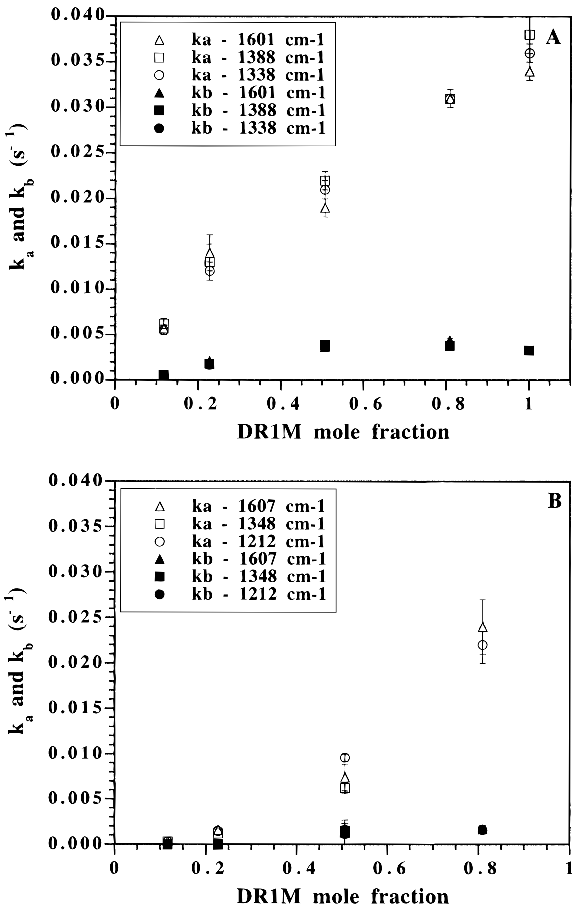


Figure 4. Effect of the polymer composition on the writing rate constants k_a and k_b of (A) DR1M and (B) BEM vibrations.

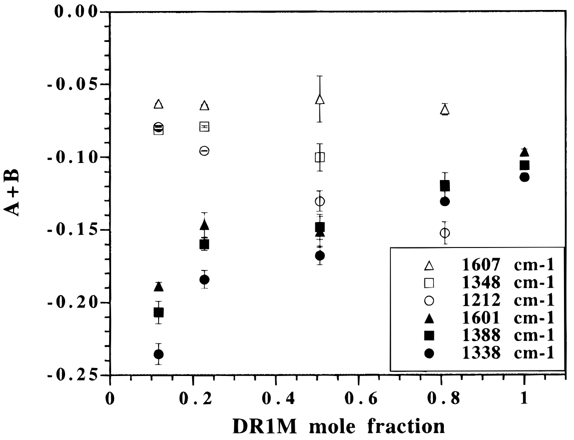


Figure 5. Effect of polymer composition on the maximum induced orientation ($A + B$) of DR1M and BEM vibrations.

azobenzene and phenyl benzoate groups do not move at the same rate. The k_a and k_b rate constants associated with the three selected bands of DR1M and BEM groups are plotted as a function of DR1M mole fraction in Figure 4. The "fast" rate constant (k_a) of the vibrations associated with the DR1M groups increases linearly with the increase of the DR1M mole fraction. Over the whole range of copolymer composition, the "slow" rate constant (k_b) is much smaller than the "fast" rate constant (k_a). In addition, k_b increases up to $x = 0.5$ and remains constant for higher DR1M mole fractions. The k_a rate constant of the BEM side groups also increases with increasing DR1M mole fraction. At low DR1M content, the value of k_a for the BEM groups is approximately 1 order of magnitude smaller than that obtained for DR1M vibrations, whereas the values of k_a for the BEM and DR1M groups are very close at high DR1M content. The k_b rate constant is nearly zero for all DR1M contents, showing that the dynamics of orientation of the BEM groups can be described by a monoexponential function. This behavior reinforces the idea that the biexponential nature of the orientation curves of the azobenzene side chains is associated with the *trans*–*cis*–*trans* isomerization process, which is not the case of the BEM groups that are not photoactive; all these observations suggest that the writing dynamics of the DR1M and BEM groups are affected by the copolymer composition. The decrease of the rate constant k_a of the DR1M side chains with the increase of the BEM content provides additional evidence for the cooperative motion of the DR1M and BEM structural units. Indeed, at high BEM content, each DR1M group is more difficult to move because it is affected by several BEM neighbors. On the other hand, for copolymers rich in azobenzene groups, the motion of the DR1M side chains is almost not influenced by the presence of the phenyl benzoate groups and the rate constant can be directly associated with the photoisomerization process. In this case, the kinetics of orientation of the isolated BEM groups is mainly governed by that of the photoactive side chains.

The maximum induced orientation ($A + B$) for DR1M and BEM vibrations is plotted as a function of the DR1M mole fraction in Figure 5. The absolute value of this parameter for the DR1M vibrations decreases with increasing DR1M content, showing that the orientation of the DR1M groups is less efficient at high DR1M concentration. In poly(DR1M-*co*-BEM), steric hindrances cannot explain the behavior of the maximum orientation since they are the same, whatever the copolymer composition. The composition dependence of the maximum induced orientation is more likely associated with the fact that the wavelength of the writing laser was always kept constant at 532 nm for all samples while the wavelength of the maximum absorption of the DR1M side chains varies from 492 nm for the poly(DR1M-*co*-BEM) containing 12 mol % of DR1M to 460 nm for polyDR1M. It has been shown that this blue shift is due to the antiparallel association of the DR1M dipoles, the paired antiparallel azo groups being more difficult to orient.[12]

The absolute value of the maximum orientation of the BEM groups calculated from the 1212 and 1348 cm^{-1} bands increases with increasing DR1M content, showing that the cooperative orientation of the BEM groups is more important when these inert groups are isolated in a polymer matrix that is richer in DR1M active groups. On the other hand, for the ν_{8a}(C=C) stretching vibration located at 1607 cm^{-1}, the maximum induced orientation remains constant over the whole range of copolymer composition. This puzzling feature might be due to the fact that for the phenyl benzoate side chains, because the two phenyl rings are linked by an ester group instead of an N=N group as in DR1M, the whole geometry of the side chain is not necessarily planar. Since the two phenyl rings can rotate more freely than in DR1M, it is difficult to predict the orientation of the transition dipole moments of the ring vibrations.

All these results show unambiguously that the BEM groups have a cooperative orientation with the DR1M groups. When the BEM groups are isolated, their writing dynamics is essentially commanded by that of the DR1M side chains. However, it is difficult to say if

Table 3. Parameters Obtained for the Relaxation Process of Poly(DR1M-*co*-BEM) witha DR1M Mole Fraction of 0.51 by Fitting with Eq 2 the Time Dependence of F_0 for Several Vibrations of DR1M Groups[a]

assignment	C_n	k_c (s^{-1})	D_n	k_d (s^{-1})	E_n	R^*
ν(C=C) 1601 cm^{-1}	0.06 ± 0.01	0.033 ± 0.011	0.09 ± 0.012	0.0009 ± 0.0001	0.85 ± 0.01	0.975
ν(N=N) 1388 cm^{-1}	0.08 ± 0.01	0.031 ± 0.008	0.07 ± 0.01	0.0008 ± 0.0002	0.85 ±0.01	0.971
ν_s(NO$_2$) 1338 cm^{-1}	0.09 ± 0.01	0.030 ± 0.003	0.07 ± 0.01	0.0008 ± 0.0001	0.84 ± 0.01	0.990

[a] R^* is the correlation coefficient. C_n, D_n, and E_n are normalized values of C, D, and E (e.g. $C_n = C/(C + D + E)$).

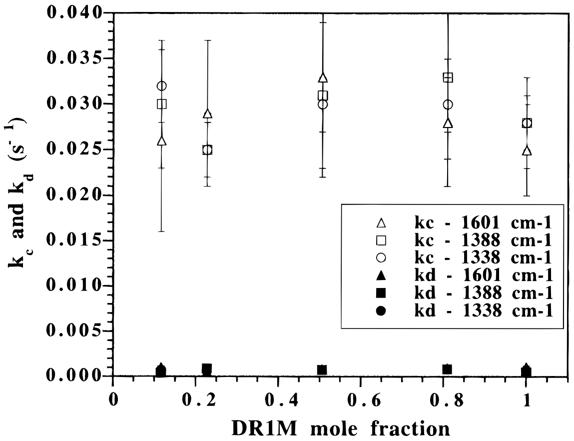


Figure 6. Effect of polymer composition on the relaxation rate constants k_c and k_d of DR1M vibrations.

this cooperative motion of DR1M and BEM groups is due to a steric effect or dipolar interactions between DR1M and BEM groups. The investigation of copolymers of DR1M with a less polar analogue of BEM should provide valuable hints to elucidate this point.

The parameters obtained by fitting eq 2 to the relaxation curves of poly(DR1M-*co*-BEM) with a DR1M mole fraction of 0.51 are given as a typical example in Table 3. As the level of orientation loss during the relaxation period is very small for all BEM vibrations, reliable fits of the relaxation curves associated with these side chains were not possible. As seen in Table 3, the k_c and k_d rate constants are approximately the same for all studied vibrations of the DR1M groups. The effect of the copolymer composition of the “fast” and “slow” relaxation rate constants are shown in Figure 6. As can be seen, the relaxation rate constants are fairly constant over the whole range of copolymer composition and the k_c/k_d ratio is approximately equal to 30. This suggests that the relaxation of the DR1M groups is not affected by the presence of the BEM groups. Similar values of k_c and k_d have been determined by infrared spectroscopy for copolymers containing azobenzene and methyl methacrylate structural units,[6] suggesting that the relaxation process depends mostly on the *cis*–*trans* isomerization and angular reorientation of the active groups and is not influenced by steric and dipolar interactions. This is further supported by the fact that the degree of orientation of the BEM groups is almost completely maintained when the irradiation of the copolymer is stopped. Therefore, there seems to be no cooperative effects during the relaxation process as opposed to the orientation period. This is most likely due to the fact that during the writing period, several *trans*–*cis*–*trans* isomerizations of the DR1M groups are necessary to move cooperatively through dipolar interactions some of the BEM groups.

The results presented in this paper demonstrate clearly that cooperative motions of the active and inert side chains occur in poly(DR1M-*co*-BEM) copolymers during the orientation process as postulated previously to explain the high birefringence of these polymers.[12] It is difficult to make a direct comparison of the rate constants and normalized parameters of the biexponential functions obtained from birefringence and infrared experiments because these parameters depend strongly on experimental conditions such as laser power and film thickness.[5,16] For example, the orientation rate constants calculated from the birefringence results are much higher than those obtained by infrared spectroscopy because of the difference in the laser power used for the two experiments. In addition, the nature of the information obtained by the two techniques is different. Birefringence provides global information on the orientation of the whole polymer, while infrared spectroscopy, depending on the studied vibration, gives specific information on either the azobenzene or phenyl benzoate side chains. Nevertheless, the results show some trends that are common to both types of measurements. First, for the orientation process, the k_a rate constant is always much higher than the k_b rate constant, and k_a increases with the DR1M content. Second, the k_c and k_d relaxation rate constants are nearly independent of the copolymer composition. Third, the two techniques show that about 80% of the orientation is conserved after relaxation of the polymer.

Conclusions

The results presented in this paper demonstrate clearly that time dependent polarization modulation infrared spectroscopy is a powerful technique to follow simultaneously the orientational behavior of different side chains in amorphous copolymers such as poly(DR1M-*co*-BEM). Cooperative orientation of both azobenzene and phenyl benzoate groups was found when the copolymer was irradiated with polarized light. In the case of the DR1M groups, the writing and relaxation curves can be fitted by biexponential equations and the two rate constants are associated with the azobenzene photoisomerization process. For the BEM groups, the orientation curves can be described by a monoexponential function and no relaxation is observed. The kinetics of orientation of the two types of side chains is markedly dependent on the copolymer composition and can be explained easily by the cooperative orientation of the two types of side chains. However, the origin of the cooperative orientation of the BEM groups is still not very well-understood. Indeed, either dipolar interactions of the photoactive and nonphotoactive groups or steric effects or a combination of both can explain the cooperative motion of DR1M and BEM groups. Studies in progress by PM-IRLD spectroscopy on copolymers of DR1M with less polar inert side chains should provide valuable information to answer this question.

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