Photoinduced Orientation in Azopolymers Studied by Infrared Spectroscopy: Cooperative and Biaxial Orientation in Semicrystalline Polymers

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ABSTRACT: A disperse red 19-containing semicrystalline azopolymer (pDR19T) with phenylene diacrylate (PD) groups within the main chain has been studied by polarization modulation and two-dimensional correlation infrared spectroscopy. The time dependence of the orientation function of azobenzene and PD groups has been followed during the orientation (linearly polarized laser on) and relaxation (laser off) periods. The results show a high degree of orientation of the different groups perpendicular to the direction of the laser polarization and a cooperative orientation of the PD groups with the azobenzene side chains. The azobenzene groups are not randomly oriented in the plane normal to the direction of the laser polarization leading to a biaxial orientation distribution. This photoinduced biaxiality has been quantified for pDR19T polymer and for amorphous copolymers containing azobenzene and methyl methacrylate structural units.

Introduction

Amorphous high-T_g polymers containing azobenzene side chains can become birefringent when they are irradiated with polarized light due to the orientation of the azobenzene groups perpendicular to the polarization direction.[1] The birefringence results from the reorientation of the azobenzene groups through *trans−cis−trans* isomerization cycles. The polarized light induces a selective optical pumping followed by an angular reorientation during the *trans−cis* isomerization and the *cis−trans* thermal relaxation. The photoinduced orientation can be optically destroyed using circularly polarized light, which restores the random distribution of orientation of the azobenzene groups. As optical information can be successively written and erased on these films, azopolymers can be used for reversible optical storage and have received a lot of attention in the past few years.[2−5]

Orientation can be achieved below the glass transition temperature (T_g) in amorphous polymers, and when the laser is turned off, the orientation is relatively stable (80% of the orientation is conserved) in polymers containing azobenzene side chains while it is less stable (35% conserved after 1 h of relaxation) when the azobenzene groups are dissolved in an inert polymer matrix. For the last case, Dumont et al.[6,7] have proposed the basis of a simple three-level theoretical model in order to explain the reorientation mechanisms of the azo molecules during the orientation (laser on) and the relaxation (laser off) processes. In this model, the orientation distribution of the azobenzene groups with respect to the radiation polarization direction is assumed to be uniaxial. The photoinduced linear dichroism, T_2, occurring during the orientation and relaxation processes can be fitted by a biexponential function which is related to the photoizomerization
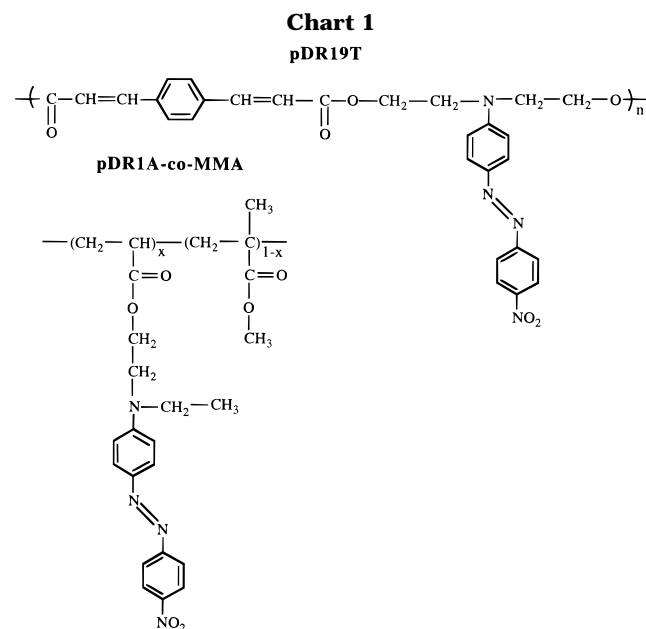
mechanism. More recently, Lagugné−Labarthet et al.[8] have shown that the slow response mode for both the orientation and relaxation processes is due to the reorientation of azobenzene molecules in various constrained environment of the inert matrix.

The understanding of the time dependence of the photoinduced orientation in amorphous polymer containing azobenzene side chains is more difficult because several structural factors may influence the reorientation of azobenzene groups. For copolymers containing azobenzene and methyl methacrylate structural units, Brown et al.[9] have shown from birefringence measurements that the degree and rate of ordering are strongly dependent on the distribution of the azobenzene units in the main chain. Similar results have been observed using time dependent infrared spectroscopy.[10] However, the question which must be asked is whether the uniaxial model for the orientation distribution of the azobenzene groups is valid for all copolymer compositions and in particular for homopolymers. Indeed, photoinduced biaxiality has been observed by Wiesner et al.[11,12] on liquid-crystalline copolymers containing cyanoazobenzene and cyanophenyl-benzoate side chains, in which the mesogens are preferentially aligned normal to the film plane. The cooperative motion of the active (cyanoazobenzene) and inert (cyanophenylbenzoate) side chains is of significant importance in the observed biaxiality because copolymers in which the azobenzene groups are statistically copolymerized with methyl methacrylate present a very low biaxiality. However, the mechanism leading to the development of biaxial order is not clearly understood.

More recently, Natansohn et al.[13] have shown that cooperative motions of azobenzene and other rigid groups are also present in semicrystalline polymers. Using both birefringent measurements and infrared spectroscopy, they have observed that in films of disperse red 19-containing semicrystalline azopolymer (pDR19T) with phenylene diacrylate (PD) groups within the main chain, the azobenzene and PD groups undergo

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Chart 1

pDR19T

pDR1A-co-MMA

Figure 1. Geometry of incoming infrared and laser beams at the sample and definition of the X, Y, Z coordinate system. The angle between the polarized laser and the infrared beam is approximately 20°.

a cooperative orientation when the polymer is irradiated with polarized light. The resulting birefringence is then about three times higher than that obtained on amorphous polymers. Furthermore, Dalton et al.[14,15] have observed that films of pDR19T are highly effective materials for nonlinear optics.

In this paper, pDR19T samples have been investigated by time-dependent polarization modulation infrared spectroscopy, to follow simultaneously the azobenzene side chains and main chains (carbonyl and phenylene groups) during the orientation and relaxation processes. The spectra obtained have been analyzed by two-dimensional (2D) Fourier transform infrared correlation spectroscopy and the orientation function, F_θ, of some bands has been calculated using the uniaxial model for the orientation distribution. The results obtained confirm the cooperative motion of rigid groups in semicrystalline polymers. In addition, photoinduced biaxiality has been evaluated from static infrared measurements using the formalism developed by Kaito et al.[16] The results obtained for the semicrystalline pDR19T polymer and amorphous copolymers containing azobenzene and methyl methacrylate (pDR1A-co-MMA) have been compared.

Experimental Section

Materials. The polymers (pDR19T, pDR1A-co-MMA) were synthesized according to published methods.[1,15] The structure of these polymers is shown in Chart 1. To prepare thin films, the polymers were dissolved in chloroform and the solutions were deposited by spin-coating onto barium fluoride disks. Film thicknesses were approximately 25 nm for pDR19T and between 100 nm and 1 μm for p(DR1A-co-MMA). The films were heated above the glass transition temperature in a vacuum oven 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.[17] The optical anisotropy in the polymer 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/cm². PM−IRLD spectra of pDR19T films were recorded during approximately 1 h for both the orientation (laser on)
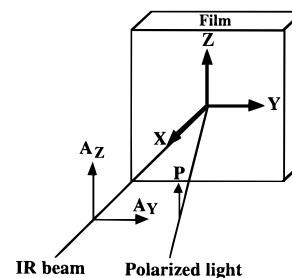
and the relaxation (laser off) periods, with a spectral resolution of 4 cm^{-1} and an acquisition time of 52s per spectrum. By using a proper calibration procedure,[18] the PM−IRLD spectrum can be related quantitatively to the dichroic difference spectrum $\Delta A = A_Z - A_Y$ where A_Z and A_Y are the absorbances with the infrared radiation polarized parallel and perpendicular to the laser polarization, respectively, as shown in Figure 1.

To measure the photoinduced biaxiality, static polarized infrared spectra were recorded, before and after the irradiation, with a Nicolet 850 FTIR spectrometer. The absorbances A_Z and A_Y were measured 1 h after the laser was turned off using a wire grid polarizer (Specac) mounted in front of the sample. The absorbance A_X was calculated by subtracting the absorbances A_Z and A_Y from the total absorbance $A_0 = (A_X + A_Y + A_Z)/3$ obtained before irradiation where the sample is assumed to be isotropic.

2D-FTIR Calculations. Synchronous and asynchronous correlation intensities were calculated from approximately 60 dichroic difference spectra using the generalized mathematical formalism developed by Noda.[19] Dynamic spectra in the time domain were calculated using the following expression:

$$\Delta \tilde{A}(\nu,\tau) = \Delta A(\nu,\tau) - \Delta A(\nu,0) \qquad (1)$$

τ is the running index of each spectrum in the time domain, $\Delta A(\nu,\tau)$ is the dichroic difference spectrum with the running index τ and $\Delta A(\nu,0)$ is the dichroic difference spectrum recorded before the laser was turned on. The discrete Fourier transforms, the synchronous and asynchronous correlation intensities were calculated as described previously by Nabet and Pézolet[20] using Mathcad 4.0 (MathSoft Inc.) while the contour maps were plotted using Transform 3.3 (Fortner Research LLC).

Results and Discussion

Assignment of the infrared bands. The infrared spectrum in the 1200−1800 cm^{-1} region of the pDR19T polymer is presented in Figure 2. This spectrum displays some bands characteristic of either the main chain (carbonyl and vinyl groups) or the azobenzene side chain. The carbonyl bands appears at 1712 cm^{-1}; its frequency is lower than that observed in pDR1A polymer due to conjugation with the vinyl group. The C=C stretching vibration of the vinyl group is located at 1634 cm^{-1}. Bands associated with the azobenzene groups are observed at approximately the same frequency as those of the pDR1A polymer.[17] The bands due to the ν_{8a} and ν_{8b} C=C stretching vibrations of the para-substituted phenyl rings are located at 1600 and 1588 cm^{-1}, respectively. The band due to the N=N stretching vibration appears at 1382 cm^{-1} whereas the band associated with the symmetric ($\nu_s(NO_2)$) and antisymmetric ($\nu_a(NO_2)$) stretching vibration of the NO_2 group occurs at 1339 and 1516 cm^{-1}, respectively.

2D-FTIR Correlation Spectroscopy. To follow the time evolution of the PM−IRLD spectra of pDR19T
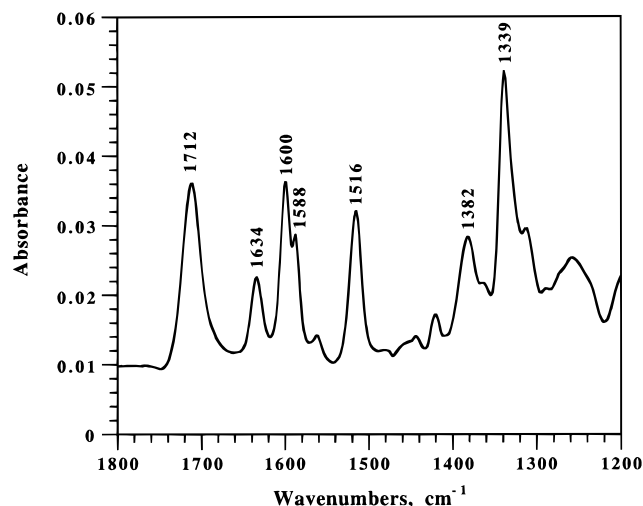
Figure 2. Unpolarized absorbance spectrum of a pDR19T film recorded before irradiation.
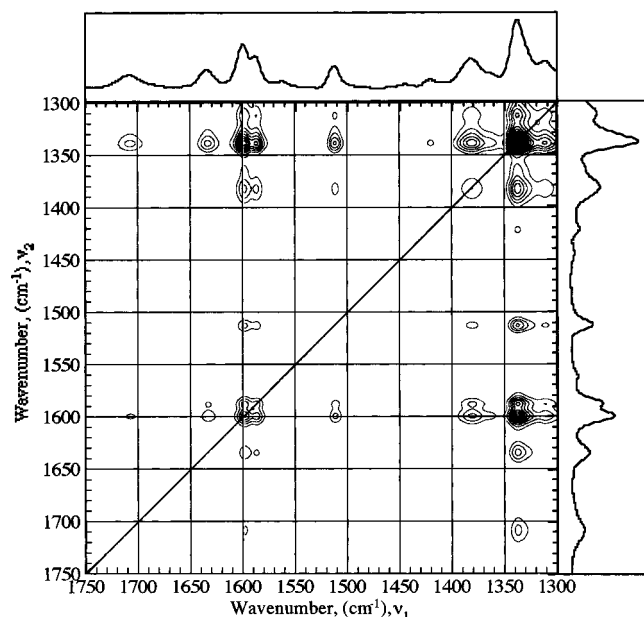

Figure 3. Synchronous 2D-FTIR correlation map of pDR19T during the photoinduced orientation process. In this figure, all peaks are positive, and the one-dimensional spectrum is the last dichroic difference spectrum recorded.
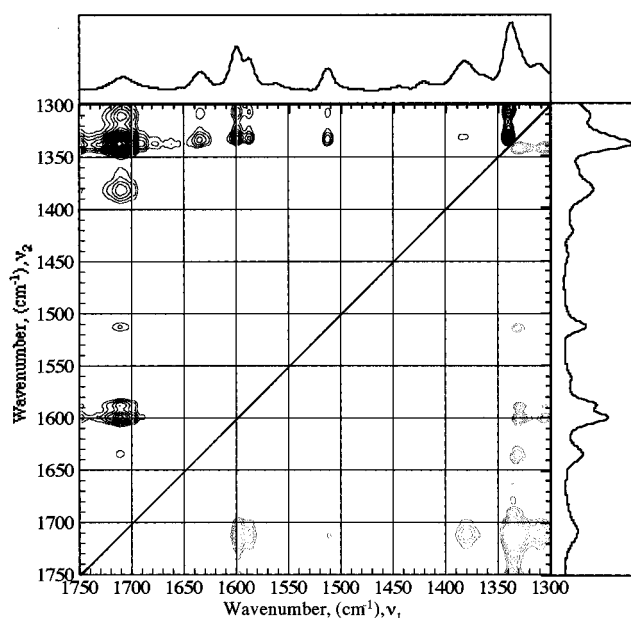

Figure 4. Asynchronous 2D-FTIR correlation map of pDR19T during the photoinduced orientation process. In this figure, dark peaks are positive while gray peaks are negative. The one-dimensional spectrum is the last dichroic difference spectrum recorded.

during the orientation process, we have performed a 2D correlation analysis using the generalized formalism developed by Noda.[19] Figure 3 shows that the synchronous correlation map of pDR19T between 1300 and 1750 cm^{-1} contains several correlation peaks. All peaks are positive, showing that the bands in the dichroic difference spectra all change in intensity in the same direction. The strongest autopeak is due to the $\nu_s(NO_2)$ band at 1339 cm^{-1} since this band undergoes the most important change of intensity during the orientation process. Strong positive cross correlation peaks between the $\nu_s(NO_2)$ at 1339 cm^{-1} vibration and other vibrations of the azobenzene side chains are also observed at 1311, 1382, 1516, 1588, and 1600 cm^{-1}, showing clearly that the azobenzene groups move as rigid rods when the polymer is irradiated with polarized visible light. Synchronous cross-peaks are also observed between the $\nu_s(NO_2)$ vibration and the C=C (1634 cm^{-1}) and C=O (1712 cm^{-1}) vibrations, revealing that the PD groups in the main chain undergo a cooperative reorientation

with the azobenzene groups, in agreement with previous results.[13]

The asynchronous map of pDR19T (Figure 4) is also characterized by several cross-peaks, providing insight into the reorientation rates of the different groups of the polymer. Interestingly, this map reveals that the $\nu_s(NO_2)$ band contains two components located at 1331 and 1341 cm^{-1}. Since the cross-peak at 1331−1341 cm^{-1} is positive above the diagonal, the use of Noda's rules[19] indicates that the component at 1341 cm^{-1} grows more rapidly than that at 1331 cm^{-1}. Since the spectra of p(DR1A-*co*-MMA) copolymers with low DR1A content show that the $\nu_s(NO_2)$ band is located at 1341 cm^{-1},[10] we tentatively assign the 1341 cm^{-1} component to isolated azobenzene groups and the 1331 cm^{-1} component to associated azobenzene groups. A strong positive cross-peak is also observed above the diagonal at 1338−1712 cm^{-1}, indicating that the carbonyl groups of the main chain of the polymer orient more rapidly than the azobenzene side chains. This surprising result suggests that the first *trans−cis−trans* isomerization cycles of the azobenzene groups induce a rapid orientation of the C=O and that this orientation is preserved during the rest of the orientation process.

Time Dependence of the Orientation and Relaxation Processes. To obtain more quantitative information about the time dependent behavior of different bands associated to phenylene diacrylate and azobenzene groups, the orientation function, F_θ, assuming an uniaxial orientation distribution, was calculated by normalizing the area under each band in the dichroic difference spectrum, ΔA, by that of the corresponding band in the unpolarized spectrum recorded before sample irradiation, A_0:

$$F_\theta = \frac{\Delta A}{3A_0} = \frac{A_Z - A_Y}{A_Z + 2A_Y} \qquad (2)$$

In this case the orientation function is associated with the orientation of the transition dipole moment of a
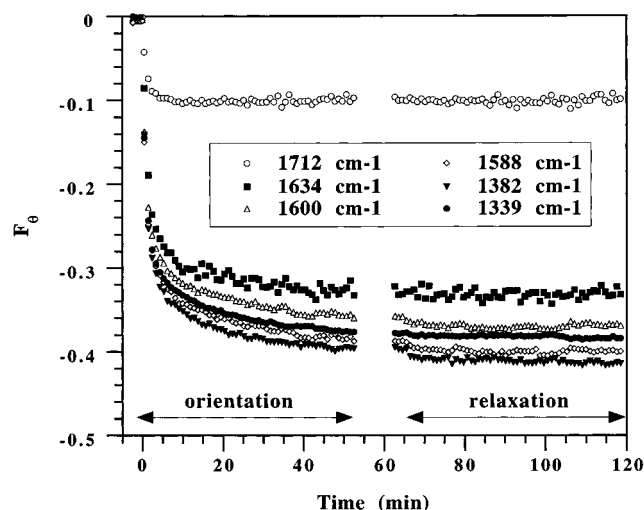
Figure 5. Time dependence of the orientation function, F_θ, for several vibrations of pDR19T. The writing laser was turned on at $t = 0$ and it was turned off at $t = 67$ min.

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.

Figure 5 shows the values of F_θ for several vibrations as a function of time for the irradiation period and after the writing laser was turned off. At time zero, all azobenzene and PD groups are randomly distributed in the film and the orientation function is zero. When the polarized laser is turned on, the azobenzene groups start moving toward a direction perpendicular to the laser polarization, producing a negative orientation functions for the bands associated with these groups. The orientation increases for the first few minutes and reaches a plateau after approximately 1 h. The orientation function has almost the same limiting value for all bands associated with the azobenzene groups, indicating that the transition moments associated with these vibrations are preferentially oriented along the long molecular axis of the azobenzene side chains. The maximum values of the orientation function observed for pDR19T are very high (between -0.36 and -0.4) in comparison with those measured for other amorphous azopolymers.[17,21] As observed from the 2D-correlation intensities, the time dependence of the orientation function of the vinyl group shows that the PD groups located in the main chain undergo a cooperative reorientation with the azobenzene groups. The value of the orientation function indicates that the PD and azobenzene groups display almost the same level of orientation perpendicular to the writing polarization direction. This result can be explained considering strong dipolar interactions between PD and azobenzene groups and a flexibility of the ester ethylene groups in the main chain. The carbonyl groups exhibit a significant dichroism and are also oriented perpendicular to the laser beam polarization. As predicted from the synchronous map of Figure 3, the C=O groups orient more rapidly than other groups of the polymer and the orientation reaches a plateau after a few minutes.

When the laser is turned off, no relaxation of the orientation is observed. This result can be explained if we consider that the polymer is perfectly ordered and that the azobenzene groups are in a constrained envi-

ronment. Dalton et al.[15] have suggested a cross-linked structure of pDR19T after irradiation. Indeed, the C=C double bonds of the PD groups could break and form molecular cross-links, which would significantly reduce the polymer mobility and the available free volume. Natansohn et al.[13] have shown that no cross-linking occurs in pDR19T films because no modification of the intensity of the C=C band is observed when the sample was exposed to UV light. The lack of relaxation of orientation during the photoisomerization cycles and the semicrystallinity of pDR19T can explain the very high degree of orientation of this polymer. These effects could also lead to a deviation from the uniaxial model of the orientation distribution of the azobenzene groups.

Photoinduced Biaxiality. The irradiation of the pDR19T film induces a reorientation of the azobenzene groups perpendicular to the direction of the laser polarization (Z), i.e., in the XY plane (see Figure 1). If the azobenzene groups are not distributed isotropically in the XY plane, a biaxial symmetry of the distribution function should be taken into account. As shown by Kaito et al.,[16] the orientation distribution function can be expressed by two orientation functions, F_θ and F_ϕ, which are given by:

$$F_\theta = \frac{3\langle\cos^2\theta\rangle - 1}{2} \qquad (3)$$

$$F_\phi = \frac{\langle\cos^2 2\phi \sin^2\theta\rangle}{\langle\sin^2\theta\rangle} \qquad (4)$$

where θ is the angle between the direction of the laser polarization and the considered transition moment and ϕ is the angle between the Y axis and the projection of the transition moment in the XY plane. If the transition moment is perfectly oriented parallel to the laser polarization, $F_\theta = 1$ and $F_\phi = 0$. A complete orientation of the transition moment along the Y and X axis gives $F_\theta = -0.5$ and $F_\phi = 1$ and $F_\theta = -0.5$ and $F_\phi = -1$, respectively. A random orientation in the XY plane leads to $F_\phi = 0$, corresponding to an average angle ϕ of 45°.

To determine the orientation functions F_θ and F_ϕ, we have to measure the three absorbances A_X, A_Y and A_Z, with the direction of the electric field of the infrared radiation oriented parallel to the X, Y, and Z axis, respectively. The absorbances in the plane of the film, A_Y and A_Z, can be measured using polarized radiation with the incident beam normal to the sample. On the other hand, the absorbance A_X has to be measured using Z-polarized incident light at oblique incidence.[16,22] This method is relatively easy to use but it requires the determination of the refractive index of the polymer in the infrared region. Another method to determine A_X is to subtract the absorbances A_Z and A_Y from the total absorbance $A_0 = (A_X + A_Y + A_Z)/3$ obtained before irradiation, when the sample is assumed to be isotropic. The orientation functions F_θ and F_ϕ are related to the absorbances A_X, A_Y, and A_Z by the following two expressions:

$$F_\theta = \frac{A_Z - (A_X + A_Y)/2}{A_X + A_Y + A_Z} \qquad (5)$$

$$F_\phi = \frac{A_Y - A_X}{A_Y + A_X} \qquad (6)$$

Table 1. Orientation Functions of the $\nu_s(NO_2)$ Vibration, Calculated from Uniaxial and Biaxial Models of the Orientation Distribution, for the PDR19T Polymer and P(DR1A-*co*-MMA) Copolymers[a]

	uniaxial	biaxial	
	F_θ ± 0.003	F_θ ± 0.007	F_ϕ ± 0.015
pDR19T	−0.364	−0.288	0.175
p(DR1A-*co*-MMA) $x = 1.00$	−0.067	−0.059	0.024
p(DR1A-*co*-MMA) $x = 0.81$	−0.068	−0.060	0.020
p(DR1A-*co*-MMA) $x = 0.44$	−0.054	−0.054	−0.001
p(DR1A-*co*-MMA) $x = 0.23$	−0.052	−0.054	−0.007
p(DR1A-*co*-MMA) $x = 0.08$	−0.100	−0.103	−0.008

[a] Orientation functions are averages of measurements on at least four different samples.

If $A_X = A_Y$ (corresponding to a random orientation of the transition moment in the XY plane), the orientation functions given by expressions 2 and 5 are equal.

The orientation functions F_θ for the uniaxial model and F_θ and F_ϕ for the biaxial model have been calculated from eqs 2, 5, and 6, respectively, and their values are given in Table 1. The high value of F_ϕ (0.175 ± 0.015) for the pDR19T film reveals an important photoinduced biaxiality in this system. The positive value of F_ϕ indicates that the azobenzene groups are rather oriented along the Y axis, that is in the plane of the film. The preferred orientation of the azobenzene groups in the XY plane affects strongly the calculation of the orientation function F_θ. As shown in Table 1, the calculated value of F_θ using an uniaxial model is too high. For such a case, only separate measurements of the X-, Y-, and Z-polarized spectra allow a precise determination of the orientation functions.

To determine if photobiaxiality also occurs in amorphous polymers, we have measured F_θ and F_ϕ for p(DR1A-*co*-MMA) copolymers of different composition. The results obtained (Table 1) indicate that value of F_ϕ is very small for high azobenzene concentration ($x = 1.0$ and $x = 0.81$) whereas no biaxiality is observed at lower concentration. In this case, the small difference in the calculated values of F_θ for the two models indicates that an uniaxial model can be used to characterize the orientation in amorphous polymers containing azobenzene side chains.

Conclusion

The results presented in this paper show clearly that cooperative motions of azobenzene and phenylene groups occur when pDR19T films are irradiated with a polarized laser. These groups orient perpendicular to the direction of the laser polarization with a preferred orientation in the XY plane. A biaxial model of orientation distribution should be used for such polymer in order to determine precisely the degree of orientation of the main and side chains. On the other hand, the orientation of azobenzene groups in amorphous p(DR1A-*co*-MMA) copolymers can be described using an uniaxial model for the orientation distribution.

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