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Azo Polymers for Reversible Optical Storage. 4. Cooperative Motion of Rigid Groups in Semicrystalline Polymers

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ABSTRACT: Polarized light induces a preferred orientation of azobenzene groups through photochemical trans–cis–trans processes. Stronger orientation tendencies exist if the azo-containing polymers are crystalline or liquid crystalline and the cooperative reorientation of nonactive mesogens of similar shape has been demonstrated. This paper shows that cooperative reorientation is a more general phenomenon and can take place even for a nonactive rigid group of a different shape which is bonded in the main chain while the azobenzene groups are in the side chains. Comparison is made between a disperse red 1-containing amorphous azo polymer (pDR1A) and a disperse red 19-containing semicrystalline azo polymer (pDR19T) with phenylene diacrylate (PD) groups within the main chain. Dichroic ratios are obtained from infrared and electronic spectra and are correlated with a writing/erasing/rewriting sequence performed with an argon laser. A maximum birefringence of 0.08 can be obtained on pDR1A, while on pDR19T the birefringence is 0.27 in similar conditions. This is the result of a combination of the semicrystallinity of pDR19T and of the cooperative orientation of PD groups along with the azobenzene groups. The drawback in terms of optical storage is the longer time required to write or erase the induced birefringence in pDR19T.

Introduction

It has been known for almost a decade that polarized light can induce a reorientation of azobenzene groups through photochemically induced trans–cis–trans isomerization cycles, thus creating optically anisotropic domains. The first material proposed was poly(vinyl alcohol) (PVA) doped with an azo dye (methyl orange).[1] The change in refractive index for such a material could reach 10^{-3}.

Liquid crystalline polymers containing azo groups on the side chain were recently proposed as materials for optical storage.[2] The mechanism of storage was similar to that described before: the laser was orienting the azo groups perpendicular to its polarization plane. The preferred mode of operation for the liquid crystalline polymers was on films which were preoriented in the presence of electric fields. The laser would then change the orientation in the areas exposed, creating differences in the refractive index of 10^{-2}, 1 order of magnitude greater than those previously reported.[2] The "writing" was fairly stable below the clearing temperature of the liquid crystalline polymer; hence, the material had long-term stability.

Since liquid crystalline polymers were used in these storage processes, it has been implicitly accepted that the presence of some spacer was needed between the rigid polymer chain (below its T_g) and the azo group. The spacer would allow the flexibility necessary for the required movement. Even the amorphous copolymers proposed for such applications contained relatively long spacers.[3] One of the most interesting observations on these liquid crystalline polymers was that, if a mixture of mesogens was present in the side chains, the nonphotoactive mesogens (such as phenyl benzoate or benzamide) undergo a reorientation together with the azo mesogens, thus amplifying the effect over the limits given by the azo groups' concentration. Initially it was proposed that the cooperative orientation was occurring only above the glass transition temperature of the polymer, in the liquid crystalline (nematic[4]) phase. This meant that, below T_g, only the photoactive mesogens (azobenzene) would change orientation, while the other mesogens will remain unchanged; in other words, the light will "address" only some of the molecules. There are a few publications that have proven this not to be true. The reorientation by "sympathy" of the nonactive mesogens takes place both above and below T_g.[5–7]

In a separate study, a series of copolymers of maleic anhydride were modified by appropriate hydrolysis in order to introduce azobenzene groups separated from the main chain by a four-methylene spacer.[8] The copolymers were then subjected to polarized light to achieve birefringence. The highest level of birefringence (0.21) was achieved on copolymers containing 90 mol % azobenzene groups, which were semicrystalline. Associated thermal treatment and comparison with Langmuir–Blodgett films of the same copolymers (which showed *no* induced birefringence) suggested that the high-birefringence level was associated with the cooperative motion of the azobenzene groups present in the side chain.

We have recently demonstrated[9] that the presence of spacers is not necessary; actually it is preferable to have materials with high glass transition temperatures, i.e., shorter or no spacers. Amorphous polymers containing electron donor–acceptor substituents on the azobenzene group exhibited a change in the refractive index of 0.08 (this is the best value obtained on a variety of samples). Most studies were performed on a disperse red 1-containing polyacrylate (pDR1A) of the structure shown in Chart 1.

In a series of papers, Dalton et al.[10] analyzed the effect of polarized light on some polymers based on disperse red 19. One of the examples is also presented in Chart 1 as pDR19T. The purpose of that work was to obtain waveguide materials. As expected, prolonged exposure to polarized UV or visible light produced a change in the refractive index of the materials. This change was attributed to the presence of trapped *cis*-azobenzene

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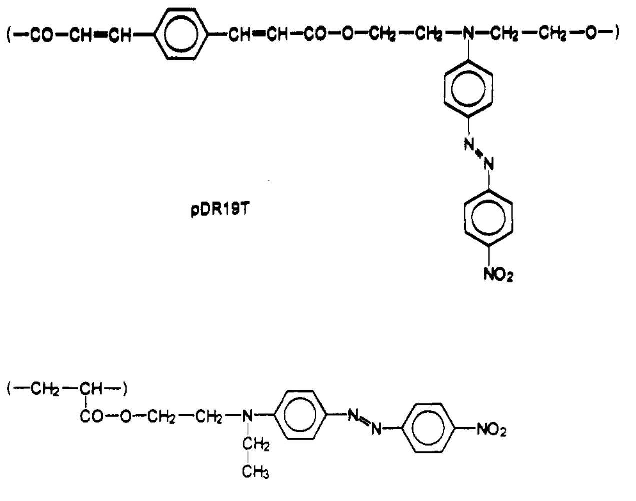
Chart 1



pDR19T

pDR1A

isomers. The cis isomers would form as a result of exposure to light, but they would be prevented from back isomerization to trans by a simultaneous cross-linking of the polymer material. The presence of the main-chain double bonds was the structural feature allowing cross-linking. The birefringence achieved by long exposure to light was 0.2–0.3, which is of the same order of magnitude as that reported for semicrystalline modified maleic anhydride copolymers[8] and higher than the levels achieved in amorphous polymers.[9]

We will demonstrate in this paper that the phenomenon described for pDR19T polymers is similar to those previously described in the literature, i.e., that the birefringence is achieved by reorientation of the *trans*-azobenzene groups and that the increased birefringence value is due to the cooperative reorientation of the *p*-phenylene diacrylate groups. Thus, cooperative motion of rigid groups induced by polarized light is a more general phenomenon. It is present not only at high azobenzene concentrations,[8] or with similar groups on the side chains,[3-7] but also with completely different groups which happen to be built into the main chain.

Experimental Section

The polymers (pDR1A and pDR19T) were synthesized according to published methods.[9,10] The procedure for reversibly storing information with a laser beam on a polymer film was also previously described.[9] Writing and erasing were performed at room temperature using a laser intensity of 5 mW on a spot of 400 μm in diameter. Films of pDR19T were also observed under polarized light with a Labophot-2 Nikon microscope equipped with a Wild-Leitz heating stage. Thermal transitions were measured on a Mettler TA-30 DSC instrument equipped with a TA-3000 processor.

Films of the analyzed polymers were deposited onto CaF_2 windows to allow spectroscopic measurements from the UV (250 nm) to the IR (10 μm). Fresh samples were exposed to a linearly polarized argon laser beam at 514 nm for enough time to reach saturation. The UV–vis transmission spectra for light polarized parallel and perpendicular to the writing polarization direction were obtained using a Shimadzu UV-160 spectrophotometer fitted with polarizing optics. X-ray measurements were performed on a Rigaku instrument equipped with a rotating Rotoflex Cu anode. Infrared spectra (400 scans at 4 cm^{-1} resolution) were recorded at room temperature with a Mattson Serius 100 Fourier transform spectrophotometer. The radiation was polarized with a rotating wire-grid polarizer (Specac) mounted in front of the sample; a reference spectrum was measured for each polarization. Infrared dichroic ratios were calculated from the peak height intensity measured in absorbance. All spectral manipulations were executed with SpectraCalc software (Galactic Industries Co.).

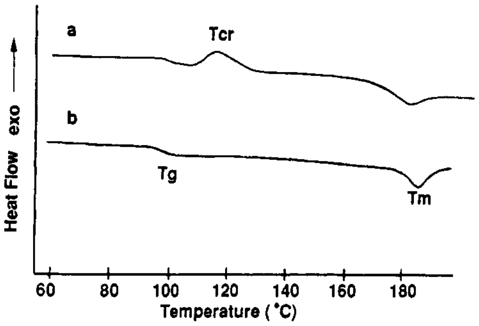


Figure 1. DSC curves of pDR19T obtained on heating: (a) first heating of a pristine sample (20 °C/min); (b) second heating (10 °C/min).

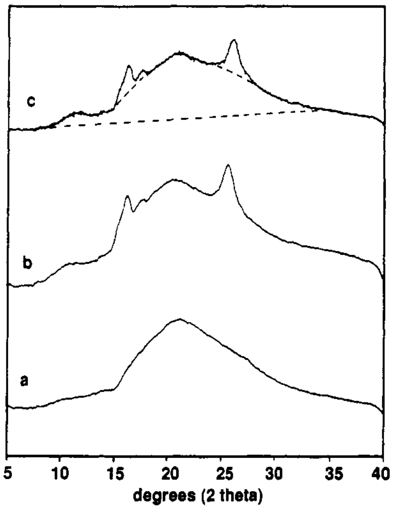


Figure 2. Wide-angle part of the X-ray diffraction patterns of pDR19T; (a) powder sample as synthesized; (b) at 160 °C; (c) after being heated to 190 °C and cooled down to room temperature (dotted lines indicate the deconvolution for the calculation of the degree of crystallinity).

Results and Discussion

pDR19T is a semicrystalline polymer, while pDR1A is amorphous with a T_g of 91 °C. DSC curves of pDR19T obtained on heating are shown in Figure 1. A first heating scan for a particular sample shows a crystallization peak immediately above the glass transition. Second and subsequent scans show only the glass transition at 96 °C and a melting endotherm at 185 °C.

Heating the sample on a polarized microscope heating stage shows that between these temperatures pDR19T has a texture which could be compared with a smectic liquid crystalline phase. The texture and the magnitude of the DSC endotherm (ca. 4 kJ/mol) both agree with a possible smectic phase, but the X-ray diffraction pattern clearly indicates that no layered structure is present (no peak below 5 2Θ). Figure 2 shows the wide-angle part of the X-ray diffraction patterns for a sample at room temperature (the sample is completely amorphous), at 160 °C (above T_g but below clearing; the sample is now semicrystalline), and upon cooling back to room temperature. The pattern at 160 °C shows a few peaks between 15 and 30 2Θ, which means that the order in the ordered parts of the sample is higher than that in a smectic liquid crystal. Hence, the endotherm at 185 °C has to be assigned to the melting of a higher ordered crystalline phase and its rather low peak area means that the degree of crystallinity in pDR19T is fairly low (16% as estimated

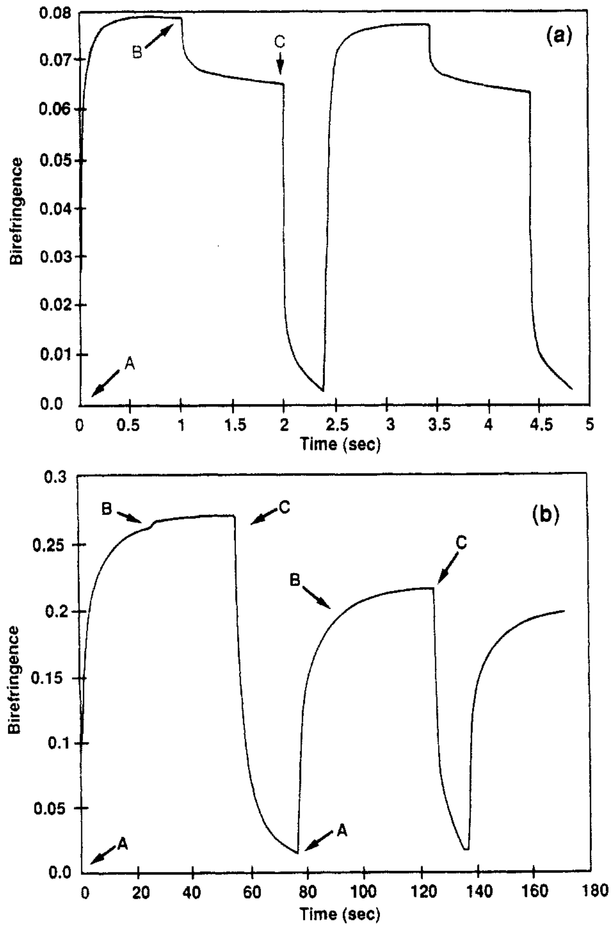


Figure 3. Typical writing curves for (a) pDR1A and (b) pDR19T. A = writing laser is turned on; B = writing laser is turned off; C = erasing laser is turned on.

from X-ray diffraction at 160 °C). (Figure 2c shows schematically how the diffraction pattern was decomposed into amorphous and crystalline parts for deconvolution.) The ordering induced by heating above T_g is being maintained on cooling back to room temperature.

Thus, pDR19T is amorphous as synthesized, and a film obtained from $CDCl_3$ or THF solution by spin coating is clear and transparent. Above the glass transition, the polymer becomes semicrystalline and the appearance of ordered domains can be observed by monitoring the polymer film. Above 185 °C, the film becomes again transparent, as the crystalline part melts. On cooling below 185 °C the polymer crystallizes and remains semicrystalline to room temperature and below. The degree of crystallinity does not seem to depend on the thermal history of the sample after the first heating. Consequently, pDR19T can produce amorphous or semicrystalline films at room temperature, depending on how the film has been prepared. These films behave very differently when subjected to polarized light.

A writing curve is presented in Figure 3 for pDR1A and pDR19T. At point A in time, the writing laser beam is turned on, activating the trans–cis–trans isomerization process which has as a consequence the preferential orientation of the azobenzene groups perpendicular to the laser polarization plane.[9] The difference between the refractive indexes of the amorphous film and of the oriented (written) part is measured as a function of time. In Figure 3 it is clear that the level of birefringence is achieved as the saturation is higher in pDR19T than in pDR1A by a factor of 4, in agreement with the literature.[9,10] However, the time required to achieve saturation in films of comparable thickness[11] is longer by a factor greater than 10 in pDR19T in comparison with pDR1A. It takes 200–300 ms to achieve saturation in pDR1A and a few seconds in pDR19T.

On turning the light off at point B in Figure 3, the birefringence of pDR1A decreases by about 20%. Part of this decrease has been associated with the thermal reorientation of some azobenzene groups. This thermal reorientation tends to restore the thermodynamically favored disordered state and is probably made possible by some local heat associated with the laser light which is dissipated through the film when the laser is turned off. Also, some of the azo groups (at the end of a chain, for example) may have more free volume available to them and are thus thermally unstable even at room temperature. Not surprisingly, turning the laser off has a different effect on pDR19T. Above T_g, the thermodynamically favored state of this polymer is ordered (semicrystalline); hence, local heating will tend to reinforce the writing effect: inducing order. This is indeed what happens when writing is performed for the first time on an amorphous film (at ca. 20 s in Figure 3b). An actual increase in the birefringence is observed. The explanation is that the dissipating heat is being used to strengthen the order induced by the writing beam. For second and subsequent writings, the polymer film is already semicrystalline and the effect of turning off the writing beam varies depending on the spot on the polymer film. The highest drop in birefringence is about 2%, and, more typically, there is no change in birefringence as shown in Figure 3b.

At point C in Figure 3 the erasing laser beam is turned on. This is the same writing beam, but its polarization is now circular instead of planar. Its effect is to randomize back the orientations of the azobenzene groups. This is achieved very fast on pDR1A, faster than the writing process, and much slower in pDR19T. One could try to erase a written sample by heating. For amorphous polymers it is enough to reach T_g and restore complete disorder in the film. For liquid crystalline polymers, erasing was proposed by heating above the clearing temperature.[2] An experiment of erasing through heating was performed on pDR19T on a heating stage of a microscope with polarized light. The sample was set in between two cross polarizers after being written. The written part was birefringent and was visible against an amorphous (black) background. Above T_g the background started also becoming birefringent, but the written part was still clearly visible. No "erasing" happened until 185 °C, and the only disorder effect induced by motions above T_g was a loss of sharpness of the edges for the written part. Above 185 °C, the whole sample became black, i.e., isotropic. On slow cooling, birefringent regions appeared on the whole film surface, due to spontaneous crystallization, but the previously written region showed a much higher luminosity. This means that the sample has a memory of its written part. This memory may be destroyed by keeping the sample for a very long time (at least 3 weeks) above its melting temperature and then cooling very slowly (2 °C/day).

Rewriting (second point A in Figure 3) is analogous to writing on a new semicrystalline sample (not in its amorphous state). In Figure 3 the writing beam is again turned on and its effect on pDR1A is to produce the same level of birefringence in the same amount of time as for the first writing on the same spot. As expected, pDR19T behaves very differently. The previously written spot has a certain amount of orientation induced by the writing beam and not erased completely by the erasing beam. Writing again on the same spot involves moving the

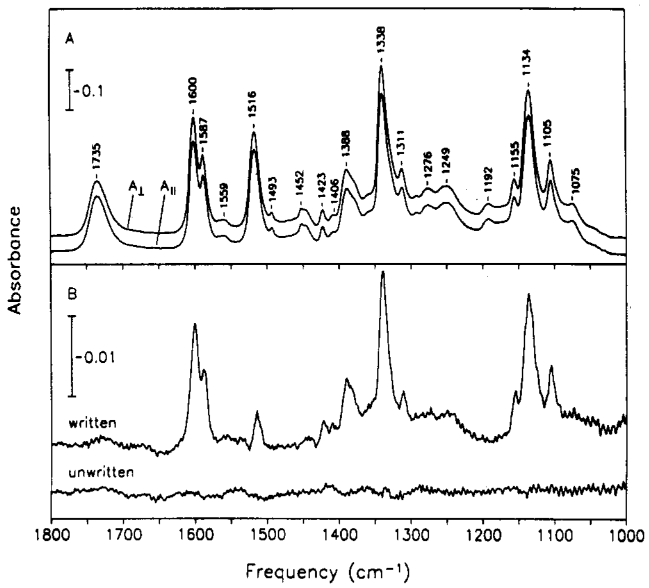


Figure 4. (A) Infrared spectra of a written pDR1A film recorded with the infrared radiation polarized parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the writing direction. (B) Dichroic difference spectra ($A_\parallel - A_\perp$) of written and unwritten films of pDR1A.

azobenzene groups from a thermodynamically stable state of domains with various orientations to another oriented state. The previous level of birefringence is never achieved on a semicrystalline sample or by writing on the same spot. Erasing can be performed completely on a previously written spot only after about 20 s, because the energy needed to achieve complete randomization in an ordered film should overcome the tendency of the semicrystalline material to stay ordered. The writing time (time to achieve saturation), however, is comparable for the initial writing and the second and subsequent ones.

The previous writing features have been interpreted in terms of induced ordering of the rigid groups present in the polymers. pDR1A has only one type of rigid groups: azobenzene. pDR19T has two types: azobenzene and *p*-phenylene diacrylate (PD). As the concentration of azobenzene is actually higher in pDR1A (85 mol %) than in pDR19T (64 mol %), one has to check if there is a contribution to the birefringence from the PD groups. In order to do this, one has to try to verify both proposed hypotheses regarding the origins of the birefringence. The first hypothesis[9] assumes that the birefringence is a result of the induced dichroism. The second hypothesis[10] postulates a different index of refraction for azobenzene in trans and in cis forms and proposes that cis azobenzene is formed and trapped in the cross-linked structure of pDR19T. The PD units present in pDR19T could act as cross-linking units, their C═C double bonds could break and form intramolecular cross-links, which would significantly reduce the polymer mobility and the available free volume.

First Hypothesis: Dichroism. The degree of light-induced molecular orientation of pDR1A and pDR19T was determined by infrared spectroscopy. The infrared spectra in the 1000–1800-cm^{-1} region of a written film of pDR1A recorded with the infrared radiation polarized parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the writing direction and the dichroic difference spectra ($A_\parallel - A_\perp$) of written and unwritten films are presented in Figure 4. The assignments of the strongest bands in these spectra as well as their dichroic ratios, $D = A_\parallel/A_\perp$, are given in Table 1.

The dichroic difference spectra of Figure 4 clearly show that unwritten pDR1A displays no preferred molecular orientation, while for the written sample several bands due to the azobenzene side chains are stronger in the $A_\perp$ than in the $A_\parallel$ spectrum and, therefore, display dichroic ratios smaller than 1 (Table 1). This is the case in particular for the strong bands due to the symmetric stretching vibration of the NO_2 group at 1338 cm^{-1} and of the C═C stretching vibrations of the para-substituted benzene rings (ν_{8a} and ν_{8b}) at 1600 and 1587 cm^{-1}. Since these vibrations have their transition dipole moment essentially parallel to the long axis of the azobenzene groups,[11] the infrared spectra clearly show that the irradiation of the polymer produces a preferred orientation of these groups perpendicular to the writing polarization direction, in agreement with previous results obtained on other polymers containing azobenzene.[6,7] On the other hand, the absence of the band due to the ester group C═O stretching vibration in the difference spectrum indicates that the main chain of the polymer remains randomly oriented.

Table 1. Assignment, Frequency, and Dichroic Ratio of the Major Bands in the Infrared Spectra of pDR1A and pDR19T

	pDR1A		pDR19T	
assignment[a]	freq (cm^{-1})	D	freq (cm^{-1})	D
$\nu_{C=O}$	1735	0.99	1711	0.87
$\nu_{C=C}$			1634	0.57
ring, ν_{8a}	1600	0.93	1600	0.48
ring, ν_{8b}	1587	0.94	1588	0.43
			1560	0.59
ν_{as,NO_2}	1516	0.98	1516	0.74
ring, ν_{19a}			1420	0.58
$\nu_{N=N}$	1388	0.94	1383	0.44
ν_{s,NO_2}	1338	0.94	1339	0.48
δ_{CH}	1311	0.92	1314	0.36
	1248	0.95	1253	0.76
δ_{CH}			1198	0.45
			1165	0.77
ν_{Ph-N}	1156	0.92	1156	0.56
ring, ν_{9b}	1134	0.94	1138	0.44
	1105	0.93	1105	0.43

[a] ν = stretching vibration; as = antisymmetric; s = symmetric; δ = bending vibration.

An interesting feature of the spectrum of pDR1A is the fact that the dichroic ratio of the bands due to both symmetric and antisymmetric stretching vibrations of the NO_2 groups is smaller than 1 (Table 1), even though these vibrations have transition dipole moments perpendicular to each other. This result reveals that, in the written polymer, the NO_2 groups, and most likely the azobenzene groups, do not display a cylindrical symmetry of orientation. Therefore, the light-induced distribution of orientations appears to be more complex than the biaxial orientation distribution of molecules with cylindrical symmetry used previously to describe the orientational behavior of written liquid crystalline and amorphous side-chain polymers.[6,7]

The polarized infrared spectra of a written pDR19T film are represented in Figure 5. As seen in this figure, and from the value of dichroic ratios given in Table 1, the level of light-induced orientation achieved is much higher for pDR19T than for pDR1A, in agreement with the birefringence results (Figure 3) and with the literature.[9,10] For example, the dichroic ratio of the 1339-cm^{-1} band due to the symmetric stretching vibration of the NO_2 groups is equal to 0.48 for pDR19T compared to 0.93 for pDR1A. In addition, the infrared spectra show that the nonabsorbing PD groups are able to follow, at least partly, the reorientation of the azobenzene side chains. The 1634-cm^{-1} band due to the C═C stretching vibration of the PD

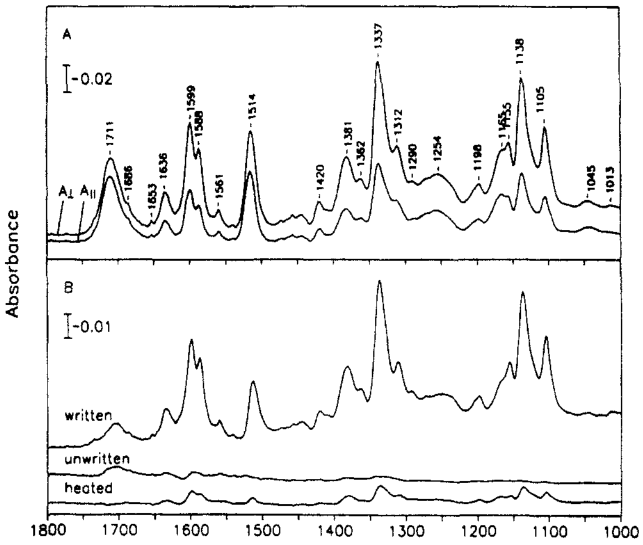


Figure 5. (A) Infrared spectra of a written pDR19T film recorded with the infrared radiation polarized parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the writing direction. (B) Dichroic difference spectra ($A_\parallel - A_\perp$) of written and unwritten pDR19T films and of an unwritten film after heating at 130 °C for 15 min.

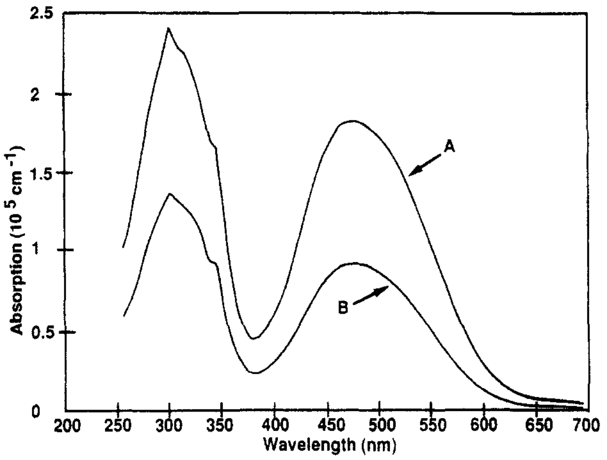


Figure 6. UV–vis absorption spectra of pDR19T for light polarized perpendicular (A) and parallel (B) to the writing direction.

groups of the written pDR19T films displays a dichroic ratio of 0.57, compared with 0.48 for the NO_2 groups. This demonstrates unambiguously that the PD groups located in the main chain undergo a cooperative reorientation with the azobenzene groups and display a preferential orientation perpendicular to the writing polarization direction.

Unlike pDR1A, pDR19T films display weak bands in the dichroic difference spectrum of the unwritten sample (Figure 5). This weak orientation is most likely associated with the fact that pDR1A is amorphous while pDR19T tends to form semicrystalline domains. These domains may have appeared during the slow evaporation of the solvent. A spectrum recorded at room temperature on the unwritten film of pDR19T that had been heated to 130 °C for 15 min is also shown in Figure 5. It shows that a significant degree of orientation of pDR19T can be induced by heating the unwritten film above T_g, confirming the X-ray diffraction results presented above.

The polarized UV–visible absorption spectra of pDR19T are presented in Figure 6. The absorption coefficient for light polarized parallel to the writing direction is substantially less than that for light polarized in the perpendicular direction. It is interesting to note that the dichroism shown in Figure 6 arises both from the UV region and from the visible region. pDR1A shows dichroism only in the visible region,[12] indicating that the π–π^* transition of the azobenzene group is the main originator. The dichroism in the UV region, which is specific for the pDR19T polymer, appears from the PD groups, and it is an important contributor to the overall dichroism of this sample. Using the previously published model of a uniaxial azobenzene orientation,[6,7] one can calculate from this dichroism an order parameter which is comparable to the liquid crystalline polymers,[7] while for pDR1A the calculated order parameter is comparable to the previously reported amorphous copolymers.[7] Obviously, this is just an approximation, as the model is clearly not valid.

The birefringence, $\Delta n(\omega)$, at 633 nm is related to the dichroism, $\Delta\alpha(\omega')$, and it can be evaluated using the Kramers–Kronig transformation:[12,13]

$$\Delta n(\omega) = \frac{c}{\pi} P \int_0^\infty \frac{\Delta\,\alpha\,(\omega')}{\omega'^2 - \omega^2}\, d\omega'$$

where P is the principal value of the integral, ω is the measurement frequency, c is the speed of light, and ω' represents the whole spectrum. For pDR19T the calculated birefringence is 0.25, while the measured one is 0.27. From the analysis it is clear that the UV part of the absorbance is an important contributor to the overall birefringence. Indeed, a similar calculation for pDR1A gave a birefringence of 0.074, compared with the measured value of 0.08.[12]

Second Hypothesis: Trapped *cis*-Azobenzene. It is fairly well-known that the azobenzene thermal cis–trans isomerization rate depends on a series of factors but that electron-donor and electron-acceptor substituted azobenzenes of the type found in pDR1A and in pDR19T have a very fast cis–trans isomerization rate.[14] Measurements of the absolute cis content are hampered by the fact that the maximum absorbance for the cis isomer coincides with the maximum absorbance for the trans isomer.[15] Nevertheless, under some approximations, a first-order kinetic constant can be measured for nitro–amino-substituted azobenzene using a procedure similar to the flash photolysis method. The polymer film is pumped with an unfocused laser beam until the absorbance reaches a stationary state. The return to the initial absorbance value is monitored as a function of time. Dumont[15] and we[16] have found that the cis–trans thermal isomerization constant is of the order of 0.2 s^{-1}. Then the cross-linking rate of pDR19T under UV light will have to be extremely fast in order to be able to trap such a short-lived isomer. Thus, we have decided to try to estimate the degree of cross-linking. A pDR19T film was irradiated with UV light under the conditions described in the literature,[10] and the degree of cross-linking was monitored using the 1634-cm^{-1} band in the IR spectrum. This band was assigned to a C=C stretching vibration. For a polymer containing the PD rigid group which undergoes cross-linking, this band has been shown to disappear altogether after ca. 100 min of irradiation.[17] For pDR19T exposed to UV light for about an hour,[10] this band showed only minor changes, thus raising a serious question mark over the proposed fast cross-linking process.[10] In our experiment, a sample of pDR19T was therefore exposed to UV light for 16 h and its infrared spectrum was recorded. No decrease in the intensity of the 1634-cm^{-1} band was detected for the irradiated sample compared with the untreated sample, showing clearly that no cross-linking occurs. Moreover, if the cis content were higher in the written sample than in the initial sample (which would happen if cis is formed and trapped in the cross-linked film), the kinetics of thermal cis–trans isomerization would be different for written and non-written specimens of pDR19T. Our experiments show this is not the case.[16]

The other argument in favor of a cross-linked product obtained after UV illumination was that pDR19T became insoluble after this treatment.[10] The loss of solubility could also be explained by the induced order (semicrystallinity) due to exposure to polarized light.

Conclusions

It seems clear from the above-mentioned data that the phenomenon described by Dalton[10] is similar to what was described previously in the literature; i.e., the azobenzene groups in pDR19T undergo trans–cis–trans isomerization cycles when subjected to polarized light, and the result of these photochemical processes is an orientation of the azobenzene groups preferentially perpendicular to the polarization plane of the light source. This orientation is known to be very stable below the T_g of the polymer.[9,18] When some other rigid groups are present in the polymer structure, they are involved in the overall orientation, providing a significant enhancement in systems which are crystalline or liquid crystalline. This phenomenon was known for side-chain polymers where the "inert" rigid groups had a shape and position in the molecule similar to those of the photochemical azobenzene group. The data presented here suggest that this cooperative motion is much more general and would involve any type of rigid groups present in the system. It will be interesting to investigate separately the cooperative motion effect in amorphous and in crystalline/liquid crystalline polymers. We are designing polymer structures which would be amenable to such a study. The next question which must be answered is whether this cooperative orientation is an energy saving or an extra expense from the point of view of the energy put into the system. We are investigating this in terms of efficiency, defined as induced birefringence per energy input or per energy absorbed by the film.[19]

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