Macromolecules **1997,** *30,* 6913−6919

Dynamic Processes of Optically Induced Birefringence of Azo Compounds in Amorphous Polymers below T_g

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Received February 5, 1997; Revised Manuscript Received June 2, 1997[⊗]

ABSTRACT: The growth and decay processes of the optically induced birefringence in an azobenzene-functionalized polymer, DR19FPOZ (full name given in the text), and in another azobenzene guest/host polymer system have been studied. The temperature dependence of the birefringence signal is studied, and possible mechanisms associated with the growth and decay segments of the signal are analyzed. Rate constants deduced from the optically induced birefringence signal are also investigated as a function of the laser excitation power and film thickness. The rate constants associated with the growth and decay processes and activation energies are obtained for the polymer system below the glass transition temperature.

Introduction

The photoinduced trans−cis isomerization of azobenzene and its derivatives has been widely studied in solution[1] and in doped and functionalized glassy polymers.[2] In hopes of producing materials that could be used for electrooptical devices, polarization holographic grating, and nonlinear optics, the mechanism underlying this isomerization process has been the subject of numerous recent studies.[3−5] This type of photoinduced isomerization process is also of particular interest because the induced changes in molecular orientation can be transferred to the surrounding molecules.[4,6] In addition, the induced birefringence and dichroism that result from molecular reorientation could potentially be used to probe the polymer environment in the vicinity of the azobenzene molecules.[2]

When first dispersed in a polymer film, azobenzene molecules exist in their lower energy, trans form and are randomly oriented throughout the film. If the polymer film is then subjected to polarized light of an appropriate wavelength (in the absorption band of the azo compound), those azo molecules that have a nonvanishing transition dipole component in the polarization direction of the excitation beam can be photoisomerized to the cis form. Through a thermal or photochemical process some molecules in the cis form can revert back to the trans form, although a given molecule may not necessarily revert to the orientation it had initially. After several repetitive photoexcitation and isomerization cycles, an excess of azo molecules with transition dipole moments perpendicular to the polarization vector direction of the excitation light can develop. The azobenzene molecules in this perpendicular orientation cannot interact with the excitation light, and therefore this light cannot convert them back to their original orientation. As a result, the distribution of molecular orientation that was isotropic before photoexcitation becomes anisotropic. This anisotropic distribution gives rise to birefringence and dichroism in the film.[3]

The time required to reach maximum birefringence is expected to depend on several factors such as the size of the azobenzene molecules, the thickness of the film and the wavelength of the excitation light and its intensity. Numerous studies on how such factors affect the dynamics of the photoinduced orientation of azobenzene-functionalized polymer have recently been performed by Natansohn et al.[7] These authors have reported the growth and decay segments of the photoinduced birefringence signal.[8] However, the underlying mechanism behind the photoinduced birefringence signal of the azobenzene-functionalized polymer has not been clarified. In addition, very few studies on the temperature dependence of the photoinduced birefringence have been performed. To clarify the mechanism responsible for the dynamic birefringence, we have studied the excitation intensity dependence, and temperature dependence, of the photoinduced birefringence. In addition, we have also measured the effects of varying the film thickness. In this paper we present the results of these studies.

Experiment

Figure 1 shows the chemical structures of the materials used in the present study. Both disperse red 19 (DR19) and the disperse red 19-functionalized polyoxazolidone (DR19FPOZ) polymer were made in house following procedures given in the literature.[9,10] To obtain the DR19FPOZ polymer, Bisphenol A diglycidyl ether (3.4 mg, 0.1 mmol) and prepolymer (8.6 mg, 0.1 mmol) were dissolved in 10 mL of dioxane. The synthesis of prepolymer containing the azobenzene chromophore was carried out using the procedure described in ref 10. The resulting solution was filtered through a 0.1 μm Teflon filter and was then spin-cast onto clean glass substrates. The resulting films were dried under vacuum at room temperature to remove solvent. After drying, the films were placed in an oven and heated to 120 °C to initiate polymerization and were kept at that temperature for at least 5 h. In order to monitor the polymerization process, a NaCl slide was used in place of the normal glass substrate for one of the films. After the polymerization process was complete, the IR spectrum of the film prepared on the NaCl slide was measured and found to be identical to that given in the literature.[10] Thus, we are confident of the successful preparation of the DR19FP0Z polymer. In addition to the DR19FPOZ polymer system, two guest/host systems were prepared: disperse red 1 (DR1) in poly(methyl methacrylate) (PMMA) (5% by weight) and methyl red (MR) in polystyrene (PS) (2% by weight). These films were prepared from solutions containing an appropriate amount of dye, polymer, and chloroform, filtering through a 0.1 μm filter and then spin coating onto clean glass slides. The film thickness was measured with using a Metricøn PC-2000 prism coupler, an instrument that determines the refractive index and thickness of a thin film using the waveguide principle; absorbance was measured with a Hewlett Packard 8452 diode array UV/vis spectrophotometer.

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[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1997.

S0024-9297(97)00164-2 CCC: $14.00

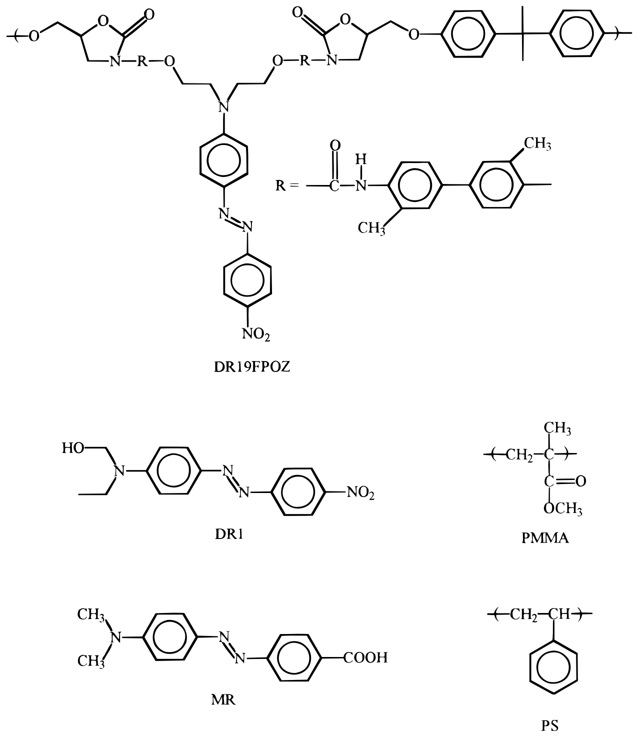

Figure 1. Chemical structures of the DR19-functionalized polyoxazolidone (DR19FPOZ), poly(methyl methacrylate) (PMMA), polystyrene (PS), disperse red 1 (DR1), and methyl red (MR).

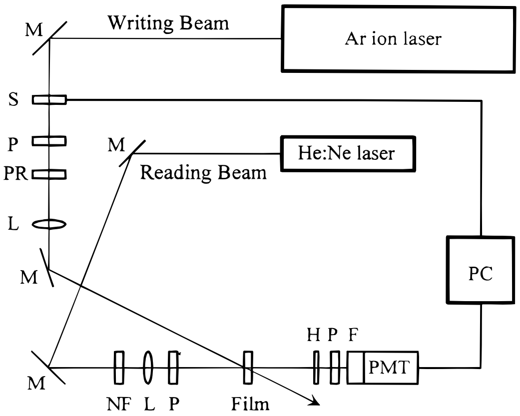

Figure 2. Experimental setup for the measurement of the photoinduced orientation of azo compounds. Labels designate various optical and electronic components: M, mirror; S, shutter; P, polarizer; PR, polarization rotator; L, lens; NF, neutral density filter; H, pinhole; F, filter set; PMT, photomultiplier tube; PC, personal computer. Lasers operating at wavelengths of 488.0 and 632.8 nm were used as a writing beam and reading beam, respectively.

Figure 2 shows the setup for the measurement of photoinduced birefringence. The 488.0 nm line from an Ar$^+$ laser was used as a pump (or writing) beam, and the 632.8 nm line from a He−Ne laser was used as a probe (or reading) beam. Unless otherwise stated, the power of the pump laser was kept low (2.5 mW) to avoid possible photodegradation or photobleaching of the sample; the diameter of the beam was approximately 0.5 cm, resulting in an optical power density of 13 mW/cm^2. The wavelength of the pump beam is in the absorption range of the DR19FP0Z polymer, and the wavelength of the probe beam lies outside of the absorption band. To carry out the experiments, a film sample was placed between a pair of crossed polarizers. To achieve maximum signal, the polarization vector of the pump beam was set to 45° with respect to the polarization vector of the probe beam. An electronically controlled shutter was used to turn on and off the pump beam. When needed, a quarter wave plate was inserted into the optical path before the sample (the quarter wave plate converted the linear polarized beam to circular polarization, which removed the birefringence that had been induced). The attached signal (i.e., the transmitted probe beam) was detected with a photomultiplier tube. To investigate the temperature dependence of photoinduced birefringence, the film was placed in a computer-controlled sample oven, which regulated the temperature to ±0.1 °C.

Results and Discussion

Photoinduced trans−cis isomerization in azobenzene is a well-known process. Azobenzene derivatives usually display a low-intensity n−π^* band in the visible region and a high-intensity π−π^* transition in the UV region associated with the N=N double bond. Due to an increase in the π orbital energy level and a decrease in the π^* orbital energy level, the n−π^* and π−π^* bands in *o*- and *p*-aminoazobenzene molecules tend to be close together or even overlap.[1] This effect is enhanced when the 4 and 4′ positions of aminoazobenzene are substituted with electron donor and electron acceptor groups, the typical configuration of nonlinear optical (NLO) chromophores.[1] Azobenzene derivatives capped at either end with an electron donor and an electron acceptor group, such as the disperse red 1 (DR1) chromophore and DR19FPOZ polymer considered here, have a transition dipole moment lying along the long π-conjugation direction. As a result of light-molecule interaction, molecules having the π-conjugation direction parallel to the polarization direction of the laser beam are promoted to the first excited state (π^*). These excited molecules then isomerize by performing a rotation about the N−N bond and then relaxing to the cis form. The cis form may be converted back to the trans form by a photo or a thermal process; this (re)isomerization may proceed via a rotational mechanism involving either rotation about the N−N bond or flip-flop inversion of one of the N atoms.[11] The essential difference between the two is that the rotational mechanism proceeds via a dipolar transition state accompanying a large volume change, whereas the inversion mechanism requires only a local motion involving hybridization of a N-atom. The photoisomerization from trans to cis or from cis to trans form is a fast process. Measurements on noninteracting molecules in the gas phase indicate that this process takes place in the subnano- to picosecond time regime. The photoinduced isomerization rate is expected to depend on the laser excitation intensity and on the environment in which the azo moiety exists.

Azobenzene with electron-donating and -accepting substituents, such as the ones considered here, should stabilize the dipolar rotational transition state, therefore making the rotational mechanism energetically favorable.[12,13] In the guest/host system, DR1 excited by a pump beam with a polarization direction parallel to the N=N bond is more likely to proceed via the rotational mechanism, as free rotation about the N−N bond can readily occur in the excited state. The trans isomer with orientation vertical to the polarization vector of the laser light can then easily be formed in the guest/host system. On the other hand, in the DR19-functionalized polymer, because one end of the azobenzene is tethered to the polymer backbone, the trans isomer with the N=N

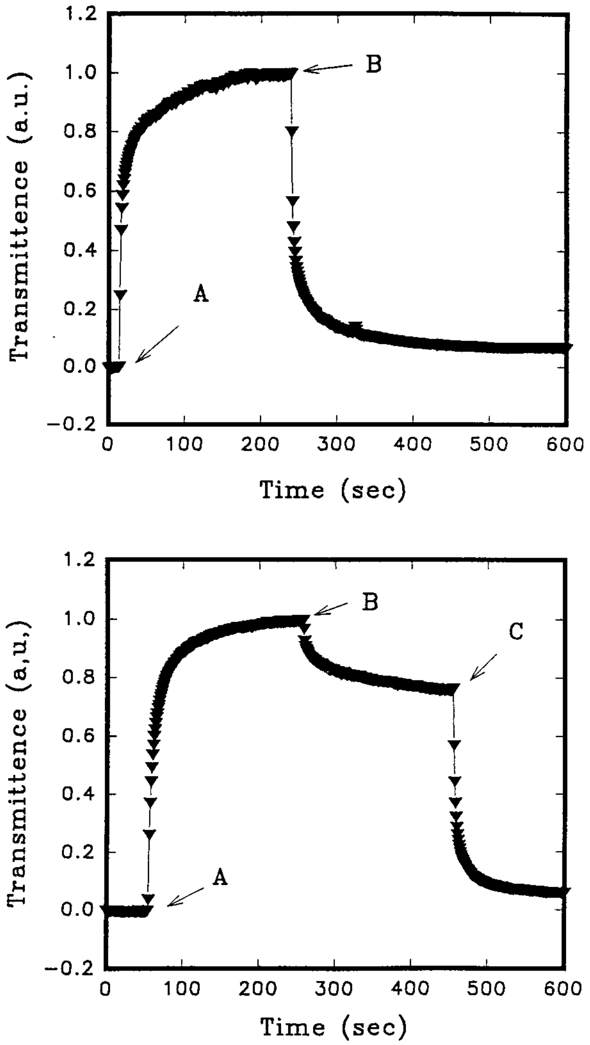

Figure 3. Typical growth and decay processes of photoinduced birefringence: (top) guest/host system with 5 wt % of DR1 in PMMA polymer, (bottom) DR19FPOZ at room temperature. The pump beam is on at “A” and off at “ B.” Circularlypolarized light was introduced at “C.”

double bond vertical to the polarization direction of the pump beam cannot easily be formed by rotation. However, the cis−trans transformation can still take place via the inversion mechanism through the N atom attached to the polymer chain. By a small adjustment of the position of the N atom in the aminobenzene group involving orbital hybridization combined with local segmental motion of the polymer chain, a trans isomer in a different orientation can be obtained. Even so, this cis to trans isomerization is expected to be a fast process (subnano- to picosecond time regime), as the process involves electronic transitions. Furthermore, the rate of this cis to trans photoisomerization is expected to depend on the light excitation power. Regardless of the mechanism, the above suggests that upon electronic excitation a conformational change in DR1 or any azobenzene-functionalized polymer in the glassy state can occur, despite the fact that rotation of the chemical group about the N−N bond is hindered and the mobility of the polymer chain is restricted. A similar conclusion has also been reached in another polymer system below T_g.[14]

Shown in Figure 3 are representative growth and decay traces of the birefringence signal from the guest/host system (DR1 in PMMA, top) and that of the DR19FPOZ polymer (bottom) at room temperature. At the beginning of the experiment, no light is transmitted through the analyzer (transmission axis oriented orthogonal with respect to the polarizer before the sample), as the azo compound is randomly oriented. As the polarized Ar^+ laser radiation (power density 13 mW/cm^2) is introduced (marked “A” in the figure), an anisotropic orientational distribution is created as a result of the accumulation of cis isomers and of trans isomers that are oriented with the transition dipole vertical to the polarization vector of the pump beam. Light is thus transmitted through the analyzer due to the onset of birefringence. When the excitation light is turned off (marked “B” in the figure), the signal starts to decay back to the initial level. In the guest/host system (top), this decay is rapid and the system reverts to equilibrium in a short time (about 100 s). On the other hand, in the DR19FPOZ functionalized polymer (bottom), the system does not relax back to equilibrium during the time frame of the experiment (many days). To remove the remaining birefringence, circularly polarized light is introduced (marked “C” in the bottom figure). Circularly polarized light effectively converts the cis isomers to the trans form for all orientations. The transmitted signal, I, due to birefringence can be shown to be proportional to $\sin^2(\pi d\Delta n/\lambda)$, where d and Δn are the thickness and birefringence of the film, respectively; λ is the wavelength of the probe beam (the He−Nelaser radiation at 632.8 nm). Since $\pi d\Delta n/\lambda$ is much less than 1, the transmitted signal is effectively proportional to $(\Delta n)^2$.

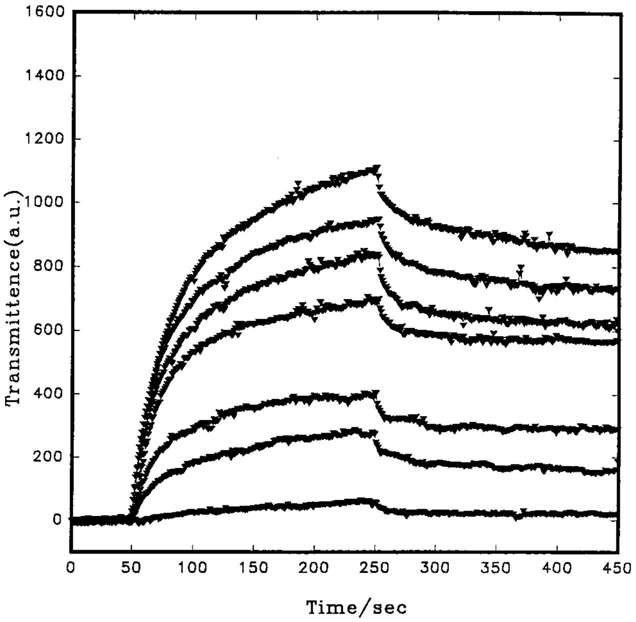

Figure 4. Temperature dependence of the photoinduced birefringence signal of DR19FPOZ. Temperatures used for this were 30, 35, 40, 45, 70, 80, and 100 °C from top to bottom.

We have investigated the temperature dependence of the growth and decay of the birefringence signal. Shown in Figure 4 are data obtained at several temperatures. As can be seen, the maximum level of birefringence obtainable decreases rapidly as the temperature is increased. Near or above T_g ($\approx$ 100 °C), the signal relaxes very quickly and a different experimental technique would be needed to accurately analyze the rapid time dependence exhibited here; this will be the subject of future work. In the present paper we focus on the dynamic process of the DR19-functionalized polymer below T_g. Signal intensities did not necessarily reach plateau levels at the various temperatures. In-

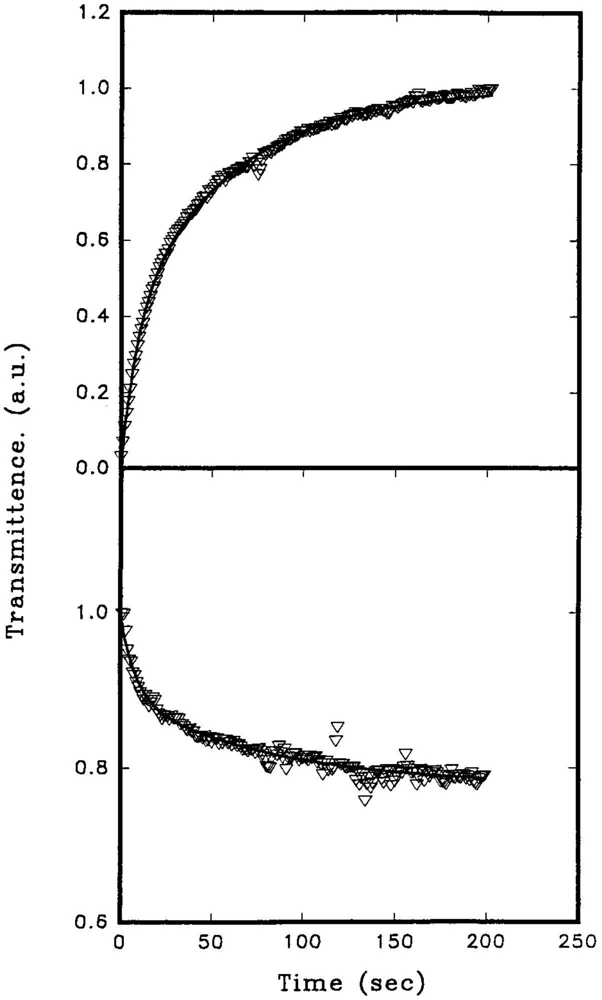

Figure 5. Comparison of the growth (top) and the decay (bottom) of the photoinduced birefringence of DR19FPOZ at room temperature. Solid lines are the fitted curves.

stead, to remove the length of exposure to the excitation laser as an experimental variable, the excitation beam was allowed to remain on for 200 s at different temperatures. After this, the excitation beam was blocked and the decay segments were measured.

We have found that the growth of the birefringence signal is not single exponential. As shown in the top plot in Figure 5, it can, however, be adequately fit to a biexponential function given by

$$I(t) = A(1 - e^{-k_a t}) + B(1 - e^{-k_b t}) \tag{1}$$

where A and B are amplitudes associated with the processes having rate constants k_a and k_b, respectively. The decay of the signal after the removal of the excitation beam is also biexponential and can be fit to

$$I(t) = Ce^{-k_c t} + De^{-k_d t} + E \tag{2}$$

(bottom plot in Figure 5), where C and D are amplitudes associated with the processes having rate constants k_c and k_d, respectively, and E is the background intensity, which can be minimized if, as mentioned above, circular polarized light is introduced to erase the residual birefringence. Since the time dependence of the transmitted signal is proportional to $\Delta n(t)^2$, one would obtain biexponential decay behavior if $\Delta n(t)$ is assumed to undergo a one-exponential decay process given by $\Delta n(t) = a + b \exp(-(t/\tau))$. However, judging from the values of k_c and k_d obtained from the fit, k_c and k_d do not have a simple ratio and the single-exponential decay mechanism can be ruled out. Equations 1 and 2 suggest that the birefringence growth and decay occur via two independent mechanisms.

Natansohn et al.[7] have also observed a biexponential kinetic process in their azobenzene systems. They have proposed a model to describe the kinetics of behavior such as that illustrated in Figure 3. In their model, only trans isomers oriented with some specially designated orientational distribution with respect to the polarization vector of the probe beam are assumed to contribute to the birefringence; molecules in the cis configuration are neglected, as they are assumed to have zero population. Although a simulation based on this model with a specially constructed set of parameters is able to reproduce the general features of the experimental results, their simulation predicts that the kinetic rate constants associated with growth and decay depend on the intensity (photon flux) of the writing beam. This model, however, does not agree with the experimental results presented here.

We have examined the dependence of the birefringence growth and decay on excitation power by analyzing the birefringence signals obtained in the DR19FPOZ polymer with different writing laser powers. The growth and decay segments obtained at each power level were well fit by the biexponential functions given above. The fitting results for the parameters A, B, k_a, and k_b for the three lowest writing laser powers are shown in Figure 6. At room temperature we find that the rate constants k_a are greater than k_b by a factor of about 10, but both display no power dependence. However, the amplitudes A and B do display a power dependence; as shown, the amplitude of the fast process (associated with k_a) increases with increasing writing laser intensity while the slow process (associated with k_b) demonstrates the opposite. As mentioned above, in the azobenzene-functionalized polymer, while the cis isomer can be readily formed by the Ar^+ laser beam, it cannot easily be converted to the other trans form by rotation, in contrast to the rotational mechanism followed in the guest/host system. However, in the presence of the laser radiation, the cis isomer can be converted back to the trans isomer by the inversion process, as described above. Until recently, it has generally been assumed that the cis form does not exist for a long enough time to contribute to the observed birefringence. However, previous work in our laboratory on several guest/host azobenzene/polymer systems[15] indicates that even in the guest/host system the cis form can exist long enough to contribute to the birefringence. Thus, we believe that in the DR19FPOZ polymer both the cis and trans isomers contribute to the birefringence signal. We therefore associate the first “fast” term in eq 1 with the formation of the cis isomer, which contributes to the observed birefringence. Furthermore, we assign k_a to the rate of formation of the cis form and k_b to the formation of the trans isomer that contributes to the observed birefringence. Both of these rates should be influenced by the polymer environment that the cis and trans isomers are in.

Figure 6 (bottom) is a plot of the rate constants k_c and k_d vs the writing laser intensity. No power dependence of k_c and k_d is found; the amplitudes C and D also do not depend on the writing laser power (data not shown). This is to be expected, as the decay segment is measured with the writing Ar^+ laser turned off.

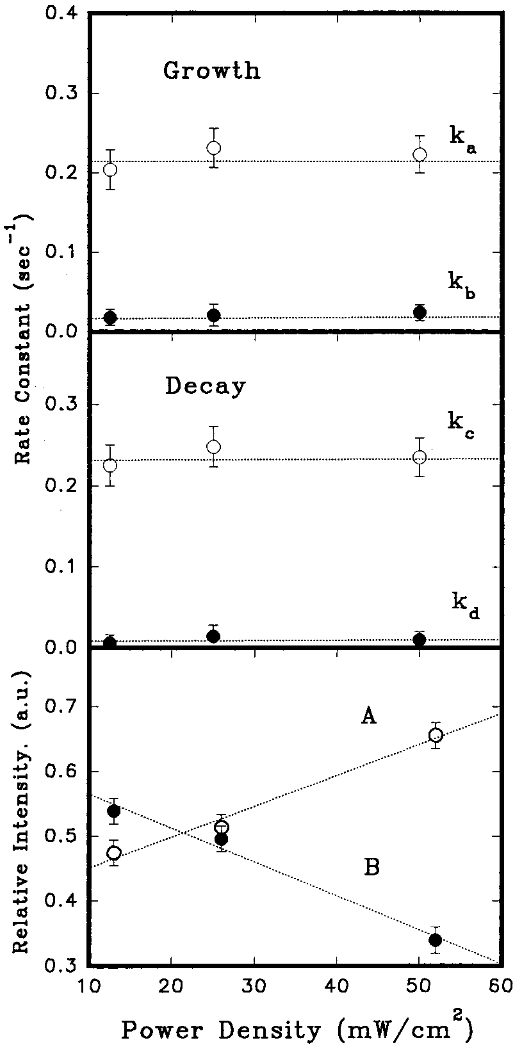

Figure 6. Writing power density dependence of rate constants (top and middle) and amplitudes (bottom) of the growth and the decay of the photoinduced birefringence in DR19FPOZ. Laser powers were 2.5, 5, and 10 mW at room temperature.

However, this result is in contrast to conclusions arrived at in ref 7 where the birefringence decay is asserted to depend on the writing laser intensity. Our results suggest that the decay of the birefringence involves both the trans form and the cis form that has not been converted to the trans isomer. To be sure, the trans form with a component vertical to the polarization of the light is formed via the cis isomer, and this formation depends on the laser power of the writing beam, but the kinetic decay rate constants should not be power dependent, as the writing laser is already off. As the rate constants were not observed to depend on laser intensity, we are confident that the effects of local heating did not significantly affect our results.

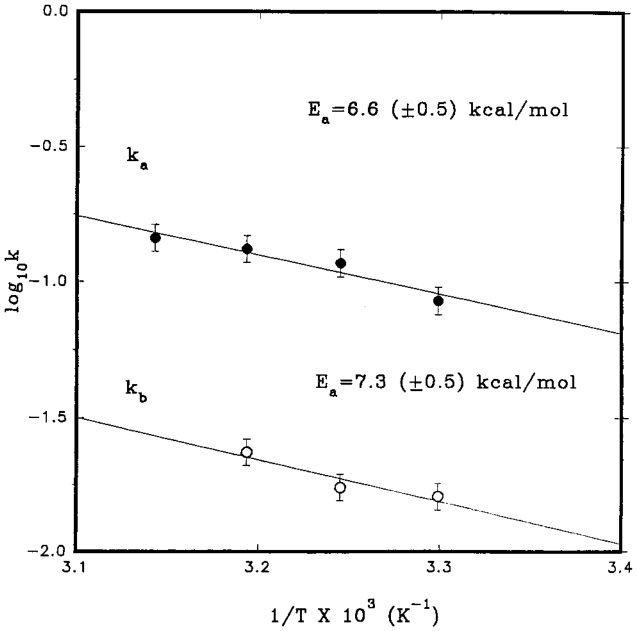

Figure 7. Arrhenius plots of the relaxation rate constants of DR19FPOZ in the growth process. Open and closed circles are for k_b and k_a, respectively. Data were obtained at 30, 35, 40, and 45 °C.

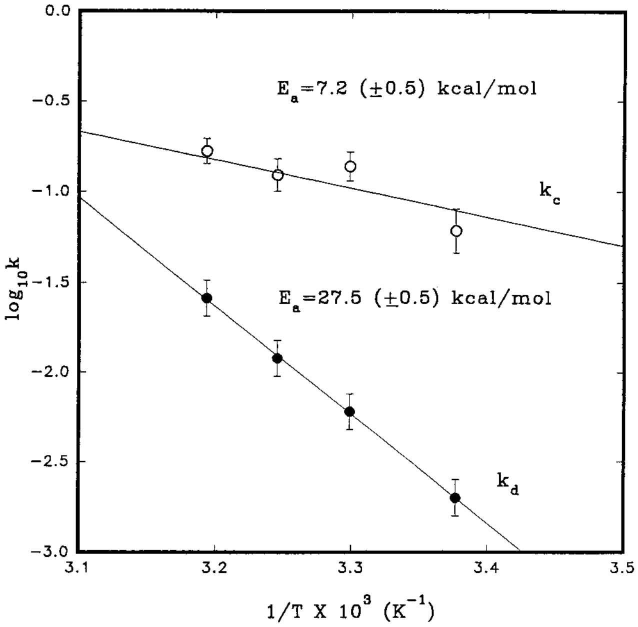

Figure 8. Arrhenius plots of the relaxation rate constants for DR19FPOZ in the decay process. Open and closed circles are for k_c and k_d, respectively. Data were obtained at 30, 35, 40, and 45 °C.

Temperature dependence data should provide additional insight into the mechanism involved in the growth/decay segments of the observed birefringence, but until now, experiments of this type have not been performed. Figure 7 is a plot of temperature vs k_a and k_b. The data presented in Figure 7 were obtained after the films had aged for about 1 month at room temperature (relaxation rates were found to gradually decrease with aging time). After this time, growth/decay results measured at a constant temperature below T_g were reproducible. Within experimental uncertainty, we have found that both k_a and k_b show a similar activation energy of about 7.0 kcal/mol. The temperature dependence of the rate constants k_c and k_d, associated with the decay of birefringence, is very interesting. As shown in Figure 8, although the rate constant k_c has about the same activation energy as k_a (or k_b), the activation energy of k_d is about 4 times larger. At room temperature, the magnitude of k_d is nearly a factor of 30 smaller (3.1×10^{-1} s^{-1} for k_c versus 1.0×10^{-2} s^{-1} for k_d). Thus, if we take the k_c rate constant to be associated with the decrease of birefringence associated with the cis isomer, then k_d is probably associated with that of the trans form having a vertical projected component of the transition dipole. The large activation energy associated with the trans form could be due to its more extended configuration, which causes it to be

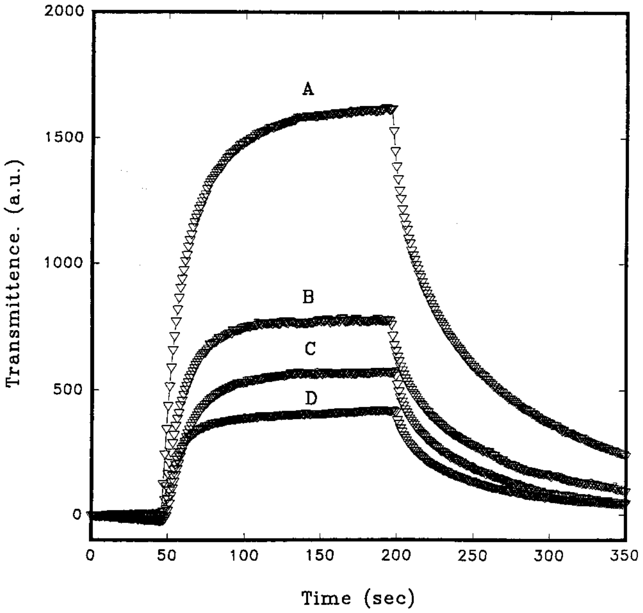

Figure 9. Film thickness dependence of the photoinduced birefringence with 2 wt % methyl red in polystyrene. Film thicknesses were (A) 2.4 μm, (B) 2.0 μm, (C) 1.7 μm, and (D) 1.5 μm, respectively.

more hindered by the polymer environment during reorientation.

Consider finally the effect of the film thickness. Rochon et al.[16] studied the maximum birefringence obtainable and investigated the growth rates as a function of film thickness. The film thickness was emphasized because of their earlier conclusion concerning the time required for the chromophores to exhibit anisotropy in their orientational distribution depending on the intensity of the writing beam. They have argued that, due to large laser intensity absorption by the azobenzene moiety, the intensity of the writing beam decreases rapidly as it propagates through the specimen. Hence, one expects to find that the molecular reorientation rates depend on the thickness of the film. These authors then presented a simulation to calculate the induced phase retardation. The phase retardation is proportional to Δn. The simulation based on their assumed model satisfactorily reproduces the thickness dependence hypothesis.

Shown in Figure 9 is a series of transmitted intensity curves obtained using a series of 2 wt % methyl red/polystyrene films of different thicknesses. Film thicknesses were measured with the Metricøn PC-2000 prism coupler and were found to be 1.5, 1.7, 2.0, and 2.4 μm, and absorbances of the films were 1.527, 1.715, 2.015, and 2.312 (obtained with the Hewlett-Packard spectrophotometer), respectively. Over the sample thickness range studied, the transmitted birefringence signal increases with the thickness of the film. We have analyzed the growth and decay segments of the transmitted signal and found that both the growth and decay segments are well fit by the biexponential functions given in eqs 1 and 2. However, as shown in Figure 10, the rate constants k_a, k_b, k_c, and k_d do not change with sample thickness. However, the amplitude factor *A* associated with the fast process decreases with increasing film thickness, whereas the reverse is true for *B*. Although the thickness dependence experiment was carried out with a guest/host system, these data are consistent with the intensity dependence shown in Figure 6 but are in contrast to the simulation results of Rochon et al. The main discrepancy between our results and those of Rochon et al. is that our results indicate that the rate constants are not laser power dependent and that therefore changing absorption due to change in sample thickness should not affect the rate constants.

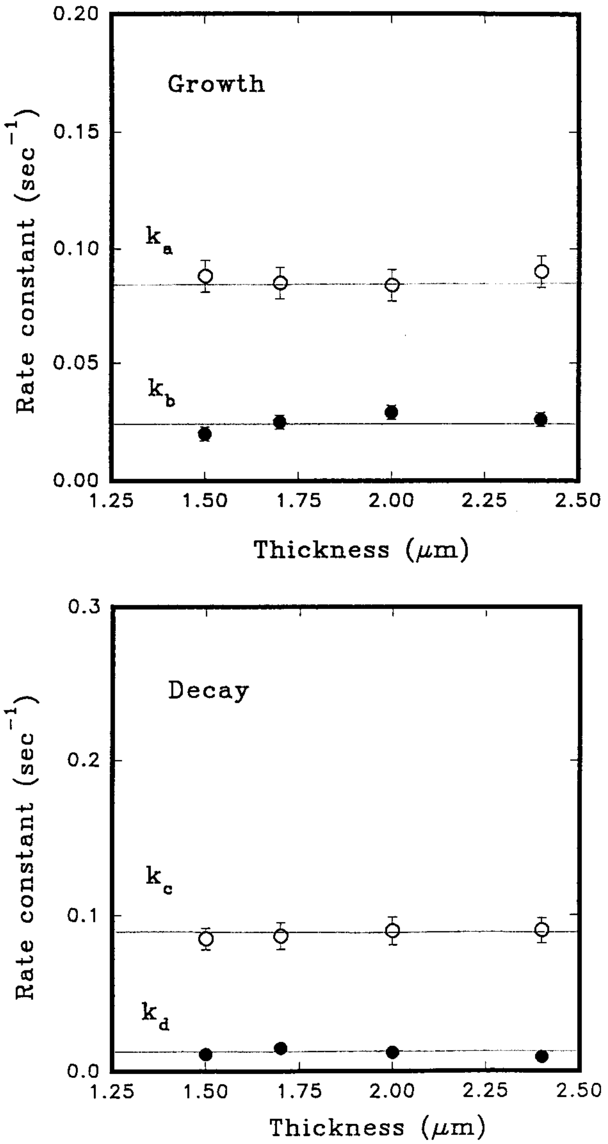

Figure 10. Rate constants obtained from the growth (top) and the decay (bottom) segments of the photoinduced birefringence signal plotted versus the film thickness of 2 wt % methyl red in polystyrene.

Summary and Conclusions

We have investigated the growth and decay processes of the optically induced birefringence in an azobenzene-functionalized polymer (DR19FPOZ) and have contrasted the results with the DR1/PMMA guest/host system. In an azobenzene-functionalized polymer, if the birefringence is not erased by circularly-polarized light, the decay segment of the signal does not decay to the initial level within the time of experiment. To account for this result, we have hypothesized that both cis and trans isomers are found to contribute to the birefringence signal. The shapes of the growth and decay segments of the birefringence signal are reflected by the formation and decay of the orientational distribution of the cis and trans isomers, and the dynamics of the decay is associated with the polymer segmental motion but not through reorientation of the azo moiety in the case of the DR19-functionalized polymer below T_g. We have found that the time dependence of both the growth and decay can be described by a biexponential function. In contrast to previously reported results in the literature, the rate constants associated with the biexponential function are found to be independent of the intensity of the writing laser, although the amplitudes of the exponentials in the growth segment are found to depend on the laser intensity. Temperature dependent studies of the birefringence signal show that the slow process in the decay segment has a significantly greater activation energy than the fast process. This allows an assignment of the fast process to be associated with the cis isomer, and the slow one with the trans isomer. The film thickness dependence study of the birefringence signal yielded results consistent with the intensity dependent data. The kinetic rate constants are independent of the film thickness.

These results can be understood because the photoinduced trans to cis or cis to trans isomerization process involves elctronic transitions associated with the breaking of a chemical bond (a π bond). Despite the rates of these isomerization processes being strongly dependent on laser power, the kinetics for the photoinduced isomerization are rather fast. In the slow time scale involving the birefringence signal measurement, as considered here, only reorientational motions of the final products of the photoisomerization process and the localized segmental motion of the polymer chains coupled to the azobenzene moiety are involved; dependence on the writing laser power should not be expected. In the case of the azobenzene-functionalized polymer, the reorientation of the azo moiety is coupled to localized polymer segmental motion and the concerted motion of both should be the mechanism for the decay of the birefringence signal. The kinetics rate constants obtained as k_a and k_b in the growth segment and k_c and k_d in the decay segment are due to the local segmental motion associated with trans and cis isomers.

Acknowledgment. Financial support of this work is from the Office of Naval Research and also from the Center of Material Research Analysis at the University of Nebraska—Lincoln.

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MA9701649