

Dynamic Processes of the Photoinduced Birefringence of Two Novel Azobenzene-Functionalized Polymers

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ABSTRACT: The growth and decay processes of optically induced birefringence in two novel azobenzene compounds [one was a hyperbranched poly(aryl ether) containing azobenzene groups, and the other was a hydrogen-bonded complex] were studied. The temperature dependence of the birefringence signal was investigated. The curves for the

buildup and decay of birefringence fit well to biexponential functions. The dependence of the fitting parameters on the temperature is also discussed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2069–2074, 2010

Key words: azo polymers; hyperbranched; orientation

INTRODUCTION

Polymers bearing azobenzene moieties (azo polymers) have been considered promising materials for optical data storage, optical switches, and electrooptical modulators and in other electrooptic areas.^{1–5} Birefringence in azo-polymer films may be created by trans–cis–trans photoisomerization processes produced with a linear polarized light, with the induced orientation of the chromophores being perpendicular to the polarization direction.⁶ The anisotropic molecular orientation results in stable photoinduced birefringence or dichroism, which can be erased by randomization of the alignment with circularly polarized light or heat.

In the simplest form of amorphous photoactive polymers, the azo dyes are dissolved in a passive polymer matrix. Such guest–host systems are flexible and cost effective as they only require the mixture of the constituents to produce a desired compound. However, the temporal and thermal stability of the induced anisotropy in these systems is typically poor.⁷ The polymer structure can be improved by covalent attachment of the chromophores to a linear polymer chain, either a side chain or a main chain; both of these have been widely studied.^{8–10} The advantage of this kind of form is the long-term sta-

bility of the induced anisotropy, which is significantly higher than in corresponding guest–host systems.¹¹

For decades, research efforts to explore new azo polymers have predominantly focused on traditional structures. In this article, we present two novel azo compounds: one is a hyperbranched poly(aryl ether) containing azobenzene groups (sample **A**), and the other is a hydrogen-bonded complex (sample **B**). In comparison with linear poly(aryl ether)s, hyperbranched poly(aryl ether)s possess a highly branched structure and good thermal properties. The presence of highly branched structures may facilitate the trans–cis isomerization of azo groups. Thus, the combination of this kind of backbone with photoactive azo groups could provide a new approach to develop novel high-performance materials with optical properties. The hydrogen bonding, although weak, enables high dye concentrations to be incorporated into the host polymer without the sacrifice of the ease of processing of conventional guest–host systems. Moreover, Banach et al.¹² reported that such specific noncovalent interactions could be used to enhance the electrooptic response of poled guest–host polymers. To our knowledge, the investigations of the dynamic processes on these kinds of structures of azobenzene compounds have not yet been reported. The temperature dependence of photoinduced birefringence in these two samples was investigated in this study. The buildup and decay curves were fitted with biexponential functions, and the dependence of the fitted time constants on the temperature are also discussed.

Additional Supporting Information may be found in the online version of this article.

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EXPERIMENTAL

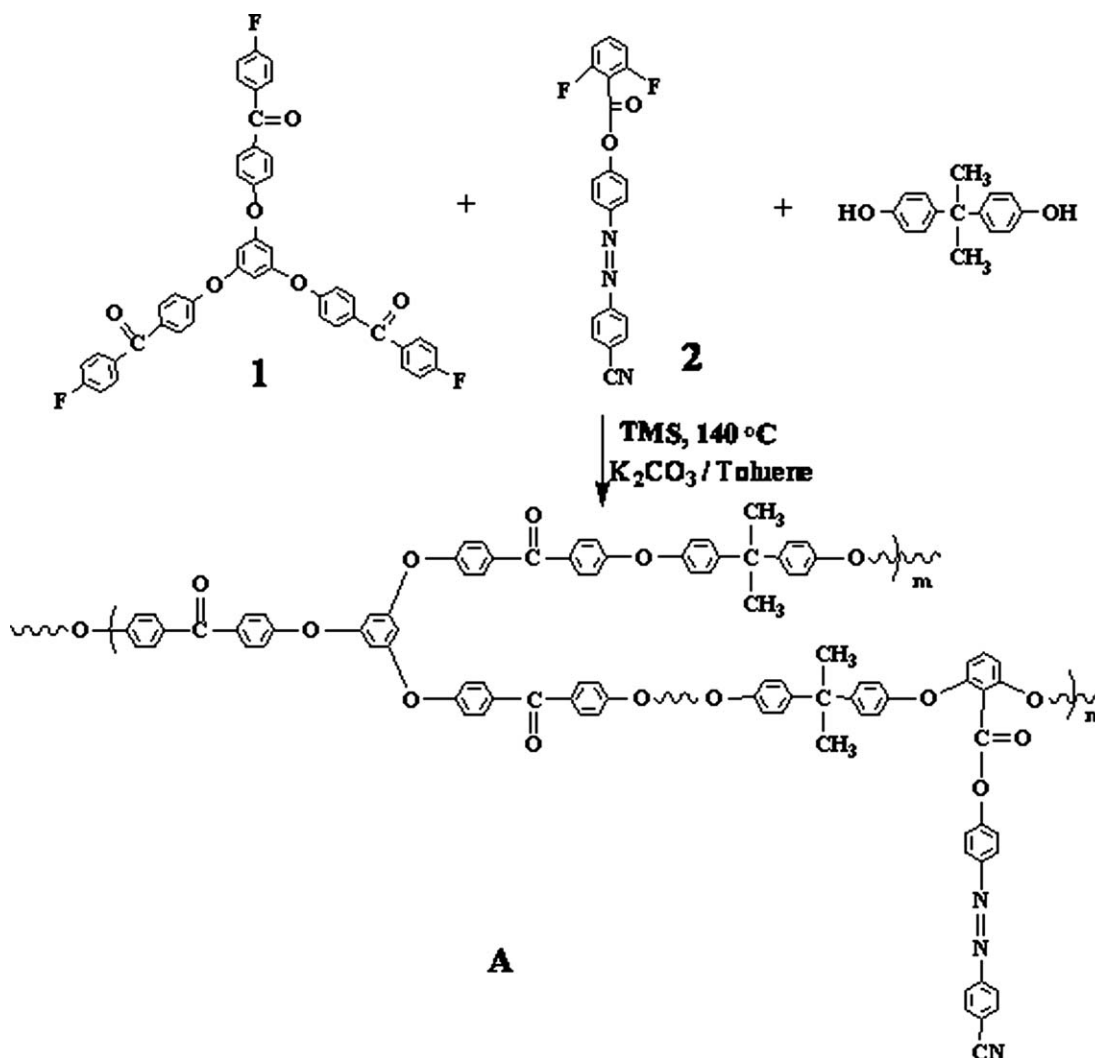
The synthesis route to sample A is shown in Scheme 1. A 75-mL, three-necked flask equipped with a mechanical stirrer, a Dean–Stark trap, a cold-water condenser, an N₂ inlet/outlet, and a thermometer were charged with monomer **1** (1.8025 g, 2.5 mmol), monomer **2** (0.91 g, 2.5 mmol), BPA [Bisphenol A (4,4'-isopropylidenediphenol)] (0.84 g, 3.7 mmol), K₂CO₃ (0.54 g, 3.86 mmol), tetramethylene sulfone (TMS; 20 mL), and toluene (15 mL). The reaction mixture was refluxed at 120°C for 2 h under an N₂ atmosphere to dehydrate the system. After dehydration and removal of toluene, the reaction temperature was then increased to 140°C and maintained at this temperature for 12 h until a viscous solution was obtained. Then, the viscous solution was slowly poured into 500 mL of water, and a thread-like polymer was obtained. After it was pulverized into a powder, the polymer was washed with hot deionized water and extracted in a Soxhlet extractor

with alcohol. The resulting product was dried at 100°C *in vacuo* for 24 h, and azo-HPAE [azo-Hyperbranched poly(aryl ether)] was obtained as an orange solid.

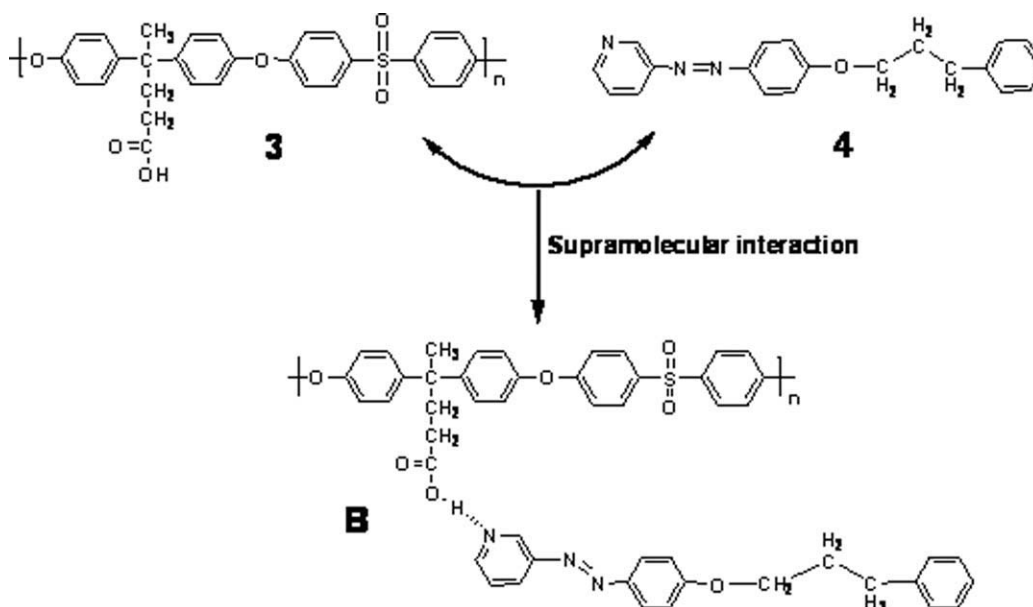
Yield = 90%. Gel permeation chromatograph number-average molecular weight = 1.3×10^4 . Polydispersity (weight-average molecular weight/number-average molecular weight) = 2.03. IR (KBr, cm⁻¹): 3030 (Ar–H), 2969 (–CH₃), 2223 (–CN), 1750 (–CO–O–), 1659 (–C=O), 1234 (–Ar–O–Ar–). ¹H-NMR (CDCl₃, ppm, δ): 8.05–7.90 (m, ArH), 7.89–7.70 (m, ArH), 7.24–6.80 (m, ArH), 6.65–6.55 (s, ArH), 1.68(s, –CH₃).

Other characterizations of this polymer can be found in our previous article.¹³

The polymer was dissolved in cyclohexanone (10 wt %) and then filtered through 0.8-μm syringe filter membranes. We obtained the polymer film by casting the polymer solution onto a glass substrate, which was subsequently cleaned in an ultrasonic



Scheme 1 Synthesis of sample A.



Scheme 2 Synthesis of sample B.

bath with dimethylformamide, tetrahydrofuran, ethanol, and distilled water. We removed the residual solvent by heating the films in a vacuum oven at 100°C for 2 days. The thickness of the film was about 60 μm .

As shown in Scheme 2, we attached the azobenzene group to the side chain of the polymer through hydrogen bonding. Polymer 3 was synthesized according to ref. ¹⁴. Polymer 3 and monomer 4 (the molar ratio of the carboxyl to the pyridine group was 10 : 4) were dissolved in cyclohexanone (10 wt %) and then filtered. We obtained the polymer film by casting the polymer solution onto a glass substrate, heating it at 100°C for 12 h, and then placing it in a vacuum oven at 120°C for 12 h. The thickness of the film was about 20 μm . The film was stored in a desiccator for further studies.

Figure 1 shows the setup for the measurement of the photoinduced birefringence. The 532-nm line from a Nd:YAG 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. To carry out the experiments, we placed a film sample 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. When needed, a quarter-wave plate (not shown in the figure) was inserted into the optical path of the pump beam before the sample (the quarter-wave plate converted the linear polarized beam to circular polarization, which removed the birefringence that had been induced). The power of the pump laser was 23 mW, and the diameter of the beam was approximately 0.3 cm. The probe light was modulated at 1000 Hz by a mechanical chopper.

The transmitted probe beam was detected with a photodetector connected to a lock-in amplifier.

RESULTS AND DISCUSSION

Shown in Figure 2 are the representative growth and decay traces of the birefringence signal. Because the azo compound molecules were randomly oriented, no light was transmitted through the analyzer in the beginning of the experiment (with the transmission axis oriented orthogonally with respect to the polarizer in front of the sample). As the pump laser radiation was introduced (point A in the figure), an anisotropic orientation distribution was created as a result of the accumulation of *cis* isomers and *trans* isomers that were oriented with the transition dipole vertical to the polarization vector of the pump beam. Light was, thus, transmitted through the analyzer because of the onset of birefringence. When the excitation light was turned off (point B in the figure), a

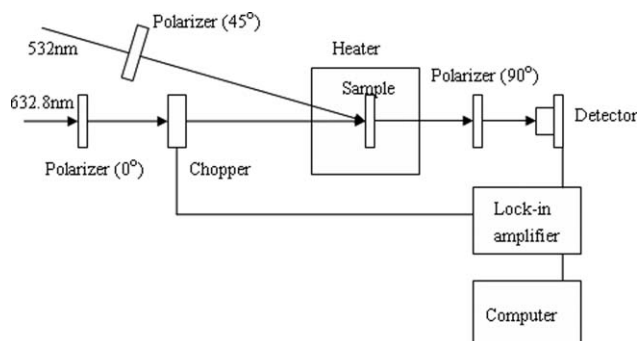


Figure 1 Experimental setup for the measurement of optically induced birefringence.

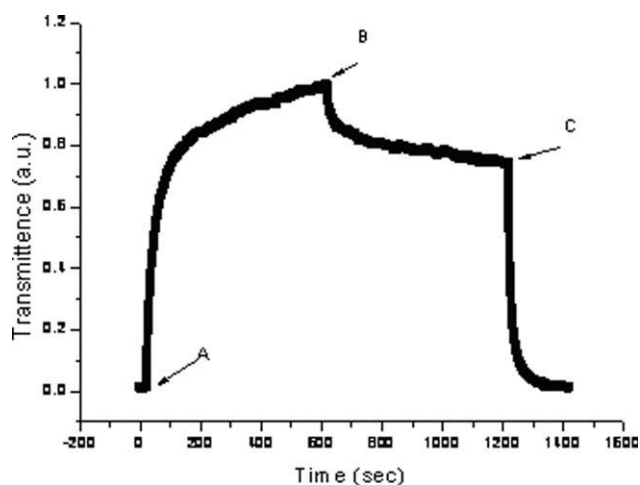


Figure 2 Typical growth and decay traces of birefringence.

relaxation of the anisotropic steady state occurred. However, the relaxation was not complete; parts of the induced birefringence were still held. To remove the remaining birefringence, circularly polarized light was introduced (point C in the bottom figure). The circularly polarized light effectively converted the cis isomers to the trans form for all orientations. The transmitted signal intensity induced by the birefringence was proportional to $\sin^2(\pi d \Delta n / \lambda)$,^{15,16} where d is the thickness of the film, Δn is the birefringence of the film, and λ is the wavelength of the probe beam (632.8 nm). Because $\pi d \Delta n / \lambda$ was much less than 1, the transmitted signal was effectively proportional to $(\Delta n)^2$.¹⁷

We investigated the temperature dependence of the growth and decay of the birefringence signal. Figures 3 and 4 show the data obtained at several temperatures for both samples. The studies reported in this article focused on the dynamic process; there-

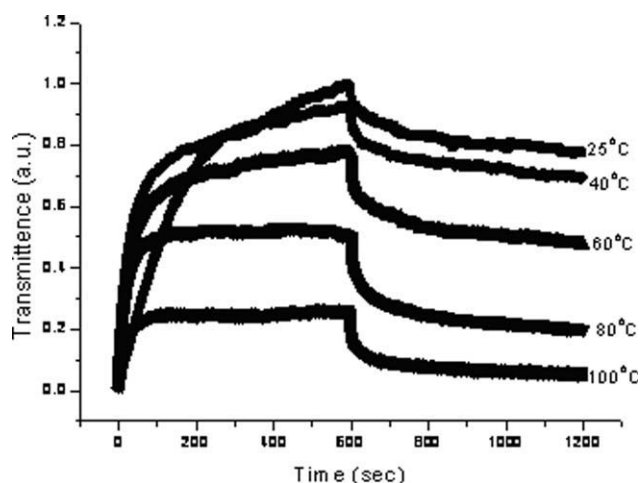


Figure 3 Experimental birefringence results for sample A at different temperatures.

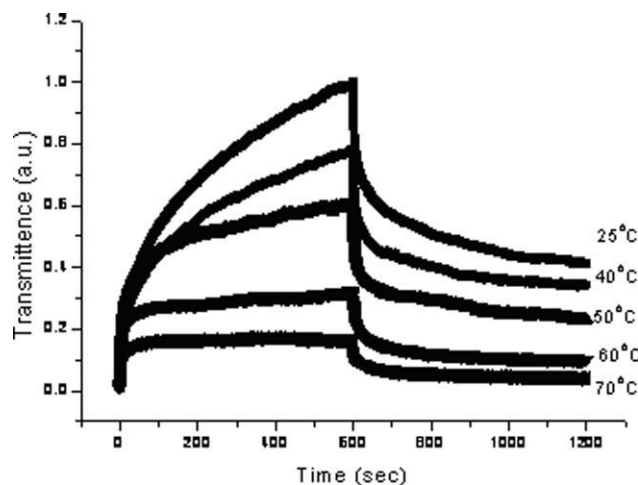


Figure 4 Experimental birefringence results for sample B at different temperatures.

fore, the signal intensities did not necessarily reach plateau levels at the various temperatures. As shown, both the photostationary (saturated value) and the stable (relaxed value) values decreased with increasing temperature. Two competing processes defined the maximum achievable birefringence: the orientation due to photoisomerization and the thermal relaxation that tended to disorientate the azobenzene groups. As the temperature increased, the second process became more important than the first one.¹⁸ These two competing processes were also likely to be relevant for the kinetics of the buildup and decay of birefringence.

The curves for the buildup process can be well fitted with a biexponential function:¹⁷

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

where A and B are preexponential factors, t is the time, and k_a and k_b are the rate constants for writing the fast and slow processes, respectively. Actually, k_a has been shown to depend on the quantum yield of the isomerization reaction, the isomerization rate, and the local mobility of the azo dye, which are affected by the size of the azo moiety, the free volume around it, and the strength of the coupling interactions between the azo dye and the polymer backbone. The magnitude of k_b depends mainly on the polymer mobility.¹⁹

The fitted dynamic parameters are listed in Tables I and II. Because the azobenzene groups were attached to the side chain through hydrogen bonding in sample B and the structure of sample A was hyperbranched, the mobility of the chromophores in sample B was much better than that in sample A. Hence, the k_a values of sample B were much larger than those of sample A. However, as the temperature increased, the parameters in the rise process for

both samples showed the same trend. k_a increased with the temperature. These results could be understood relatively easily and were consistent with the results of other studies.^{17,20} With increasing temperature, the mobility of the chromophores increased, and the process became faster. However, the percentages that increased as the temperature rose were quite different for the two samples; the ones of sample **A** were much larger than those of sample **B**. For example, the k_a of sample **A** at 100°C was more than 10 times that of the value at 25°C. This indicated that the mobility of the chromophores in sample **A** changed much as the temperature was increased.

However, the parameter k_b for the slow process did not change much as the temperature increased for the two samples. As mentioned previously, there were two competing processes (the orientation process and the relaxation process) that defined the photoinduced birefringence. Because the slow process was associated with the mobility of chains, the disorientation caused by the increase in temperature seemed to be more important than in the first kinetics process. The temperature dependence for the disorientation apparently compensated for the dependence on the chain mobility.²⁰

The curves for the decay could also be fitted with another biexponential function:

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

where C and D are the 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, the circular polarized light is introduced to erase the residual birefringence. The fast decay was due to the fast component of the thermal cis–trans isomerization and dipole reorientation, whereas the slow decay was associated with the mobility and relaxation of the polymer backbone.

The fitted fast rate constant (k_c) of sample **B** increased with temperature, which was understandable because the cis isomer was very thermodynamically unstable, and hence, the cis–trans back-reaction was accelerated at higher temperatures.²¹ The slow rate constant (k_d) was almost invariable, even if it increased slightly. This indicated that, as the temper-

TABLE I
Fitted Dynamic Parameters at Different Temperatures for Sample **A**

	25°C	40°C	60°C	80°C	100°C
k_a (s ⁻¹)	0.007	0.048	0.055	0.052	0.080
k_b (s ⁻¹)	0.004	0.005	0.005	0.004	0.002
E_n	0.78	0.71	0.62	0.40	0.21

TABLE II
Fitted Dynamic Parameters at Different Temperatures for Sample **B**

	25°C	40°C	50°C	60°C	70°C
k_a (s ⁻¹)	0.109	0.128	0.133	0.184	0.206
k_b (s ⁻¹)	0.004	0.004	0.004	0.003	0.003
k_c (s ⁻¹)	0.133	0.142	0.153	0.222	0.227
k_d (s ⁻¹)	0.005	0.005	0.004	0.007	0.007
E_n	0.40	0.42	0.35	0.31	0.23

ature rose, the mobility and relaxation of the backbone changed little. However, the fitted rate constants for sample **A** did not show any dependence on the temperature. The reason for this remains unclear. We think it may have been caused by the structure of the sample. Because the backbone of sample **A** was the highly branched rigid aromatic structure, and the azobenzene chromophore substitutes were located in the side chain of the branched arms, the movement of this structure must have been more complicated than the regular linear ones.

$E_n = E/(C + D + E)$ is an important parameter that represents the fraction of the induced birefringence that was stable over time. In other words, E_n represents the relative long-term stability of the photoinduced birefringence. As shown in Tables I and II, with increasing temperature, the values of E_n for both samples **A** and **B** decreased. This means that as the temperature rose, the fraction of the induced birefringence that reserved decreased. As shown in the tables, at lower temperatures, the values of E_n for sample **B** were much larger than those for sample **A**. This is also shown in Figure 3 and 4, at lower temperatures; when the pump laser turned off, the decreased values of birefringence for sample **B** were much larger than that for sample **A**. This was relatively easy to understand. It was the rigid aromatic structure for sample **A** that limited the relaxation process of the oriented chromophore groups.

CONCLUSIONS

We investigated the growth and decay processes of two novel azobenzene-functionalized polymers whose structures were different from the others that were fully studied earlier. Both the saturated value and the relaxed value decreased with increasing temperature as the thermal relaxation of the chromophores was facilitated. Both the growth and relaxation processes involved a fast and a slow process caused by different mechanisms. As the temperature rose, the fitted k_a of the fast buildup process increased, whereas k_b changed little for both samples. In the decay process, k_c also increased with temperature, whereas k_d was invariable for sample **B**. A comparison between the two samples was also

discussed. These conclusions may be a helpful guide for the further development of practical materials in the fields of reversible, high-density optical storage, optical switching, and other photodriven devices.

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