Articles

Stability of Photoinduced Orientation of an Azo Compound into a High-T_g Polymer

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Optically induced birefringence on films containing disperse red 1 (DR1) doped into poly(methyl methacrylate) (pMMA) and into a very high-T_g poly(ether ketone) (pASH) is compared with birefringence induced in films of a copolymer and a blend containing a similar azo moiety in the side chain. The level of the induced birefringence depends mainly on the film absorbance, as expected. The stability of the induced birefringence in the absence of illumination depends on the difference between room temperature (at which the experiment is performed) and the T_g of the material. Doping DR1 in a polymer depresses the material T_g, producing a material that loses the birefringence very fast when the matrix is pMMA. All other materials, including pASH doped with DR1, show the usual high stability of the induced birefringence. Hence, doped high-T_g polymers may be as suitable for reversible optical storage materials as the previously reported copolymers and blends, which had the azo moiety bound on the side chain.

Introduction

Various azo compounds are being used to produce second-order nonlinear optical phenomena either dissolved in a polymer matrix or as part of a polymer structural unit, usually in the side chain.[1] The azobenzene structure provides the π conjugation which allows the electrons to move from the electron-donor substituent to the electron-acceptor substituent and create polarization. Bulk polarization is achieved when the individual dipoles are parallel aligned in an electric field while the polymer is heated above its glass transition temperature. Cooling of the polymer while maintaining the electric field is used to "freeze" the dipole alignment and conserve the bulk polarization. There is a whole body of literature that studies the stability of this induced alignment, because it is extremely important for the long-term functioning of these materials as second order nonlinear materials. Intuitively, one would expect that polymers with azobenzene groups bound into the structure would be more stable over time than the doped systems, because of the motional hindrance introduced by chemical bonding. This was however demonstrated to be true only at temperatures below T_g −50 for a variety of guest–host and bound systems.[1] Above this temperature, the alignment is as unstable in doped polymers as in polymers having bound azobenzene groups. Consequently, building a polymer containing bound azobenzene appears to be the preferred choice, especially since doping a polymer with a small azobenzene molecule will inevitably depress the glass transition of the resulting material in comparison with the pure polymer.

Our research group is studying amorphous high-T_g polymers containing azobenzene groups and their orientational behavior. Orientation of the azobenzene groups can be achieved through a series of photochemically trans–cis–trans isomerization cycles induced by polarized light.[2] Nonpolarized or circularly polarized light restores the random orientation of the azobenzene groups through the same mechanism. While the light is on, a photostationary state is achieved which contains a certain amount of cis isomers,[3] together with a saturated concentration of aligned dipoles which translates into induced birefringence. A typical induced order–disorder cycle is illustrated in Figure 1.

The main difference between the photoinduced alignment and the poling procedure used for nonlinear optical applications is that the photoinduced alignment is only

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1995.

[1] Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.

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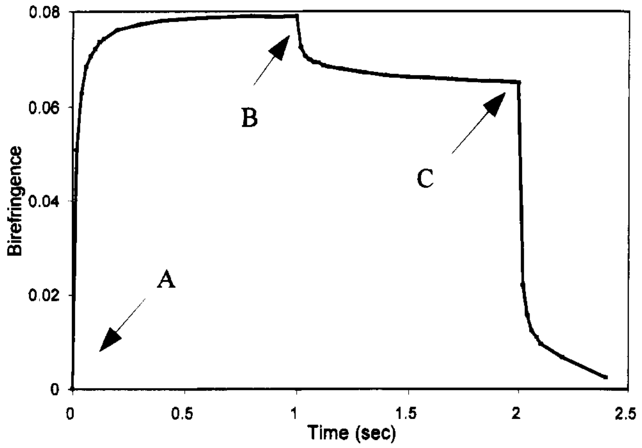


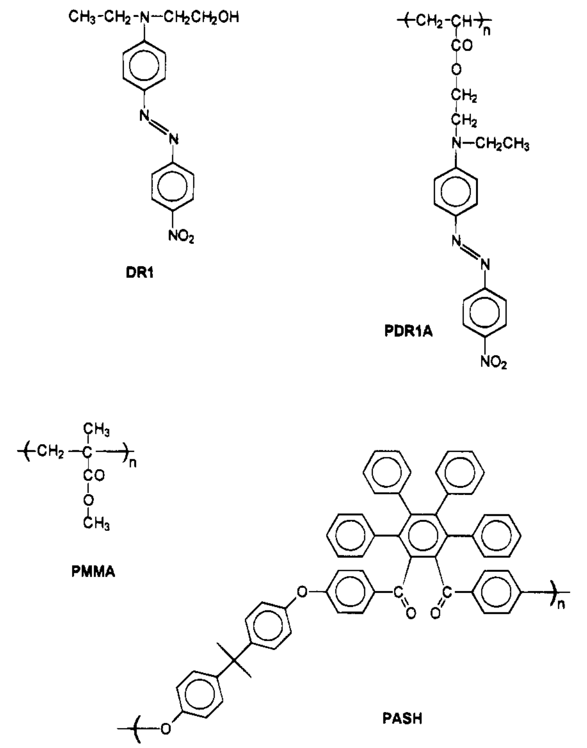
Figure 1. Typical write/erase curve on a polyDR1A film. The structure of the polymer is shown in Chart 1. At point A, a plane polarized laser (514 nm) is turned on; at point B it is turned off; at point C the same laser, but circularly polarized, is turned on for erasure.

directional, along an axis perpendicular to the light polarization but with the dipoles pointing randomly up or down the axis. In fact, the absorbance spectra strongly suggest that the dipoles are preferentially antiparallel.[4] For parallel dipoles obtained by a poling procedure, a shift to longer wavelength has been observed,[5] while azobenzene-containing homopolymers show a shift to shorter wavelengths in comparison with copolymers in which the azobenzene units are isolated. The photochemically induced orientation of the azobenzene groups involves fairly small changes from the initial orientation. A model calculation indicated that in order to achieve an overall birefringence of 0.08 in a homopolymer, every azobenzene group has to move by an average of 11° from its initial position.[6] This means that the initial antiparallel orientation of the azobenzene groups will be reinforced by the photochemical alignment.

At point B in Figure 1, the photostationary state is interrupted by switching off the light. The cis azobenzene groups isomerize to trans fairly fast,[3] with a rate constant of about 0.2 s^{-1}, producing some of the decay of the birefringence. This decay must also be associated with some heat dissipation after the laser is turned off. After a few seconds, the birefringence level stabilizes to about 70–80% of its initial value, and this value does not change for years. This phenomenon is very similar to what happens to the orientation achieved by poling when the electric field is turned off. The main difference is that the preferential antiparallel arrangement obtained by photochemical orientation is thermodynamically favorable, while the parallel alignment obtained by poling is not.

As mentioned above, there is a whole body of literature dealing with the stability of orientation in poled polymers,[1] and quite a few research groups are investigating procedures that would improve this stability. To our knowledge, there are no reported data analyzing the stability of the photoinduced orientation. This paper presents some stability data obtained on our samples. It will be demonstrated that the most important parameter affecting the stability is the difference between the operating temperature and the glass transition temperature of the material. Thus, doped high-T_g polymers are as suitable for optical storage as copolymer and blends of comparable glass transition temperature. This correlation is analogous to that observed for poled polymers.

Chart 1



Experimental Section

Disperse red 1 (Aldrich) was recrystallized from ethanol prior to use. Poly(methyl methacrylate) (pMMA, Aldrich) was used as received. Poly[4′-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitrobenzene] (pDR1A)[2] and pASH[7] were synthesized as described. All structures are given in Chart 1. The glass transition temperatures of the relevant polymers are 91 °C (pDR1A), 120 °C (pMMA), and 265 °C (pASH). Also used was a copolymer of MMA with DR1A containing about 8 mol % DR1A structural units[8] with a glass transition temperature of 105 °C. All glass transition temperatures were measured on a Mettler TA-3000 DSC instrument. Mixtures of DR1 and each of the polymers, and one blend of pDR1A with pASH, were obtained by dissolution in THF followed by slow solvent evaporation to generate films used for reversible optical storage. The procedure was described previously;[2] the parameter measured was birefringence as a function of time and illumination. The light source for "writing" was an argon laser at 514 nm, and the signal was "read" at 633 nm by a HeNe laser. To ensure that the various films could be compared,[9] the thickness of the films were selected to give absorbances below 4.

Results and Discussion

A comparison between writing curves on films obtained by dissolving DR1 in pMMA and, respectively, pASH, is shown in Figure 2. The actual levels of

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(6) Rochon, P., unpublished results.

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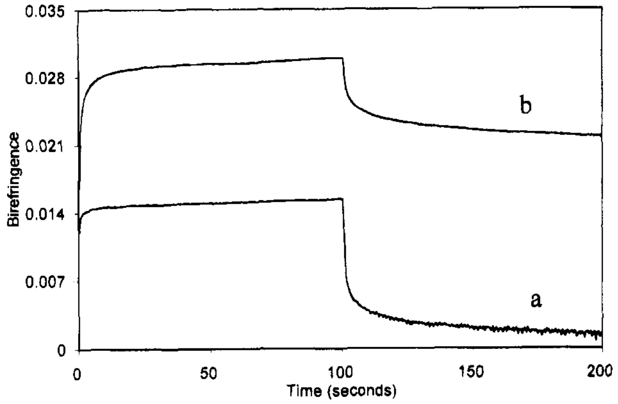

Figure 2. Photoinduced birefringence on (a) a film of 12 mol % DR1 in pMMA of 1313 nm thickness and (b) a film of 41 mol % DR1 in pASH of 530 nm thickness. The writing laser is turned on at time zero and off at 100 s.

birefringence achieved at saturation depend on the azo content of each sample; hence it is understandable that DR1 dispersed in pASH shows a level which is double that shown when the matrix is pMMA, because the level of doping is much higher in pASH. The rates of achieving saturation are fairly similar. The main difference, as expected, is related to the relaxation of the ordered azobenzene groups after the writing laser is turned off. While the film based on pASH retains about 76% of its birefringence in the long term, which is comparable with the level retained by pDR1A,[2] the film based on pMMA shows a significantly more pronounced decay to a level of about 20% of the initial value. In fact, the birefringence level of this film after the light has been switched off is close to zero within the experimental noise after about 200 s.

Is this difference between the two films due to a difference in kinetics of the cis–trans isomerization or is it due to the difference in the glass transition temperature of the two films? The rate constants for the thermal cis–trans isomerization of DR1 in the two films have been measured and found to be essentially equal within experimental error.[10] Hence this difference in relaxation has to be due to the different mobility allowed in the two samples by the matrix polymers. Indeed, the T_g of the doped pMMA sample is now 60 °C, while the T_g of the doped pASH has decreased to 171 °C. The induced birefringence experiments are performed at room temperature, which is now fairly close to the T_g of doped pMMA, in any case within the range of T_g −50. It is important to mention that translational diffusion phenomena and aggregation may occur, and they would affect the outcome of the photoinduced orientation process in these two doped polymer cases. No aggregation was observed via observation with a polarized microscope, but molecular-level association was not investigated by solid-state NMR, hence it cannot be ruled out. Overall, however, the films are remarkably homogeneous and transparent.

Figure 3 presents the photoinduced birefringence experiments on the p(DR1A-*co*-MMA) (8 mol % DR1A) copolymer and on the pDR1A/pASH blend. The azo content of these two samples is very different, with the blend containing much more azo than the copolymer.

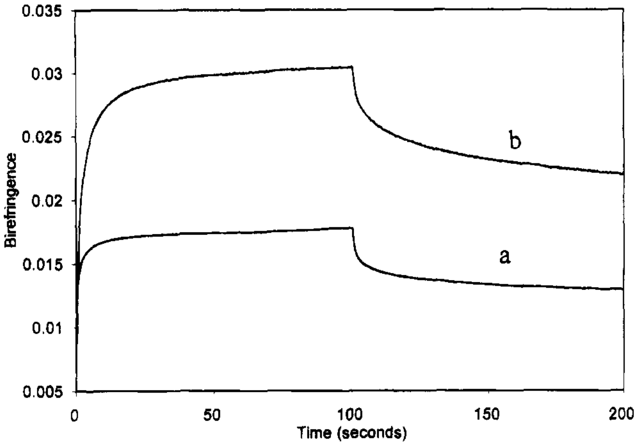

Figure 3. Photoinduced birefringence on (a) a film of a blend of pASH with pDR1A containing 39 mol % pDRA1 of 1783 nm thickness and (b) a film of poly(DR1A-*co*-MMA) copolymer containing 8 mol % DR1A of 2783 nm thickness. The writing laser is turned on at time zero and off at 100 s.

It is not very clear why the level of induced birefringence is so much higher in the copolymer. The absorbance of the copolymer film is about double that of the blend, and this may be at least part of the explanation for the difference. Another possible explanation would be that the mostly isolated DR1A groups in the copolymer have more freedom to move around than in the blend, where the azo groups are very close to each other. Indeed, copolymers show higher birefringence than similar blends of the same composition.[4] The fact that in the copolymer the azo groups have more freedom to move also produces a slower rate of achieving the birefringence in the copolymer, as observed for previous systems. Also, there is a difference in the T_g of the two films analyzed in Figure 3. The copolymer has a T_g of 105 °C, while the blend—with one of the components a polymer of very high T_g—has a T_g of 171 °C.

It is fairly surprising that the film of the blend is perfectly transparent and has a single T_g, indicating compatibility of the two components. pDR1A has been shown to be compatible at the molecular level with pMMA,[11] and part of the explanation was the relatively low molecular weight of pDR1A. This may be the reason that pDR1A appears to form compatible blends with pASH as well.

The birefringence relaxation when the light is turned off produces a remnant birefringence of 77% of the initial value in the copolymer and of 76% of the initial value in the blends. This is similar to the doped pASH sample and the previous results on pDR1A.[2]

For comparison purposes, the decay of birefringence when the light is turned off (the equivalent of point B in Figure 1) was analyzed by fitting for exponential decay. The decay is neither monoexponential nor biexponential. At the time the light is turned off, the decay of birefringence must be governed by a relaxation to equilibrium, as well as by a temperature gradient. The laser heats the polymer film, because it is absorbed, and when it is turned off, the heat dissipates through the film, changing the temperature of the analyzed spot. This process is quite different from what happens when the electric field is switched off in a poling process. In

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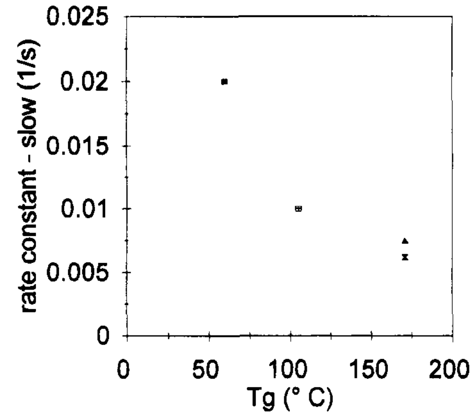

Figure 4. Rate constant of the birefringence decay after 110 s after the laser has been switched off as a function of the Tg of the sample: (■) DR1 in pMMA; (□) p(DR1A-*co*-MMA); (▲) DR1 in pASH, and (×) pDR1A-*b*-pMMA.

Table 1. Remnant Birefringence and Rate Constants for the Decay of the Birefringence When the Laser Light Is Turned off

sample	remnant birefringence	rate constant	
		slow, s^{-1}	medium, s^{-1}
DR1 in pASH	0.0205	0.0075	0.0078
DR1 in pMMA	0.0003	0.0200	0.0210
p(DR1A-*co*-MMA)	0.0200	0.0100	0.0750
pDR1A-blend-pASH	0.0210	0.0062	0.0098

that case, the film temperature has already been brought back to equilibrium, and it does not change when the field is removed. Hence, in the poling case, the decay of the signal is a direct consequence of the stability (or instability) of the orientation, while in the present case, a thermal process is superimposed on the decay phenomenon. It is always possible to fit a stretched exponential to the decay of the photoinduced birefringence, but in the present case, the difference between T_g and room temperature is too dissimilar, hence the fits would be misleading. Instead, a "long-term" exponential fit was used for the decay after 110 s after the light was turned off, and another "medium-term" exponential was used for the time interval between 100 and 110 s. Any decay prior to 100 s was considered to be too influenced by the film temperature and hence discarded. Table 1 shows the results obtained for the rate constants of the two exponential decays: the long-term (slow process) and the medium-term decay.

It is clear in Table 1 that both samples having DR1 dispersed into a polymer matrix show no difference in the decay behavior at "medium" and "long" time. It is also fairly clear that some samples are more stable than others. A plot of the slow rate constant as a function of the T_g of the sample is shown in Figure 4. There is a clear correlation of the birefringence stability with the sample T_g, as was reported previously in the literature for poled samples.[1] Since this is a phenomenon different from poling and since the number of samples analyzed here is small, a comparison with the previous data on the same type of master curve is not strictly valid. Nonetheless, the results definitely suggest that DR1 dispersed in pASH shows a birefringence as stable as that of the pDR1A-*blend*-pMMA.

The long-term stability of the induced birefringence was not investigated, apart from monitoring the signal continuously for about 24 h where the induced birefringence was found to be stable. Copolymer and blend samples previously written in our laboratory have shown practically constant birefringence for about 4 years. It is also important to mention that if long-term stability of the alignment is monitored continuously by "reading" the signal with the HeNe laser, the system is actually slightly affected. The HeNe laser has its wavelength at the edge of the sample absorbance, and hence it does induce some orientation, at a 45° to the initially induced orientation, due to the optical geometry used. The longer the laser is on, the more it will change the initial orientation, thus slowly erasing the signal. No measurable erasing was observed within 24 h, but in principle, this is a built-in error which would make the stability to appear worse than it actually is. Monitoring over long intervals should not be done continuously.

Conclusions

In terms of using materials for reversible optical storage, DR1 dispersed in pASH provides very good results as it is probably more stable than any copolymer involving MMA units, because the glass transition temperature of the doped pASH is much higher than that of—say—a copolymer containing DR1A and MMA units. Blends of azo polymers with some of the available high-T_g polymers are also very good candidates for reversible optical storage materials, provided that the mixtures are compatible and form homogeneous films.

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