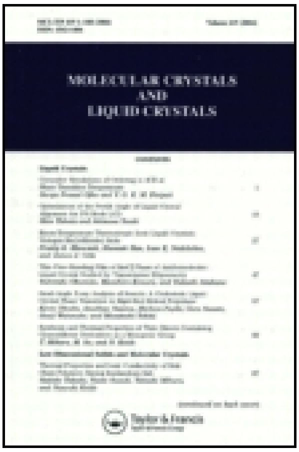

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RELAXATION DYNAMICS OF NONLINEAR OPTICAL CHROMOPHORES DISPERSED IN POLED PHOTO-POLYMER COMPOSITES

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Abstract The relaxation dynamics of nonlinear optical chromophores in photo-polymer composites is studied for a basic understanding of the poling mechanism. The composite films are made up of a photo-polymer containing 0.5 % by weight of 4-dimethylamino-4'-nitrostilbene. They are poled under an external dc electric field at room temperature, followed by UV curing. It is found that for such composite films both the optical retardation and the second harmonic generation (SHG) intensity clearly decay as similar stretched-exponentials in time, and their relaxation behavior is predominantly governed by the period for UV curing. It is suggested that the optical retardation involves mostly the axial order while the SHG intensity is strongly correlated to the degree of polar ordering of the chromophores.

INTRODUCTION

The polymeric nonlinear optical (NLO) materials such as NLO organic molecules dispersed in photo-polymer composites have attracted much attention for potential use in integrated optics[1-2]. The additive non-centrosymmetric ordering of the NLO molecules, required for the second-order NLO processes, can be achieved by the electric field poling[3-5]. However, the induced orientational order in the poled state usually becomes to relax into an isotropic state after removing the electric field[6,7]. For practical applications, the poled state must possess a high degree of the induced order, and it should maintain thermal and chemical stabilities in time as well. Although a temporal stability of the NLO polymer has been recently reported[8], a complete picture of the relaxation mechanism has not been obtained so far. Therefore, it is of great importance to understand the underlying physical mechanism for the relaxation of the induce order in time. The study of this relaxation process in photo-polymer composites may also provide useful information about the dynamical behavior of the NLO polymers in a restricted geometry.

In this paper we have studied the relaxation dynamics of the axial as well as the polar order present in guest-host polymer composites. The guest NLO molecules are dispersed in a host photo-polymer system, followed by UV curing. In this type of the polymer composite, it is simpler to control microscopic environments of the NLO chromophores at a molecular level and to extract information about how they interact with each other in a restricted geometry. In Sec. II, we briefly describe the experiments, and present the results for the linear (optical retardation) and the second order NLO (the second harmonic generation) properties of the photo-polymer composites, along with discussions. In the remaining section, some concluding remarks are then made.

EXPERIMENTAL

The NLO composites used in this study is NOA 61 UV-curable epoxy (curable wavelengths: 320 to 400 nm) of Norland Corp., doped with 0.5 % by weight of 4-dimethylamino-4'-nitrostilbene (DANS) of Aldrich Chemical Co. The DANS/NOA material was filled into a cell made with conductive indium-tin-oxide coated glass substrates. The polyimide layers of about 2.5 μm thick were prepared on the inner surfaces of the cell by spin coating. The cell gap was maintained using glass spacers of 10 μm thick, giving about 15 μm for the total thickness between two electrodes. The samples were then cured with UV light during the electric poling at room temperature. The electric field used for poling was 13 MV/μm, and the intensity of UV light for curing was about 100 watt at 365 nm.

The polarization modulation method was employed for measuring the optical retardation of the poled NLO composite films[9]. The measurements were made with a He-Ne laser of 632.8 nm, crossed polarizers, an intervening photo-elastic modulator, and a detector. Each poled composite film, placed between the first polarizer and the modulator, was able to rotate with respect to an axis in the plane of the film. The modulated output from the detector was monitored using a lock-in amplifier. The optical retardation was then calculated from the output signals of the first and the second harmonics from the amplifier. The SHG measurements were carried out with a Q switched Nd-YAG laser operated at 10 Hz. The fundamental beam at 1064 nm with the p-polarization was incident on the film. For various poled films, both the optical retardation and the SHG intensities were measured as a function of time at an angle of 50° to the normal incidence.

RESULTS AND DISCUSSION

Since the poling field makes the DANS molecules in the host photo-polymer oriented along the field direction[3-5], the optic axis of the poled film coincides with the field direction, and thus the film has the ∞_{mm} symmetry. For convenience, the axis 3 is assumed to be the field direction. From the absorption spectra of the DANS molecules at 450 nm in the DANS/NOA film, the axial order parameter $< P_2 >$ was found to be about 0.03 for the poling field less than 200 V/μm. Here, the axial order $< P_2 >= (1/2)(3 < \cos^2\theta > -1)$ where θ is the angle between the axis 3 and the molecular axis, and $< \ >$ denotes an average over all the molecules.

Since the axial order present in the DANS/NOA film is negligibly small, the associated optical retardation may be analyzed in the isotropic model[2,5]. In this model, the optical retardation B of the poled film of thickness d can be written as

$$B = \frac{2\pi\Delta n \ d}{\lambda}\sin\phi\tan\phi \ , \tag{1}$$

where ϕ is the incident angle of the input beam of wavelength λ. Here, the birefringence $\Delta n = 3\pi N/\bar{n}\Delta\alpha < P_2 >$ with N the number of the guest molecules, $\bar{n}$ the mean index of refraction, and $\Delta\alpha$ the anisotropy of the molecular polarizability[10]. As expected from Eq. (1), the relaxation of the axial order $< P_2 >$ of the guest molecules can be determined from the change of B in time. We measured $B(t)$ for the poled DANS/NOA and a pure NOA one at a fixed angle of $\phi = 50°$ as a function of time, t, with varying the curing time T_{cure}. The measured $B(t)$'s in both cases indicate that the relaxation for the DANS/NOA film mostly results from the reorientation of the DANS molecules.

For studying the relaxation dynamics of the DANS/NOA films, the optical retardation is rewritten as $\Delta B(t) = [B(t) - B_g]/[B(0) - B_g]$, which is shown in Fig. 1. Here, B_g represents the background after a full relaxation of each film in time.

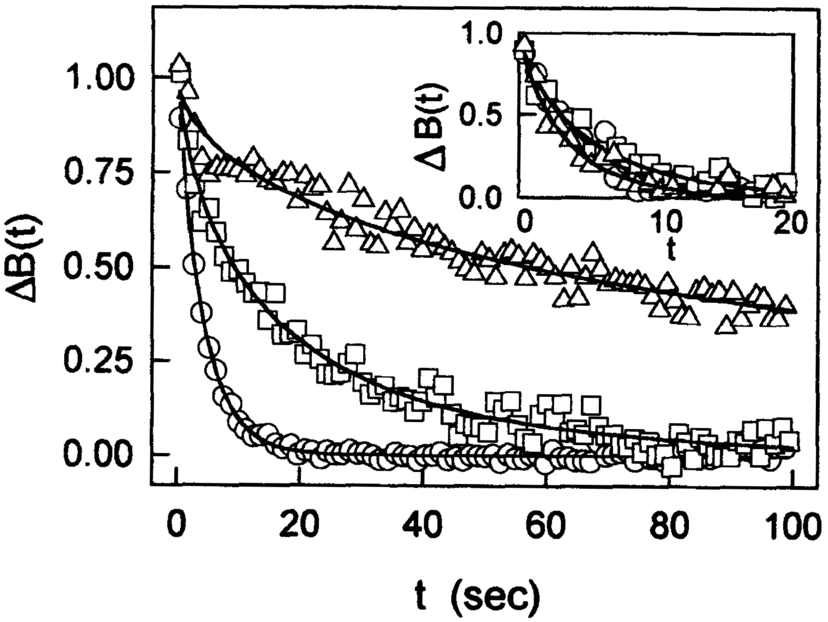

FIGURE 1 The normalized optical retardation, $\Delta B(t)$, for the poled DANS/NOA films with different T_{cure}'s as a function of time. The inset shows $\Delta B(t)$ for the pure NOA films. The circles, squares, and triangles represent $T_{cure} = 0$, 10, and 30 min, respectively.

As shown in Fig. 1, it is clear that $\Delta B(t)$ for the cured DANS/NOA film decays as a stretched-exponential in time, showing a considerably long time tail, while $\Delta B(t)$ for the uncured DANS/NOA one follows a single exponential. Moreover, the cured pure

NOA film exhibits almost the same exponential behavior as the uncured one irrespective of the curing time, T_{cure}. This also suggests that the stretched-exponential type of $\Delta B(t)$'s for the DANS/NOA films is mainly caused by the reorientation of the DANS molecules.

We now attempt to interpret the essential features of the data in a relaxation model applicable for complex systems[11]. Assume that a physical quantity $S(t)$ is associated with various temporal processes (labelled by i), all of which decay exponentially with different relaxation times (τ_i) and contribute to $S(t)$ with different weights ($w(\tau_i)$. In this description, the relaxation processes of the chromophores in the photopolymer composites may be expressed as the following stretched-exponential.

$$S(t) \sim \int w(\tau_i)\exp(-t/\tau_i)d\tau_i \sim \exp(-t/\tau_{eff})^{\beta} \;, \quad 0 \leq \beta \leq 1 \;, \qquad (2)$$

where τ_{eff} denotes the stretched relaxation time and β the stretched exponent which characterizes the distribution of the relaxation processes. Here, $\Delta B(t)$ may be represented by $S(t)$, and the relaxation for the rotational diffusion of the process i is given by[10] by $\tau_i = 1/D_2$ where $D_m = m(m+1) < [\theta(t) - \theta(0)]^2 > /4t$ with D_m the rotational diffusion constant of the order m.

The solid lines in Fig. 1 represent the best fit of $\Delta B(t)$'s to Eq. (2). For the uncured DANS/NOA films, the distribution $w(\tau_i)$ is extremely narrow ($\beta \approx 1$), and thus $\Delta B(t)$ decays as a single exponential. For the cured DANS/NOA films, however, the free volume accessible to the guest DANS molecules will be different from one site to another, which gives rise to distributed relaxation rates. Therefore, β becomes less than 1, and $\Delta B(t)$ is expected to follow a stretched-exponential. Accordingly, the stretching effect of β becomes profound with increasing the curing time, T_{cure}, as shown in Fig. 1.

The polymerization of the host NOA, produced by the curing process, will affect the relaxation dynamics of the polar ordering as well as the axial ordering of the guest DANS molecules. We now discuss the polar ordering of the DANS molecules and the associated relaxation in the poled DANS/NOA 61 films, determined from the SHG measurements. Using the Maker fringe method, one of the second-order NLO coefficient, d_{33}, was found to be about 1.34 pm/V. This is in reasonable agreement with a theoretical value of 1.2 pm/V, estimated in the isotropic model at low fields.

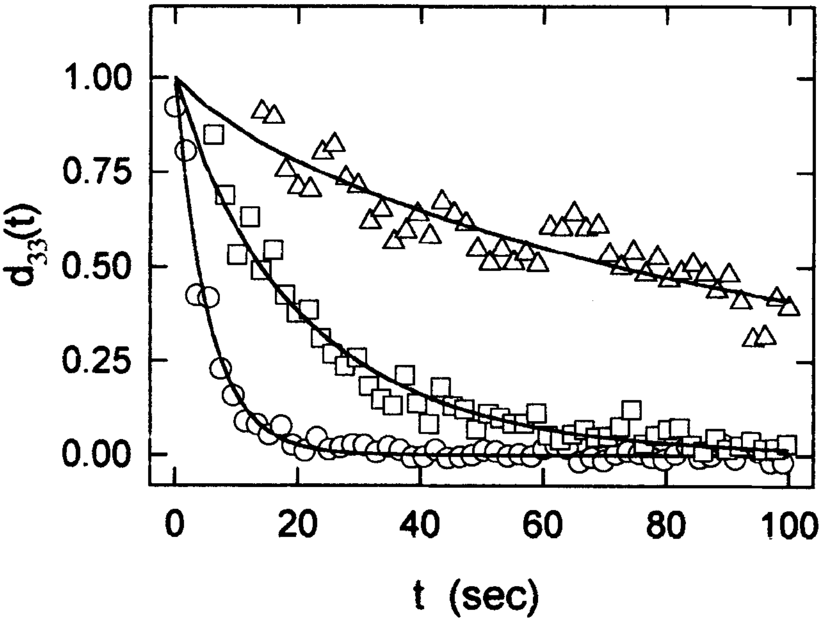

FIGURE 3 The normalized $d_{33}(t)$ for three differently cured DANS/NOA films. The circles, squares, and triangles represent $T_{cure} = 0$, 10, and 30 min, respectively.

Fig. 2 shows the normalized $d_{33}(t)$ for three differently cured DANS/NOA films. In the cured state, $d_{33}(t)$ decays as a similar stretched-exponential, Eq. (2), but with the relaxation rate different from that of $\Delta B(t)$. For the rotational diffusion[10], τ_i for the polar order is given by $1/D_1$. The solid lines represent the best fit of $d_{33}(t)$'s to Eq. (2). The stretched exponent β becomes less than 1, and τ_{eff} increases with increasing the curing time.

One interesting feature is that the relaxation rate of $d_{33}(t)$ is slower than that of $\Delta B(t)$. This would be expected from the fact that the polar ordering process $(1/D_1)$ is 3 times slower than the axial ordering one $(1/D_2)$. As a consequence, the average relaxation time for $d_{33}(t)$ will be 3 times slower than that for $\Delta B(t)$. In fact, $< \tau_i >$

is given by $\tau_{eff}\ \Gamma(\beta)/\beta$ with $\Gamma(\beta)$ the gamma function. All the measured and fitted parameters were collected in Table 1.

Table 1 The stretched relaxation time τ_{eff}, the associated exponent β, and the average relaxation times $< \tau_i >$'s for $\Delta B(t)$ and $d_{33}(t)$ for three differently cured DANS/NOA films (T_{cure} = 0, 10, 30 min).

	ΔB			d_{33}			
T_{cure} (min)	τ_{eff} (sec)	β	$< \tau_i >$ (sec)	τ_{eff} (sec)	β	$< \tau_i >$ (sec)	ratio of $< \tau_i >$
0	4.17	1.00	4.17	11.08	1.00	11.08	2.655
10	15.71	0.71	19.69	44.33	0.92	46.04	2.339
30	111.11	0.55	187.90	281.51	0.78	324.11	1.728

Clearly, Table 1 shows that the ratio of the average relaxation time of d_{33} to that of ΔB is close to a theoretical value of 3, calculated under the assumption of a perfectly uniform background or host system. In our case, the relaxation of ΔB for the host material NOA itself was probably involved, making the ratio a little smaller than 3.

CONCLUDING REMARKS

We have studied the relaxation dynamics of the optical retardation, ΔB, and the second-order NLO coefficient, d_{33}, for the poled photo-polymer composites. It was found that both ΔB and d_{33} decay as a stretched-exponential type in time, and the ratio of the average relaxation rates is close to a theoretical value of 3, calculated under the assumption of a perfectly uniform host system. This stretched behavior may be attributed to the change in the accessible free volume during polymerization of the host NOA material. The thermal behavior of the relaxation dynamics of the poled NLO photo-polymer remains to be explored.

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REFERENCES

1. See, for example, Molecular Nonlinear Optics ed., J. Zyss (Academic, New York, 1994).
2. P. N. Prasad and D. J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers (Wiley, New York, 1991).
3. Y. Shuto, H. Takara, M. Mano, and T. Kaino, Jpn. J. Appl. Phys. 28, 2508 (1989).
4. K. D. Singer, J. E. Sohn, and S. Lalama, Appl. Phys. Lett. 49, 248 (1986).
5. K. D. Singer, M. G. Kuzyk, and J. E. Sohn, J. Opt. Soc. Am. B 4, 968 (1987).
6. K. D. Singer and L. A. King, J. Appl. Phys. 70, 3251 (1991).
7. H. W. Guan, C. H. Wang, and S. H. Gu, J. Chem. Phys. 100, 8454 (1994).
8. M. Stähelin, C. A. Walsh, D. M. Burland, R. D. Miller, R. J. Twieg, and W. Volksen, J. Appl. Phys. 73, 8471 (1993).
9. J. C. Kemp, J. Opt. Soc. Am. 59, 950 (1970).
10. J. W. Wu, J. Opt. Soc. Am. B 8, 142 (1991).
11. See, Non-Debye Relaxation in Condensed Matter, ed., T. V. Ramakrishnanan and M. Rajlakshmi (World Scientific, Singapore, 1987).