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RELAXATION OF POLAR ORIENTATIONAL ORDER IN NONLINEAR OPTICAL POLYMERS BY SECOND HARMONIC GENERATION

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ABSTRACT

An investigation of the decay of the second harmonic generation (SHG) signals from a main chain accordion and a guest/host nonlinear optical (NLO) polymer has been carried out. The shape of the decay of the SHG signal from the main chain polymer is stretched exponential with the width parameter, β, increasing with increasing temperature. The increase in β indicates a narrowing of the distribution of relaxation times. On the other hand, the SHG decay signal from the guest/host system polarized with contact electrode poling is found to be better described by the sum of two single exponential functions with the first short time component affected strongly by the surface charge effect and the second slow component associated with the relaxation of the macroscopic polarization. The time constant of the slow component is found to be successively increasing with the poling/decay cycle and reaches a steady state value after several cycles. The relaxation time lengthening effect is obtained both above and below T_g. The effect is considered to be due to trapped charges that enhance the polar orientation correlation. The temperature dependence of the steady state relaxation time over a 30°C temperature range can be satisfactorily either described by the Vogel-Fulcher-Tamann or the Arrhenius equation.

Introduction

Because of their potential applications in integrated optics, interest in polymeric nonlinear optical materials has grown rapidly during the past decade.[1] It is now well established that molecules containing an electron donor-acceptor substituted conjugated system exhibit large quadratic hyperpolarizabilities,[2] β. To obtain bulk quadratic nonlinear optical (NLO) effects, non-centrosymmetric materials are required. By incorporating these molecules into the polymer system and then polarizing them with a strong DC electric field (near the glass transition temperature of the NLO polymer) to remove the centrosymmetric environment, one can prepare a second order NLO material. The electric field polarizing process is know as poling. For applications in frequency doubling or electro-optic devices, the poled polymer must maintain the polar order that has been created. Therefore, an understanding of the underlying mechanism responsible for the relaxation of polar orientational order is of great interest.

In this paper we report recent results from our laboratory of an investigation into the relaxation behavior of two types of NLO polymers. One type involves NLO chromophores dissolved in a polymer host as guests and the other has the NLO chromophores covalently attached to the polymer to form a main chain polymer.

Experimental

The synthesis of the main chain accordion polymer used in this work has been described elsewhere by Lindsay et al.[3] The synthesis of nitroaminostilbene (NAS) was carried out in our laboratory. NAS served as the NLO chromophore, and the host polymer used in this work was polymethylmethacrylate (PMMA) (M_w >100 K, Aldrich).

The NLO polymers were dissolved in appropriate solvents. For the main-chain accordion polymer system, the solution was cleaned by centrifugation at 9,000 G for three hours to remove undissolved particulates. For the guest/host systems, various amounts of NAS were dissolved in the polymer solution to obtain different NAS concentrations. The solutions were filtered to remove undissolved particulates; thin, optically clear films (about 1 μm thickness) were prepared by spin coating the solution onto transparent conducting substrates (indium tin oxide, ITO, coated soda lime glass slides). The film thickness was measured with an α-stepper. The ITO coated slides containing polymer films were first placed in a vacuum oven at about 50°C for over 24 hours and then baked for another 24 hours at higher temperature (slightly above T_g) to obtain solvent-free films. The glass transition temperatures, T_g, of all films were determined by a differential scanning calorimeter (DSC, Perkin Elmer, delta series). Over a 0 to 12 weight% NAS concentration range, the T_g of the NAS/PMMA system decreases linearly with increasing NAS concentration, due to the plasticization effect of the NAS chromophores. In the NAS/PMMA system no evidence of phase separation was observed after film preparation for samples containing up to 30 weight% NAS; however, after cycling the poling/cooling steps several times, phase separation occurred for films containing more than 15 weight% of NAS. The concentration of the chromophores was monitored by UV-visible absorption spectroscopy. To complete the assembly of the guest/host sample for the optical experiment, two identical glass slides coated with NLO polymer films were then placed in a vacuum oven at a temperature above T_g to fuse them in a sandwich configuration for contact electrode poling. The corona poling technique was used to pole the main chain accordion polymer. For corona poling, a positive voltage potential of 3 kV was applied to a sharp tungsten needle located 1 cm in front of the polymer film surface. The contact poling or corona poling was conducted in dry air in an oven that housed the sample. The establishment of polar order due to poling and subsequent relaxation of the polar order were monitored by measuring the second harmonic generation (SHG) signal. Optical measurements were carried out at the same temperature as the poling process. The setup for SHG measurement was similar to that used in our previous work[4]. Basically, it consisted of a Q-switched Nd:YAG laser operated at 10 Hz. The fundamental beam (1.064 μm) impinged on the sample with the electric field polarized in the plane of incidence. The SHG intensity of each sample was referenced to quartz. The intensity was detected with a photomultiplier tube and processed with a boxcar integrator that was interfaced to a personal computer.

RESULTS

We show in Figure 1 the rise and decay SHG signals for the main chain accordion polymer at 176°C with and without first being subjected to thermal annealing before the corona poling field is applied. Note that the T_g of the accordion polymer is 193°C. Isothermal annealing below T_g is a common method to densify and decrease the free volume of the amorphous polymer. Without annealing, the SHG signal of the fresh sample overshoots and then decreases to a steady state after about 1 hour. On the other hand, the SHG signal of the sample with 6 hours of annealing at 176°C increases steadily to a steady state value. In both cases the rise in the SHG signal is very rapid; the decay is, however, considerably slower and depends on the thermal treatment of the sample. One notes from the expanded decay portions shown in Figure 2 that the fresh film decays much more rapidly than the film subject to 6 hours of annealing at 176°C. In both cases the decay behavior is not single exponential. Best fits of the $\chi^{(2)}$ data (proportional to the square root of the SHG intensity) to the Kohlrausch-Williams-Watts (KWW) function (the stretched exponential) given by

$$\chi^{(2)} = a \cdot e^{-(t/\tau)^{\beta}} \qquad (1)$$

yields values for τ and β. Here τ is the characteristic relaxation time, and β is the width parameter whose value is $0 < \beta_i \leq 1$. Values of β and τ for the fresh and annealed films at 176°C are given in Table I. The annealed film has a much smaller β value, indicating a wider distribution of relaxation times. We have further studied the temperature dependence of the decay of the annealed film. The KWW function fit to the decay curve gives the β and τ values as a function of temperature. These results are also given in

Table I. One notes that above T_g the τ value decreases rapidly with increasing temperature; on the other hand, the β parameter increases with increasing temperature.

In Figure 3 we show the SHG intensity relaxation curves obtained for a 5 weight% NAS in PMMA sample subject to contact poling at 110°C under two different field strengths. Contact poling is carried out by increasing the voltage stepwise to a desirable level and then holding the poling voltage at that level until a steady SHG intensity is reached. To examine the SHG intensity decay behavior, we then turn off the poling voltage through a manual switch and record the signal decay. At a field strength of about 7.2×10^5 V/cm, two components are clearly evident (Figures 3a and 3b). At this poling strength, the magnitude of the short time component is about 20% of the total intensity, but at a higher field strength, 9.0×10^5 V/cm, the short time component is nearly covered by the stronger long time component (3c or 3d). The relaxation curves shown (Fig. 3a or 3b) can be fit satisfactorily to the sum of two single exponentials, with one single exponential representing each relaxation component. Similarly, a single exponential is sufficient for curve 3c (or 3d) provided that the short time component is excluded. One notes the two exponential decay curve shown in (Figure. 3b) is displayed more clearly when the time axis is set in the logarithmic scale. Except for the short time portion, a single exponential decay curve fits rather satisfactorily the decay curve portrayed in Fig. 3d. On the other hand, one can also fit the whole decay curve in terms of a KWW function with a β parameter equal to about 0.26, consistent with that reported previously.[6,9] However, a two single exponential fit gives a smaller standard deviation.

Shown in Figure 4 is a detailed "shot to shot" record of the SHG signal after the poling field is turned off for the 10% NAS/PMMA sample ($T_g \approx 95$°C) poled at 96°C. In trace (a) the cathode is shorted immediately after the poling field is turned off. In this case, the SHG signal takes a step decrease to the background intensity. Traces (b) and (c) correspond to decays with a $10^5 \Omega$ and a $10^{10} \Omega$ resistor connected to the cathode, respectively. Clearly, these signals decay gradually, with the $10^{10} \Omega$ resistor case decaying with a longer time constant.

We have observed an interesting memory effect associated with the establishment of the NLO macroscopic polarization. Shown in Fig. 5 is a series of SHG relaxation curves for the NAS/PMMA sample (5 weight% NAS) at 100°C. In curve (a) the sample was poled with a field of 8.4×10^5 V/cm. After the SHG signal decays completely, the poling field with the same strength is turned on and within a few seconds, an SHG intensity of about the same initial level is recovered. However, upon turning off the poling field, the SHG signal is found to have a longer relaxation time than the previous one, as shown in (b). As the process is repeated, the relaxation times become successively longer until a plateau value of about 4000s is obtained for the sample poled at this field strength. After the plateau value is reached, there is no longer any change in the decay curve, regardless of the number of times that the sample is repoled. These results are also observed for the sample above T_g, but the relaxation time lengthening effect above T_g is somewhat reduced.

We have studied the plateau relaxation time as a function of temperature. Over the narrow temperature range (≈ 30°C), studied as shown in Figure 6, the temperature dependence of the relaxation time can either be fit to an Arrhenius or Vogel-Fulcher-Tamann (VFT) [or equivalently, the Williams-Landel-Ferry (WLF)] form given by

$$\tau(T) = \tau_\infty \exp\left[\frac{B}{T - T_0}\right], \quad T > T_0 \tag{2}$$

However, statistics obtained from the fit favor the VFT equation and we shall interpret the data in accordance with this equation. For the 5 weight% NAS/PMMA system, we have found that τ_∞ equals 6.8×10^{-8} s and T_0 equals 293.8K. Two remarks are in order. Since the WLF parameter C_2, is equal to T_g-T_0, we obtain for this sample a C_2 value equal to 90 K. This is consistent with C_2 = 80 K for PMMA reported in the literature,[12] as the C_2 value will increase as the polymer is plasticized. The other remark is the VFT equation appears to describe all data above and below T_g. This is in contrast to the result of reference 6, which requires different equations to describe results above and below T_g.

Discussion

The SHG signal is proportional to the square of the second order optical susceptibility $\chi^{(2)}$, which in the case of the electric field poled amorphous NLO polymer consists of only two elements $\chi_{33}^{(2)}$ and $\chi_{31}^{(2)}$. For a molecule with a dominant β element, one can show that if the field-dipole interaction is less than kT, $\chi_{31}^{(2)}$ is equal to $\chi_{33}^{(2)}/3$. On the other hand, $\chi_{31}^{(2)}$ is larger than $\chi_{33}^{(2)}/3$ if the poling field is large such that the field-dipole interaction is greater than kT.[5] The study of the decay of the SHG signal provides information on the time dependence of $\chi_{33}^{(2)}$ as a result of the reorientation of the chromophore dipoles.

The time dependence of $\chi^{(2)}$, as represented by the decay of the SHG signal after the poling field is removed (as shown in Figures 1 and 2), is due to reorientation of the electric dipoles, which results in decreased polar order. The KWW functional representation suggests that the decay either has a distribution of relaxation times or has a complex non exponential single relaxation process. In any case, we can infer the relaxation process by both the characteristic relaxation time τ and the width of distribution β (Table 1). The increase in β implies that the distribution of relaxation times narrows to a single exponential as temperature is increased. This result is consistent with that found in side chain NLO polymers;[6] however, the data in reference 6 corresponds to temperatures below T_g.

Figures 1 through 3 above illustrate the use of two competing methods of obtaining polar order in polymers, corona and contact polymers. It is known that when a voltage is applied to a two-layer dielectric consisting of a layer with mobile ions and an insulating layer, a space-charge layer will be built up at the interface between the two layers due to the migration of mobile ions in one of the layers.[7] The space charge will create a static electric field, which prolongs the decay of $\chi^{(2)}$.[8] For *in situ* corona poling

(Figures 1 and 2), positive ions continue to be deposited on the polymer films some of which are transported across the film and trapped. The decay of trapped charges will affect the relaxation of the SHG signal after the corona field is turned off.[8] However, without a detailed knowledge of concentration of mobile ions, impurities, and the dynamics of the trapped charge decay, it is difficult to separate the effect of trapped charges on the behavior of the SHG intensity decay. In addition, surface charges can also affect the decay behavior of the SHG signal. Surface charges in corona poled films can, however, be removed by wiping of the film surface. Contact electrode poling (Figure 3) provides an alternative method for polarizing the polymer film and presumably is a better method for studying the relaxation behavior of $\chi^{(2)}$ after the poling field is turned off, as the surface charges that are built up at the interface can be readily bled off by short-circuiting the electrodes. However, at high poling field, charge injections still occur in contact electrode poling.

The results shown in Figure 4 indicate that the fast component of the decay is closely associated with the surface charges produced at the cathode. These surface charges will polarize the dipoles of the chromophores near the surface and in the bulk. Due to rapid relaxation of surface charges, it is not difficult to see that at high voltages and at high temperatures ($T>T_g$) the SHG signal from the dipoles induced by the surface charges will relax with a shorter time constant than that associated with the dominant macroscopic polarization in the bulk. As a result, the fast decay component that is only barely apparent in Figure 3d is nearly covered by the dominant slower decay component. Since the fast decay is closely associated with the surface charges, the study of the orientation of the dipoles induced by the surface charges will require constructing faster switching electronic circuitry that needs to turn on and off the poling field. In this work we emphasize the study of the second slower decay component associated with the relaxation of the macroscopic polarization. The relaxation of the SHG signal is associated with the fluctuations of macroscopic polarization owing to the correlated dipolar reorientation of the NLO chromophores in the bulk.

In our previous work we have shown that the SHG decay associated with the macroscopic polarization is strongly affected by the pair orientational correlation.[10] Due to the pair orientational correlation, the relaxation time of the slow component is affected by the poling field strength. In the case of NAS/PMMA system, the relaxation time increases with increasing poling field strength.[10] The pair orientational effect is expected to be reinforced when charges are injected to the polymer if it is poled with a large field.

While we do not at present have a quantitative theory for the memory effect shown demonstrated in Figure 5, we can offer a qualitative explanation of the observation. By poling, the dipoles overcome the viscous barrier of the surrounding polymer to orient along the electric field direction. Since the medium is also elastic (considering the fact that the polymer system is viscoelastic), the elastic stress imposed by the poling field results in electrostriction that also helps align the dipoles. This explains why the medium can be repoled rapidly after the SHG signal has decayed. At high poling field, charges (more likely electrons in the case of contact electrode poling) are injected and trapped in the medium. Due to the charge-dipole interaction, the presence of the trapped charges is expected to enhance the polar orientational correlation that should then lengthen the SHG decay time. The trapped charges have a life-time longer than the relaxation time of the macroscopic polarization for SHG,[11] and additional charges are further injected into the medium following each poling cycle. As a result, the SHG signal relaxation time will become longer as the system is repoled. Once the medium is saturated with charges; no more charges can be injected into the medium and a plateau SHG relaxation time will be obtained. Thus, as the medium is poled, we expect to observe the gradual lengthening of the SHG signal decay of the medium either above or below T_g. This is indeed experimentally found. We have observed the relaxation time lengthening effect both above and below T_g. However, below T_g an additional mechanism associated with physical aging also plays a role. The lengthening of the relaxation time as dipoles are polarized below T_g is also associated with the decrease of the amount of space surrounding the dipoles owing to the densification of the polymer chains. Polymer chain densification would decrease the available free volume and hinders subsequent reorientation of the dipoles. As a result, the relaxation time becomes longer. Thus, as the system is repoled below T_g, less and less free volume is made available for chromophores to reorient and the SHG signal will assume a progressively slower decay.

Due to the relaxation time lengthening effect, it should be emphasized that in order to obtain reproducible relaxation time results one needs to successively pole the medium until the plateau relaxation time is obtained. At a given poling field, the plateau relaxation time is a function of temperature.

Finally, we should mention that our steady state relaxation time τ in the vicinity of T_g is considerably longer by at least two orders of magnitude than that reported by Dhinojwala, et al.[13] who used the repetitive pulsed voltage with spacing variable from 200 μs to 0.5 s to pole the sample. In their work, they have not discussed the surface charge complication or the relaxation time lengthening effect that we have observed. No allowance is provided to remove the surface charge in their work. On the other hand, the poling field strength used by Dhinojwala et al. was only 3.2×10^4 V/cm, which is almost two orders of magnitude less than the poling field employed in the present work. Charge injection probably does not occur to a significant extent at such a poling field level, and the effect of trapped charge induced polar orientational correlation is probably unimportant in their case. However the poling geometry used in reference 13 may not have the unusual uniaxial symmetry. In this poling geometry, anomalous effects are known to occur.[14]

Conclusion

In summary, we have carried out a rather detailed investigation of the decay of SHG signals from a main chain accordion NLO polymer and a guest host NLO polymer system. The decay of the SHG signal from the main chain polymer is KWW, with the width distribution parameter ß increasing with increasing temperature, thus indicating that the distribution of relaxation times narrows as the temperature increases. In the case of the guest/host system polarized with the contact electrode poling method, the KWW function also gives a reasonable fit to the data, but the result is better described by the sum of two exponentials, with the fast component arising from surface charges and the slower component from the decay of macroscopic polarization of the medium. Due to the presence of trapped charges, the dielectric property of the medium is modified to some extent. Experimental results show that the amplitude of the slower component increases with increasing strength of the poling field. If the fast component is subtracted from the data, the single exponential function gives an excellent fit to the decay of the SHG signal. We have found that the time constant of the slow component successively increases as the poling-decay cycle is repeated, reaching a plateau value after several cycles. The memory effect is present in the sample above and below T_g and is believed to be associated with the presence of injected charges that also enhances the polar orientational correlation factor. The Vogel-Fulcher-Tamann equation gives a satisfactory fit to temperature dependence relaxation time data.

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FIGURE CAPTIONS

Fig. 1: Rise and decay curves of two main chain accordion NLO polymer films with and without thermal annealing. Trace associated with the lower horizontal axis corresponds to a fresh film, and that with the upper horizontal axis corresponds to an annealed film.

Fig. 2: Decay curves of the corona poled main chain accordion NLO polymer films with (solid circles) and without (empty circles) thermal annealing.

Fig. 3: SHG intensity relaxation curves for 5 wt. % NAS in PMMA poled at 100°C obtained with two field strengths. The abscissa for curves (a) and (c) are in linear scale and those for (b) and (d) are in logarithmic scale. The field strength is 7.2×10^5 V/cm for (a) or (b), and is 9.0×10^5V/cm for (c) or (d).

Fig. 4: Detailed shot to shot SHG intensity curves with different values of resistor connected to the cathode. Resistance for (a) is 0 ohm, for (b) is = 10^5 ohm and for (c) is 10^{10} ohm.

Fig. 5: Lengthening of the relaxation curves as the sample is progressively poled at a constant temperature.

Fig. 6: Temperature dependence of the steady state relaxation time. (——Vogel-Fulcher-Tamann fit; . . . . . Arrhenius fit).

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TABLE I

KWW parameters associated with the decay portion of the dynamic SHG intensity curve.

Temperature (° C)	τ (s)	β
175		
a. Fresh film	19.5	0.42
b. Annealed film	3276.8	0.36
198	2097.1	0.52
204	884.7	0.73
210	395.4	0.88