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Optical poling in a crosslinkable polymer system

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Abstract. Efficient optical poling of a crosslinkable polyurethane film, in which a high crosslinking density can result, is experimentally investigated and compared with corona poling. The photoinduced orientation and the crosslinking processes of the chromophores can be performed separately. The heating rate and the final curing temperature are crucial for the optical poling procedure. Through thermal curing of the sample, the stability properties of photoinduced polar order are demonstrated to be dramatically enhanced, especially its photostability. It is also shown that corona poling is more effective than optical poling in the case of a crosslinkable thick film.

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Much attention has been paid to the research of second-order nonlinear optical (NLO) materials in recent years for their great potential in photonics applications [1, 2]. A key issue in this field is to exploit methods to arrange the NLO molecules into noncentrosymmetric structures. One of the available routes benefits from the short-range interaction between molecules, such as the techniques of crystal growth, Langmuir–Blodgett films, liquid crystals, and ferroelectrics. But in most cases, the NLO chromophores are randomly dispersed in the polymer matrix and a dc-electric-field poling is applied, which is the most popular route so far [3, 4]. Recently, a novel poling method with which the polar order can be achieved completely by light has been demonstrated by Charra et al. [5–7]. This so-called all-optical poling is very attractive for its various advantages. One most important feature of this method is that it results in an induced $\chi^{(2)}$ with a spatial period automatically satisfying the phase-matching condition for frequency doubling. Additionally, it offers the possibility of optical two- or three-dimensional tailoring of NLO molecules [8].

The physical mechanism of this method is quite different from that of electric-field poling, in which the molecules rotate through the coupling of the dipole to the external electric field. For all-optical poling, molecular rotation results from the effects of orientational hole burning and the photoisomerization reorientation [6, 9]. In detail, the coherent interaction of two beams at fundamental and its doubled frequencies leads to a polar-selective excitation of azo dye molecules. Through the processes of *trans-cis-trans* isomerization cycle and orientation redistribution, a polar alignment of the molecules is yielded and hence a nonzero second-order susceptibility is induced inside the material. By optimizing the preparation conditions such as the relative phase and the intensity ratio of the two seeding beams, a high conversion efficiency for second-harmonic generation (SHG) is obtainable.

However, a critical problem is also encountered in all-optical poling: the induced polar orientation of the chromophores appears unstable and suffers from a gradual relaxation [7, 10]. To stabilize the induced polar order, thermal or photo crosslinkable polymer systems have been demonstrated to be efficient in case of conventional electric-field poling [11, 12]. In these polymer systems, the nonlinear molecules can be aligned and chemically bonded together to form long-range, three-dimensional networks. Such networks dramatically retard the mobility of the NLO molecules, thereby preserving their polar order.

Recently, we have first introduced the concept of crosslinking into optical poling [13]. The experimental data preliminarily evidenced that the stability of induced polar order was greatly improved via crosslinking of polymer matrix. Here we further study this work in a new crosslinkable polyurethane system which differs from the previous in that here not only the matrix but also each NLO chromophore participate in the crosslinking reaction. A practicable poling procedure is also proposed and we find that the heating rate and the final curing temperature are two crucial factors for the optical poling of a crosslinkable system. The dynamic thermal stability of the optically poled sample is investigated and compared with that of corona poling. In particular we show that the polymer exhibits excellent photostability after completion of crosslinking process.

1 Experiments

1.1 Sample preparation

The crosslinkable polymer system consists of two kinds of monomers, as shown in Fig. 1. Monomer (a) is a prepolymer containing isocyanate and azo dye group, and monomer (b)

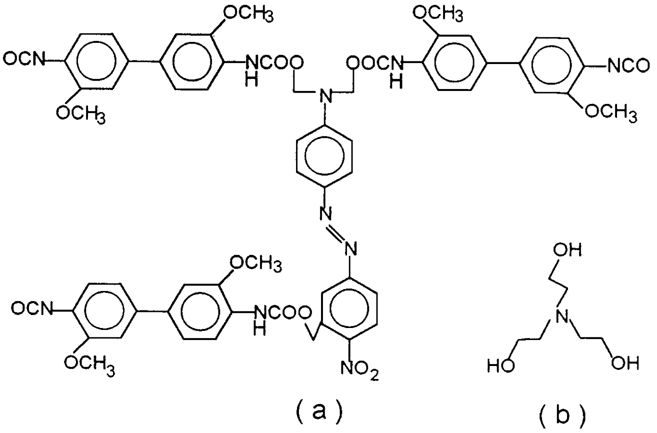

Fig. 1a,b. Molecular structures of monomer (**a**), the prepolymer, and monomer (**b**), the crosslinker. Crosslinking can be thermally carried out through chemical reaction between the hydroxyl (OH) groups of the crosslinker and the cyanate (CNO) groups of the prepolymer

is the crosslinker. Crosslinking can be thermally carried out through chemical reaction between the hydroxyl (OH) groups of the crosslinker and the cyanate (CNO) groups of the prepolymer. Obviously, the isocyanate as well as the azo group are all involved in crosslinking reaction during thermosetting.

The azo dye was synthesized based on the diazo coupling reaction between the substituted aniline with substituted N,N-dialkyl aminobenzene. 3-hydroxmethyl-4-nito azo N,N-dihydroxyethyl aminobenzene was synthesized according to [14]. Purified dioxane was used as solvent. 4,4′-diisocyanato-3,3′-dimethoxydiphenyl was added to form the prepolymer and made sure that the molar ratio of the functional group OH/NCO was 1 : 2. Trihydroxyethyl amine was added as crosslinker and the solution was heated to 90 °C for 0.5 h. The resulting solution was filtered through a 0.2 μm Teflon filter and spun-cast onto glass slides. After these samples were dried in vacuum overnight at room temperature, we got red-transparent optical-quality films. The thicknesses of the films and their transmissions at 532 nm were measured to be about 2.5 μm and $10^{-2.2}$, respectively. Figure 2 shows the absorption spectra of the film before (solid line) and after (dash line) being poled with corona poling method.

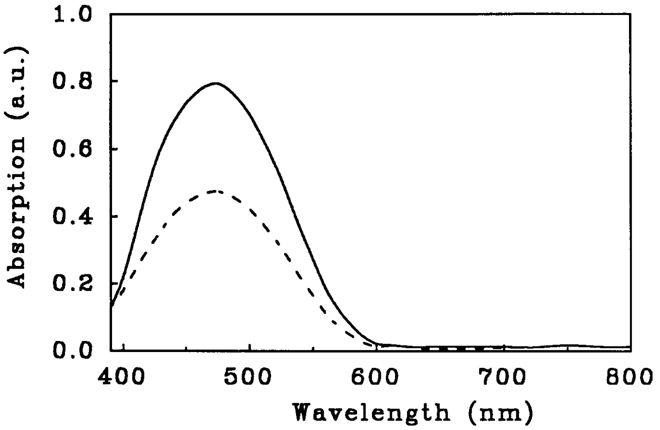

Fig. 2. Absorption spectra of the uncrosslinked prepolymer (*solid line*) and the crosslinked polymer poled with corona poling method (*dash line*, 160 °C, 2 h). The thickness of the film was 2.5 μm

1.2 Experimental setup

For optical poling, a setup as schematically shown in [13] is adopted. The source was a Q-switched Nd:YAG laser delivering 8-ns pulses at 1064 nm with a 10 Hz repetition rate. The polarized source beam was split into two branches by a beam splitter. One branch is frequency doubled by a KDP crystal (2ω beam here) and served as one of the seeding beams; the other, which passed through a polarizer to adjust its polarization, served as another seeding beam (ω beam). These two beams copropagated and are focused on the sample with the same spot of 0.6-mm diameter. Two filters for 1064 nm, respectively placed behind the KDP crystal and the sample, were used to intercept the ω beam. A pair of electronically controlled shutters were used to alter the seeding and probing processes. The shutter set in front of the KDP crystal was turned on while the other is turned off during the seeding process and vice versa during the probing process. The optically induced second-order susceptibility of the sample was measured via SHG of the ω beam when the 2ω seeding beam was blocked by the shutter set in front of the KDP crystal. The signal was detected by a photomultiplier tube (PMT). The sample was placed in an oven, which was controlled by a digital temperature controller. The pulse energies were about 3.8 mJ for the ω infrared beam and 4 μJ for the 2ω green beam.

2 Results and discussion

There exists big difference in poling procedure between corona poling and all-optical poling method for a thermal crosslinkable polymer system. For the former, both orientation and crosslinking of the NLO molecules need to be performed at elevated temperature [11]. However, crosslinking before poling greatly hinders the mobility of the NLO moieties and therefore results in a reduction of nonlinearity. On the other hand, before the crosslinking reaction is completed enough, the high electric poling field would cause the sample film to be damaged. So, a complicated optimized poling procedure is required for achieving a large second-order coefficient and a good thermal stability. But for all-optical poling, some convenience is available because samples can be poled at room temperature. This means the two processes, orientation and crosslinking of the molecules, can be performed separately. Thus, in our experiments we first optically poled the sample at room temperature (30 °C), then kept the seeding condition and raised its temperature at an appropriate rate.

In order to identify the influence of crosslinking on the thermal stability of the induced polar order, we compared the decay behaviors of the samples which had experienced different thermal histories. The poling and heating procedures were carried out as follows. First, we optically seeded the polymer until the induced SHG signal reached its saturation level, then heated it to a final temperature at a rate of 2 °C/min. After the sample was kept at that final temperature for 1 h, the seeding condition was terminated and the isothermal relaxation of the polar order was monitored via SHG. Figure 3 shows three such cases in which the final temperatures are respectively set at 30, 60, and 90 °C. The experimental results show that relaxation of the induced polar order becomes much slower

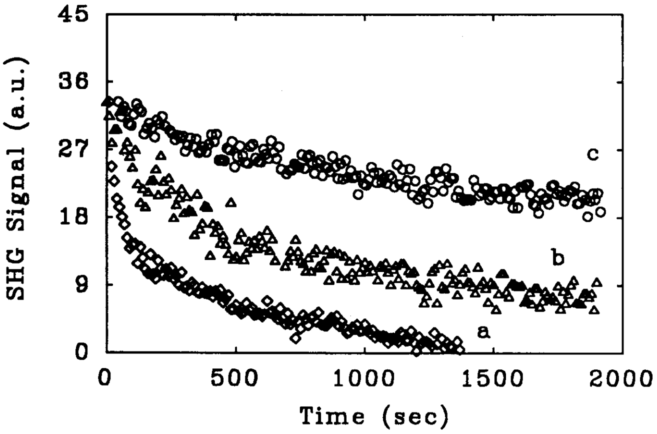

Fig. 3. Isothermal relaxation of the photoinduced SHG signal under different sample temperatures, 30, 60, and 90 °C from curve (a) to (c), respectively. The optical poling and thermal procedures were carried on as follows: we optically poled the sample first, then kept the seeding condition and raised its temperature at 2 °C/min. The samples were kept at that final temperatures for 1 h

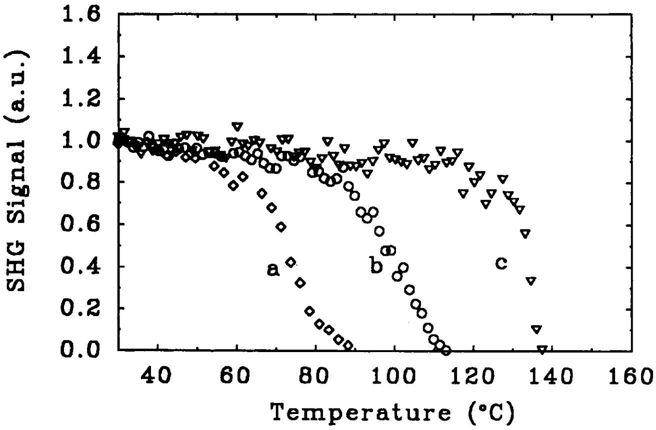

Fig. 4. Dynamic thermal analyses for the poled samples, optically poled without (a) or with (b) crosslinking, and poled via corona poling (c). In all cases, the heating rate is 10 °C/min

with increasing the final temperatures. Note the fact that the degrees of crosslinking reaction increase at higher temperatures, thus we concluded the improved thermal stability of the induced polar order benefits from the effect of thermal crosslinking. Indeed, thermal crosslinking directly results in a rigid three-dimensional polymer network in the sample and much restricts the mobility of the NLO chromophores [11].

We also found that, in the three cases described above, the induced saturation level of SHG was almost not affected by the increase of temperature. However, when the heating rate was increased a lot, for example 10 °C/min, the saturation level decreased, though the seeding process was kept on. Additionally, a final temperature too high, such as above 100 °C, could result in a breakdown of the induced polar alignment of the chromophores. These limitations in temperature results from the molecular orientational diffusion and the glass transition temperature (T_g) of the polymer. With increasing temperature, the crosslinking reaction is sped up, but a higher thermal randomization energy is obtained simultaneously for the NLO moieties. Thus, the induced order will be maintained much better by crosslinking on one hand, but destroyed by the enhanced molecular orientational diffusion on the other hand. A high heating rate is possible to make orientational diffusion overwhelm the effect of crosslinking. For the present sample, the suitable heating rate and the highest final temperature are about 2 °C/min and 95 °C, respectively.

The dynamic thermal properties of the poled samples were also investigated. Three cases are compared, as shown in Fig. 4. Curve (a) in the figure shows the case in which the sample was optically poled at room temperature but without a heating history. Obviously, no crosslinking happened in this sample. Curve (b) shows a case of optical poling with crosslinking. After the induced SHG reached its saturation level at room temperature, the sample was heated to 95 °C at a rate of 2 °C/min and kept at that temperature for 2 h. Finally it was cooled down to room temperature at the same rate. Curve (c) shows the situation of corona poling. The poling procedure was described in [15], in which the final poling temperature was 160 °C. From Fig. 4, one confirms that crosslinking really has a great contribution to the thermal stability of the induced polar order. However, the case of corona poling shows much better thermal stability than that of optical poling. We believe such difference is attributed to their different heating processing. For optical poling, although the poling temperature can be increased to complete the crosslinking reaction, it must be kept far below the T_g of the sample due to the enhanced orientational diffusion [16]. As to the corona poling, such limitation of the poling temperature does not exist, the sample can be poled around the original T_g of the sample. This is the reason why the sample was heated only to 95 °C in the case of optical poling, but poled at 160 °C in the case of corona poling. On the other hand, the T_g of a crosslinkable polymer is not a constant but increases with the curing temperature. Consequently, the resulting T_g of the sample heated at 95 °C in optical poling is much lower than that poled at 160 °C in the case of corona poling. That is to say, corona poling leads to better thermal stability just as shown in Fig. 4.

Experiments were also carried out to demonstrate that crosslinking can dramatically enhance the photostability of the polar order. In fact, poor photostability is another obstacle for the application of all-optical poling [7]. During reading, the intense ω beam would destroy the previously induced polar order through an axial photostimulation process. Figure 5 (top) shows the case where the induced polar order of the optically poled sample was read out by different intensities of the ω reading beam. The sample was poled on the condition of curve (a) in Fig. 4, which did not experience a heating procedure. One can see that the induced order is very unstable and sensitive to the reading conditions. A higher intensity of the reading beam leads to a faster decay of the polar order. But for the crosslinked sample, the induced polar alignment of chromophores exhibited excellent photostability. As shown in Fig. 5 (bottom), the read-out SHG signal of the crosslinked sample (poled on the condition of curve (b) in Fig. 4) could be kept unchanged at least for 2 h. Even when the reading intensity was increased twofold, 90% of the initial value could be maintained. Experimentally, we also found that this enhanced photostable behavior was almost the same as in the case of corona poling.

The resonantly enhanced nonlinear coefficient d_{33} of the optically poled sample was measured to be 16 pm/V. This value was almost eight times smaller than that of corona pol-

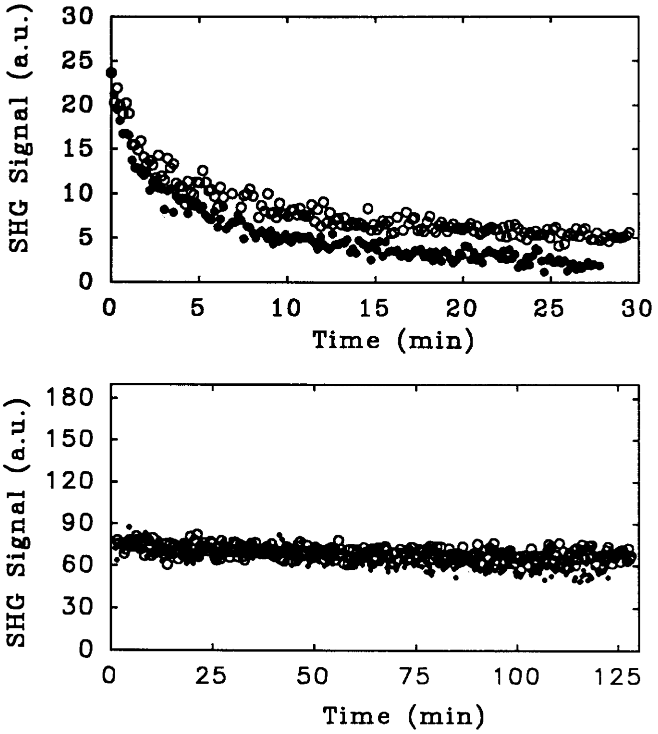

Fig. 5. Decay behaviors of the photoinduced SHG signal for the uncrosslinked (*top*) and already crosslinked (*bottom*) samples. In both cases, the photoinduced $\chi^{(2)}$ was read out with different reading intensities: 3.8 mJ (*open circles*) and 7.5 mJ (*filled circles*)

ing, 120 pm/V at 1064 nm. Such difference we believe lies in the absorption of the poled sample. As shown in Fig. 2, the absorption is greatly reduced after the sample has been subjected to the corona poling procedure. Though some effects such as dichroism of dye polymer may also cause an absorption reduction at 532 nm during optical poling, the strength is not so pronounced as that of corona poling.

Usually, the preparation conditions, involving the relative phase and the intensity ratio between the two seeding beams, are optimized to achieve an efficient optical poling. However, in the present experiments the relative phase has not been considered. This is reasonable for the thickness of the sample. In fact, only very thin film is required to optimize the relative phase, because its thickness is usually below the coherent length, namely $l < l_c$. For this crosslinkable sample, its l_c is estimated to be 1.3 μm, which is half of the sample's thickness ($l \approx 2.5$ μm). In this case, the relative phase of the two seeding beams would not make a big difference during the measurement of photoinduced $\chi^{(2)}$ [7].

3 Conclusion

We have investigated the efficient optical poling in a crosslinkable polymer. The photoinduced orientation and the crosslinking processes of the chromophores can be performed separately. The heating rate and the final curing temperature are crucial for the optical poling procedure. After thermal crosslinking, the photoinduced polar order of the sample showed excellent stability properties, especially its photostability. The resonantly enhanced nonlinear coefficient d_{33} of the optically poled sample was measured to be 16 pm/V. Experimentally, it was also shown that corona poling is more effective than optical poling in case of a crosslinkable thick film.

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