

# RAPID COMMUNICATION

## Improved Optical Quality of Crosslinkable Nonlinear Polymer Waveguides by Anchoring the Diffusive Small Molecules

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### INTRODUCTION

Using nonlinear optical (NLO) polymeric materials to fabricate electrooptic (EO) devices has several well-recognized advantages such as compatibility with different substrates, ease of fabrication, and possibly low costs compared with the inorganic counter parts such as lithium niobate. As a result, a lot of NLO polymers have been synthesized in recent years.<sup>1–5</sup> However, the progress of the fabrication of practical devices has been impeded by the lack of processability of the materials. A low loss waveguide with a high and stable NLO coefficient is needed for any practical device. Polyimide NLO materials offer the best stability; however, the NLO active materials have relatively high optical losses ( $>3$  dB/cm) and it is often the case that the losses and processability remain unreported.<sup>2</sup> Other materials, however, do not possess a thermal stability satisfying commercial or military requirements.<sup>6</sup> Much higher stability can be achieved by crosslinking both of the ends of a NLO chromophore into the polymer network. Although many efforts have been made, only a few NLO materials have achieved long term stabilities near or up to 100°C,<sup>1–3,5</sup> and one material (LD-3) turns out to have a long term thermal stability satisfying the military requirement of 125°C.<sup>4</sup> LD-3 is a thermally crosslinkable NLO polymer consisting of a poly (methyl methacrylate) (PMMA) backbone and an azobenzene-sulfone chromophore [Fig. 1(a)]. It can be crosslinked by a diisocyanate crosslinker. Using Dianisidine diiso-

cyanate (Pfaltz & Bauer, Inc.) as the crosslinker [Fig. 1(b)], a  $r_{33}$  value of 13 pm/V at 633 nm was achieved and a long-term stability at 125°C is proved through annealing a sample at this temperature for over 1250 h.<sup>7</sup>

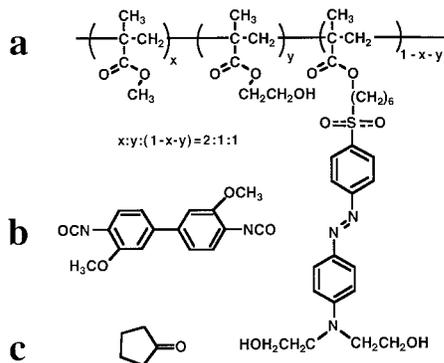
It is both technically and commercially interesting to use crosslinkable NLO polymer to fabricate EO devices. However, only very few materials have been reportedly used in making any kind of useful devices.<sup>3,5,8,9</sup> The excellent stability and the good EO coefficients make LD-3 polymer an ideal candidate for fabrication of EO polymer devices, but some unsolved processing problems with this material impede the progress of its practical application. Even some researchers who first published this material turn their attention to other materials which have much inferior stability.<sup>4,8,9</sup> The PURDR19 is most frequently used to fabricate waveguide devices.<sup>8,9</sup> Test devices made of other two materials BIN2-HDT and Red-acid Magly are also reported by other researchers. However, BIN2-HDT, PURDR19 and Red-acid Magly have long term stabilities only up to 100, 90, and 85°C, respectively.

It is significant if the processing problems of LD-3 can be solved because its superior stability allows a much wider range of applications. More importantly, some insight into these problems might also apply to other crosslinkable NLO polymer systems. The key part of fabricating LD-3-based NLO polymer devices is the preparation of the NLO polymer films. For a crosslinkable polymer, we need to first dissolve the polymer and the crosslinker together to make a spin-coatable solution. Then the chromophores need to be aligned into a noncentrosymmetric order to obtain second order nonlinearity. The alignment of the chromophores is accomplished by applying a high electric field across the film while heating the film to above the glass transition

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**Figure 1.** (a) The structure of the LD-3 polymer; (b) the diisocyanate crosslinker; (c) the cyclopentanone.

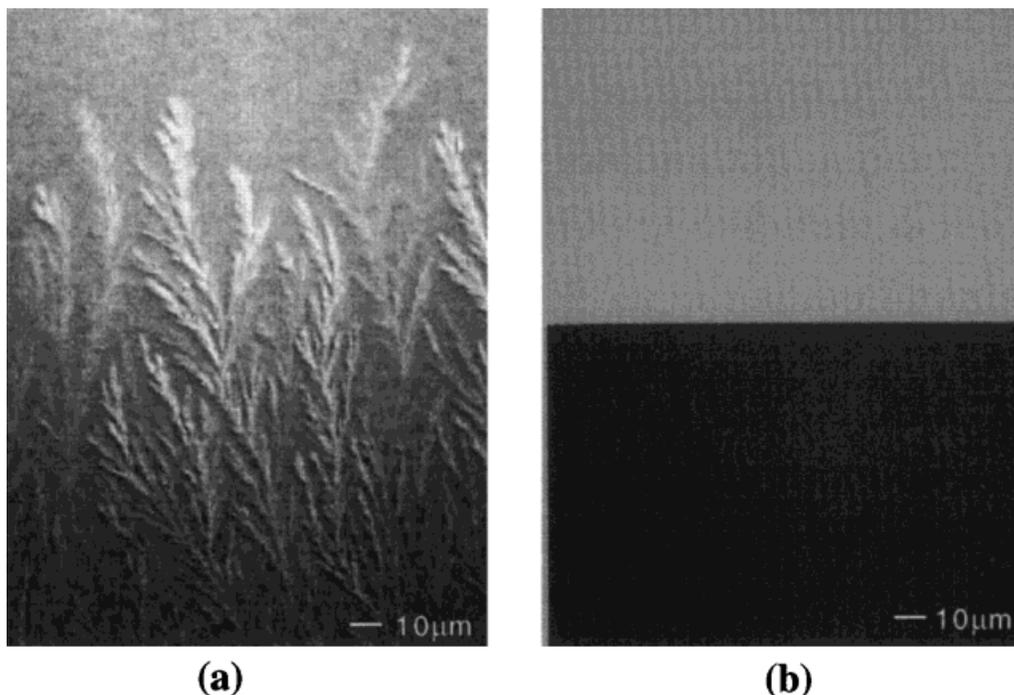
temperature  $T_g$  of the polymer. The fix of the alignment is realized by crosslinking both of the ends of a chromophore into the polymer network at an elevated temperature.

### SEARCHING FOR COMPATIBLE SOLVENTS

The first attempt at fabricating a planar waveguide out of LD-3 polymer has failed because of the lack of an appropriate solvent compatible with all the fabrication processes.<sup>7</sup> The only solvent previously reported is tetrahydrofuran (THF), which was also suggested to us by the material supplier. However, due to the high volatility of THF, it is impossible to make smooth films thicker than 0.5  $\mu\text{m}$ .<sup>7</sup> Such a thin film is not useful in making devices because the insertion loss is very large. Even if other kinds of losses are neglected, the coupling loss would make a device unacceptable, simply considering the mismatch of the mode profiles between a 0.5  $\mu\text{m}$  waveguide and a single-mode optical fiber that typically have a mode diameter from 5 to 10  $\mu\text{m}$ . It is important to understand the dominating interactions in the polymer to find a good solvent for it, because the interaction among the molecules in a solution determines the solubility of a solute in a solvent. High solubility is possible when the interactions among the molecules in the solute are similar to those in the solvent. For polymers with known solubility parameters, a compatible solvent can be found among the solvents that have solubility parameters close to those of the polymers. However, LD-3 polymer is a new material and the solubility parameters are unknown. But we can deduce some information from the molecular structure. Unlike PURDR19 or BIN2-HDT, which consists of small molecules before crosslinking and is much easier to be dissolved in many common solvents, LD-3 polymer is a long chain polymer [Fig. 1(a)]. The many OH groups in the polymer produces strong hydrogen bonding and the push-pull structure of the NLO chromophore results in a very strong dipole-dipole interaction

in the polymer. It is well known that some long-chain polymers with many OH groups such as polyvinyl alcohol, poly (acrylic acid), etc., can only be dissolved in water or alcohol. Therefore, the difficulty of dissolving LD-3 polymer into some commonly used NLO polymer solvents such as cyclohexanone, dioxane, chloroform, etc., is understandable. Our results show that the solubility of LD-3 polymer at room temperature is less than 10% (weight percentage) in cyclohexanone, very poor in dioxane, and actually zero in chloroform. The solubility in THF is better, but no more than 20%. The cross-linking process prohibits the use of any solvent that reacts with the crosslinker; as a result, water or any alcohol has to be excluded. Considering the strong hydrogen bonding interaction and dipole-dipole interaction in the polymer, we chose other solvents with vapor pressures lower than that of THF but with stronger hydrogen bonding and dipole-dipole interaction. More than 10 solvents have been tested, and several solvents do have good solubility to LD-3 polymer. However, most are not compatible with the film fabrication processes. For example, pyridine offers good solubility (>20%) to LD-3, but it catalyzes the crosslinking reaction between the polymer and the crosslinker and, therefore, makes the solution quickly turn into a useless gel before spin coating. After exclusion of these solvents, which are either chemically reactive or difficult to be removed, only one solvent, cyclopentanone, remains. The structure of cyclopentanone is shown in Figure 1(c). The solubility of LD-3 polymer in cyclopentanone is high, measured to be higher than 50%. The dissolving speed of LD-3 polymer in cyclopentanone is very slow. To prepare a high concentration solution, we let the solution sit overnight to allow the polymer to be totally dissolved. This might explain why other researchers have not found cyclopentanone as a compatible solvent for LD-3 polymer, although it is a common solvent.

Removal of the solvent is not a trivial issue. One important criterion for choosing cyclopentanone is its mild volatility. A proper solvent volatility is required for preparing high quality optical films with required thicknesses. For spin-coated films, the thicknesses are proportional to the concentration of the solution. If a solvent evaporates too quickly, it is impossible to prepare thick films because the solution quickly becomes too viscous to be able to spread. On the other hand, if a solvent evaporates too slowly, it is necessary to heat the film to have the solvent removed, which would cause undesirable crosslinking and make poling inefficient. During all the processes before poling, any crosslinking should be minimized to allow the chromophores enough freedom to align themselves with the electric field when the poling voltage is applied. Vacuum drying is necessary to remove the solvent. Thicker films are fabricated by using cyclopentanone as the solvent. The films are prepared by dissolving both the polymer and crosslinker in the solvent and then filtered and spin coated onto silicon wafers, or on indium tin oxide (ITO)



**Figure 2.** Microscope view of the LD-3 polymer films: (a) high solvent evaporation speed results in crystal grains; (b) low solvent evaporation results in smooth films (upper part: LD-3 on metal, lower part: LD-3 on glass).

coated glass slides for measuring EO coefficients. The ratio of the crosslinker to the polymer is 60 : 100 in weight. This ratio ensures the chromophores to be fully crosslinked and, hence, ensures a high thermal stability. The resulting films have thicknesses from 1.2 to 2.4  $\mu\text{m}$ , which are determined by an Alpha Step 200 surface profiler. The solvent cyclopentanone can be removed from the polymer film within 8 h at room temperature by a mechanical pump. A slow reaction between the polymer and the crosslinker in the solution is observed. After the solution is prepared, it has to be used within half an hour if the concentration is high (>15%). Otherwise, the solution will turn into a nonspincoatable gel.

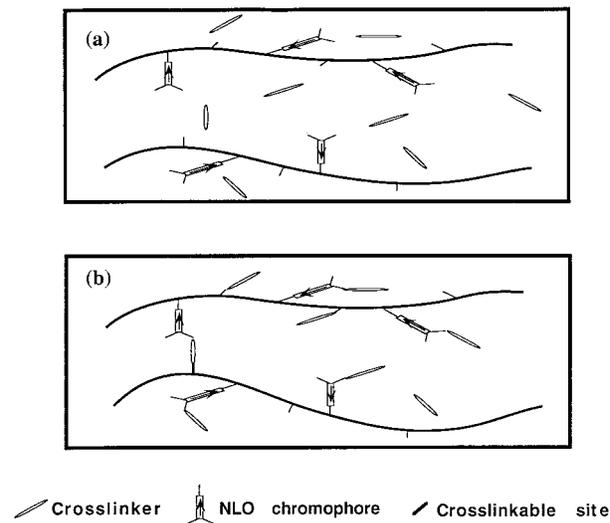
#### ANCHORING THE CROSSLINKERS TO STOP THEIR CRYSTALLIZATION

The crystallization of the crosslinker on the film surfaces is another obstacle. This phenomenon also bothers other researchers working on the same material. Figure 2(a) shows a microscope picture of the crosslinker crystal grains formed on a LD-3 film surface. The crystals form tree branch patterns on the polymer surface. Usually there are more crystals formed along the edge of the silicon wafer than at the center. In extreme cases, the tree shape pattern can cover areas of several square centimeters in total along the edge. We have tried other substrates, including glass slides, met-

als, polymers, but the crystallization always occurs. Therefore, it is not a problem of substrates. To solve this problem we carefully investigate when the crystallization occurs. We observed that no crystal appears just after the spin coating. The grains are formed during drying of the film in the vacuum. This indicates that the crystallization occurs when the solvent is being removed from the film and there is a phase segregation between the polymer and the crosslinker during this process. The role of the solvent in the crosslinker crystallization is not clear, but the phase segregation is dictated by the free energy of the system of the crosslinker and the polymer. If the crystallization of the crosslinker lowers the free energy of the system, it will occur no matter what solvent is used. This means the solid solubility of the crosslinker in the LD-3 polymer is low. One way to solve this problem is to reduce the crosslinker to polymer ratio. However, the ratio is determined by the stoichiometry of the crosslinking reaction and does not allow change. Another way is to use other crosslinkers that might have higher solid solubility in LD-3 polymer. Because this will change the composition of the resulted NLO films, the stability of the NLO properties might also change. Other crosslinkers tested do result in inferior stability.<sup>7</sup>

The slow reaction between the polymer and crosslinker in the solution gives a clue for us to solve this problem. Clearly, there are three competing processes: the polymer–crosslinker reaction, the solvent evapora-

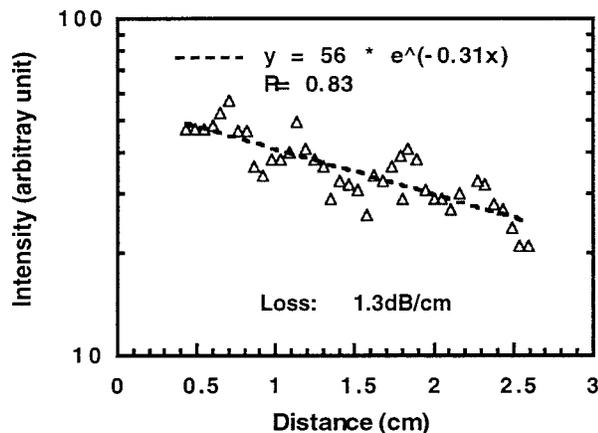
tion, and the crosslinker diffusion and crystallization. If the polymer–crosslinker reaction rate could consume enough crosslinkers so that the concentration of the free crosslinkers could be maintained lower than the solubility of the crosslinker in the polymer–crosslinker–solvent system during the solvent evaporation process, then the crosslinker would not crystallize. The simplest way to do this is by slowing down the solvent evaporation speed during vacuum drying. However, there might be another problem. Once the crosslinker has had enough time to react with the polymer, most of the chromophores might be crosslinked before poling, so the  $r_{33}$  value might be drastically reduced. There might be a possibility that only one of the two ends of a crosslinker has reacted to the LD-3 polymer within a certain length of time so that the segregation of the crosslinker is not possible, but the chromophore can still be aligned to the electric field because a crosslinking bridge forms only when both of the ends of a crosslinker are reacted. Statistically it is not possible to have all the crosslinker have only one end reacted. However, if the crosslinking density is very low (e.g.,  $< 1\%$ ), there will be no appreciable decrease in the EO coefficient. Different levels of vacuum, from  $10^{-2}$  Torr to 1 Torr, are used to control the evaporation rate. When a vacuum of 1 Torr is used, good films free from crystal dots of the crosslinker are consistently obtained, when observed under microscope. For higher vacuum, some crystal dots always appear on the film surface. Of course, longer drying time is needed when the vacuum is lower. About 48 h are needed to totally dry the films with 1 Torr vacuum. The measurement of the EO coefficients show that this method causes no observable decrease in the  $r_{33}$  value. We obtain  $r_{33}$  values around 16 pm/V in corona poled films at the wavelength of 633 nm, which is at least as good as the previously reported one at the same wavelength (13 pm/V). Directly measuring the crosslinking density is difficult and is beyond our interest. The resulting  $r_{33}$  values indicate that the unwanted crosslinking density should be very low. An insight into the method can be obtained if we analyze microscopically the drying process. Figure 3 shows the microscopic mechanism of anchoring the crosslinkers. The crosslinker has a high mobility with the presence of the solvent so that it has a great chance to encounter the crosslinkable sites within the polymer matrix. Once one end is attached to the backbone, the mobility of the crosslinker is drastically reduced. As a result, the probability for the second end of a crosslinker to encounter a crosslinkable site is much smaller. Therefore, it is possible to have most of the crosslinkers anchored to the polymer but without forming many crosslinked bridges. This is difficult to be realized in a solution. First, the polymer chains can move in the solution, so there might still be a considerable chance for the second end of a crosslinker to encounter a crosslinkable site associated with another backbone. More importantly, the solution will turn into a nonspincoatable gel as



**Figure 3.** Mechanism of anchoring the crosslinker. (a) Free crosslinker can diffuse and crystallize out; (b) slow evaporation rate allows a crosslinker to have time to attach one end to the polymer backbone, but the second end of a chromophore has much less chance to encounter a crosslinkable site.

mentioned before even if there is only a small amount of crosslinking. However, the motion of the polymer is greatly reduced due to the loss of most of the solvent and the large molecular size of the polymer after the solution is spin coated onto the substrate and a film is formed. Therefore, a well-controlled evaporation rate will ensure that most of the diffusive crosslinkers are attached to the polymer while most of the chromophores can still have the rotational freedom. There is no report of any kind of crystallization in the previously mentioned NLO polymers. This is not unexpected. No crosslinker is used with the Red-acid Magly. For the other two materials, a precuring is conducted after the crosslinker is added. Although no one reported why a precuring step is necessary, we can understand that precuring has combined small molecules into larger molecules; hence, the precipitation of any small molecules is prevented. Because the starting materials of PURDR19 or BIN2-HDT are all small molecules with molecular weights of a few hundred atomic units, a well-controlled precuring will not turn the polymer solution into a nonspin coatable gel. On the other hand, the average molecular weight of LD-3 polymer is expected to be at least tens of thousands atomic units. Precuring before spin coating is not viable in LD-3 polymer for the reason mentioned before. Through this comparison we can see that the slow evaporation of the solvent plays the same role as the precuring step in the other polymers, but it happens after spin coating.

Polymer films prepared in this way show no observable crystallization, regardless of what substrates were used. The films prepared on silicon wafer were very



**Figure 4.** Optical loss measurement of a planar LD-3 polymer waveguide with NOA 61 as the cladding material.

smooth and featureless under microscope observation. To show some contrast, we prepared a film on a microscope slide with chromium patterns. Figure 2(b) is a microscopic picture of the film. The upper part of the film is on chromium, so it is bright due to the reflection. The lower part is on glass, so it is darker due to the transparency of the glass and the film.

#### LOSS MEASUREMENT AND CONCLUSION

The ultimate check of the effectiveness of the film preparation method is the waveguide losses. A multilayer planar waveguide on a 4-inch silicon wafer is fabricated. First an aluminum layer is deposited as the ground electrode. Then 3  $\mu\text{m}$  optical adhesive NOA61 is coated as the lower cladding, then 1.2  $\mu\text{m}$  LD-3 polymer, and finally 1  $\mu\text{m}$  of NOA61 as the upper cladding. An infrared light with a wavelength of 1.32  $\mu\text{m}$  is coupled into the waveguide from a prism located at the center of the wafer. The propagation of the light from the center of the wafer to the edge is clearly observed using a CCD camera. It propagates nearly 5 cm and then emerge from the wafer edge. The loss is determined by measuring the scattered light intensity along the light streak.<sup>10</sup> Figure 4 shows the loss measurement result. Relatively low loss of 1.3 dB/cm is achieved. Lower loss (less than 1 dB) can be expected if the core and the lower cladding thicknesses are increased. There is no reported loss data of LD-3 polymer. Compared with other reported results in NLO polymers,<sup>3,9</sup> this loss is acceptable.

In conclusion, the crosslinker crystallization problem has been solved by balancing the polymer-cross-

linker reaction rate and the solvent evaporation rate. The different reaction probabilities of the two ends of a crosslinker resulting from the reaction sequence is understood as the underlining mechanism. Good optical quality multilayer planar waveguides with relative low loss have been fabricated. Although this discussion is limited to LD-3 polymer, the same principle can be applied to fabricate other polymer films involving the use of a crosslinker. Based on the mechanism discussed, the processing time might be shortened by using different drying schemes. This investigation is in progress.

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