

Fabrication of high quality crosslinked LD-3 nonlinear optical polymer waveguide films

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ABSTRACT

Crosslinked polymers offer the promise of great long term temporal stability and chemical resistance. However, a crosslinkable nonlinear optical (NLO) polymer is more difficult to be processed into high optical quality thin films than other type of NLO polymers such as side-chain, main-chain or guest-host polymers. The crosslinking process imposes more stringent requirements on the solvents. The process of searching for a compatible solvent for a crosslinkable NLO polymer is described. Two detrimental phenomena during the fabrication of electrooptic waveguides from crosslinkable polymers are reported. One is the crystallization of the crosslinker. The other is the formation of wavy surfaces when a commercially available optical adhesive is used to prepare the cladding. By anchoring the small molecules to the long chain NLO polymer and precuring the optical adhesive, good optical quality polymer waveguides are prepared.

Keywords: nonlinear optical polymer, electrooptic, optical film, waveguide fabrication, crosslinker crystallization, optical adhesive

1. INTRODUCTION

Although today's dominant electrooptic devices today are still made from inorganic materials such as lithium niobate, it is difficult to integrate these devices with electronic circuits which are usually fabricated on semiconductor wafers. This difficulty prevents the reduction of the fabrication cost and hence the wider use of these devices. Compared with the inorganic counter parts, nonlinear optical (NLO) polymeric materials have several well recognized advantages such as compatibility with different substrates, ease of fabrication and possibly low cost. As a result, a lot of NLO polymers have been synthesized in recent years^[1,2,3,4,5]. 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 ($>3\text{dB/cm}$) and it is often the case that the losses and processability remain unreported^[2]. Other materials, however, do not possess a thermal stability satisfying commercial or military requirements^[6]. 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 $100\text{ }^\circ\text{C}$ ^[1,2,3,5] and one material (LD-3) turns out to have a long term thermal stability satisfying the military requirement of $125\text{ }^\circ\text{C}$ ^[4]. LD-3 is a thermally crosslinkable NLO polymer consisting of a poly (methyl methacrylate) (PMMA) backbone and an azobenzene-sulfone chromophore (figure 1(a)). It can be crosslinked by a diisocyanate crosslinker. Using Dianisidine diisocyanate (Pfaltz & Bauer, Inc.) as the crosslinker (figure 1(b)), a r_{33} value of 13pm/V at 633 nm was achieved and a long term stability at $125\text{ }^\circ\text{C}$ is proved through annealing a sample at this temperature for over 1250 hours^[7].

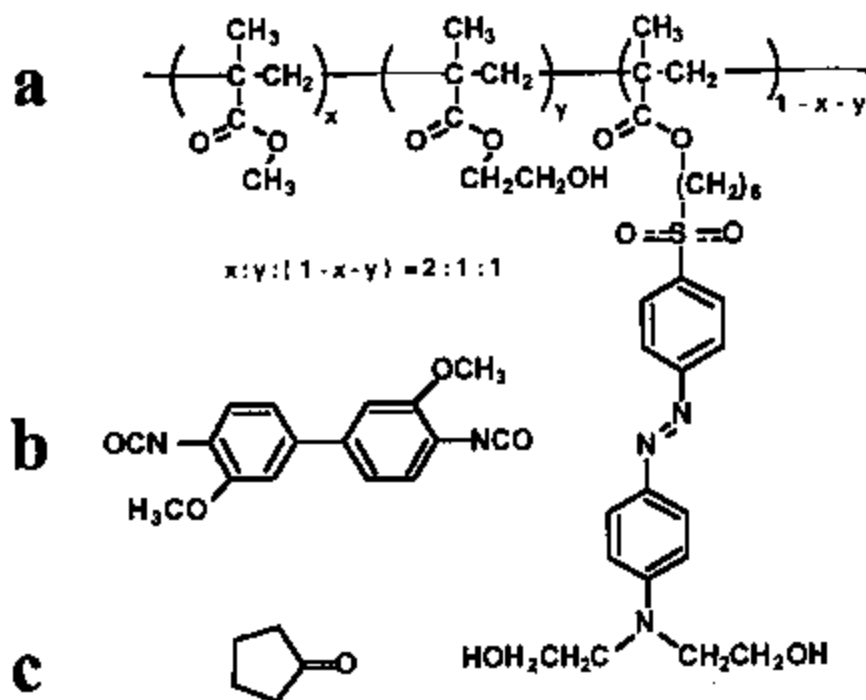


Figure 1. (a) the structure of the LD-3 polymer (b) the diisocyanate crosslinker (c) the cyclopentanone.

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^[3,5,8,9]. 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^[4,8,9]. The PURDR19 is most frequently used to fabricate waveguide devices^[8,9]. 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°C, 90 °C 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 using a crosslinker, 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 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.

For any NLO polymer, a compatible cladding material is also important for fabrication of low loss waveguides. Optically it should have a lower refractive index than the NLO polymer and low absorption at the working wavelength; electrically it should be more conductive than the NLO polymer at the poling temperature to ensure poling voltage can be effectively applied across the NLO polymer layer; chemically it should be resistant to the acid, the base and the organic solvents

used in the photolithographic process for patterning the waveguide channels and the modulation electrodes. A good choice to use are optical adhesives because the data of the refractive indices, solvent resistance and thermal stability etc. are available. However, most such adhesives are in liquid state and the films obtained by direct curing usually show wavy surfaces. Therefore, it is significant to understand the cause of the waviness and to find a solution

2. PREPARING LD-3 NONLINEAR OPTICAL POLYMER FILMS

2.1. Searching for a compatible solvent for LD-3 polymer

A solvent for a crosslinkable NLO polymer must be compatible with all the fabrication processes. It should have good solubility to both the NLO polymer and the crosslinker, neither react with the polymer nor the crosslinker, nor cause any other side effects. To avoid unwanted crosslinking before poling, it also should be able to be removed by vacuum drying. The lack of an appropriate solvent for LD-3 has failed the first attempt of fabricating a planar waveguide out of LD-3 polymer^[7]. 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 μm ^[7]. 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 μm waveguide and a single-mode optical fiber which typically have a mode diameter from 5 to 10 μm . It is important to understand the dominating interactions in the polymer in order to find a good solvent for it since 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 which 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 (figure 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 crosslinking 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 spincoating. 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 over night 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 not a quite uncommon 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 in order 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) 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 μm to 2.4 μm which are determined by an Alpha Step 200 surface profiler. The solvent cyclopentanone can be removed from the polymer film within 8 hours 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 non-spincoatable gel.

2.2. Anchoring the crosslinkers to the polymer chains to prevent the crosslinker 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 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

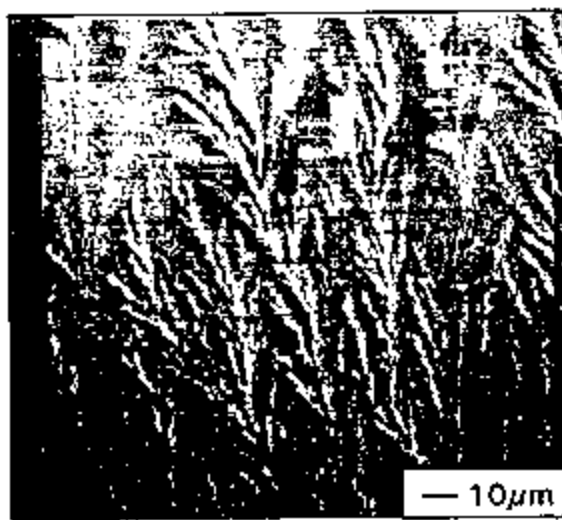


Figure 2. The tree-branch pattern of the crosslinker crystal grains formed on an LD-3 film due to fast removal of the solvent

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, metals, 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 which might have higher solid solubility in LD-3 polymer. Since 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^[7].

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 evaporation 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 (for example, <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 hours 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 16pm/V in corona poled films at the wavelength of 633nm which is at least as good as the previously reported one at the same wavelength (13pm/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. 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 non-spincoatable gel as 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 previous 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 non spin 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 smooth and featureless under microscope observation.

3. PREPARING NOA61 CLADDING LAYERS

The cladding material chosen for LD-3 polymer is NOA61 which is a one-component UV curable optical adhesive and a liquid at room temperature. We observed that directly curing the NOA61 films, regardless of light intensity, always resulted in an unwanted wavy surface although the surface was quite smooth before curing. The newly purchased material gives even worse results than the old out-of-date one. Similar problems are also observed in other optical adhesives which are in a liquid state.

The formation of wavy surfaces is mainly due to the volume change during curing. This is confirmed by the following experiment. A layer of NOA61 is directly coated on a 1" x 1" microscope glass slide. Then two opposite edges of this film are brought in contact with two pieces of microscope slides, hence a restriction is formed at the two edges. After curing, only ridges parallel to the two restricted edges are formed. This is different than the surfaces formed after curing with no restriction at the edges where the ridges go in every direction. The formation of ridges parallel to the two restricted edges indicates that the film expands in the film plane. The diffusion of the small liquid molecules to more reactive sites can also cause thickness fluctuation, but the above experiment implies that this is not the major source of the surface waviness. To reduce the volume change and the diffusion of the molecules in NOA61 during the curing, an UV precuring is performed before spin coating. The newly bought NOA61 is dissolved in dry cyclopentanone and vigorously stirred by a magnetic stirrer. A UV light with an intensity of 10mW/cm^2 is used. Controlling the precuring time is critical. If the precuring is too short and the resulting molecule size still small, a substantial volume change can still occur. On the other hand, if the precuring is too long, the solution will turn into a gel. This happened to us in the first few trials. Even though the solution was not turned into a gel, sometimes it could not go through a $0.2\ \mu\text{m}$ syringe filter. The curing time determined from the experiments ranges from 10 seconds to 5 minutes depending on the concentration of the solution. The resulting solutions can easily go through the syringe filters and good films are always obtainable.

4. WAVEGUIDE FABRICATION AND LOSS MEASUREMENT

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 μm optical adhesive NOA61 is coated as the lower cladding, then 1.2 μm LD-3 polymer, and finally 1 μm of NOA61 as the upper cladding. An infrared light with a wavelength of 1.32 μm is coupled into the waveguide from a prism located at the center at 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^[10]. Figure 3 shows the loss measurement result. Relatively low loss of 1.3dB/cm is achieved. Lower loss (less than 1dB) 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^[3,9], this loss is acceptable.

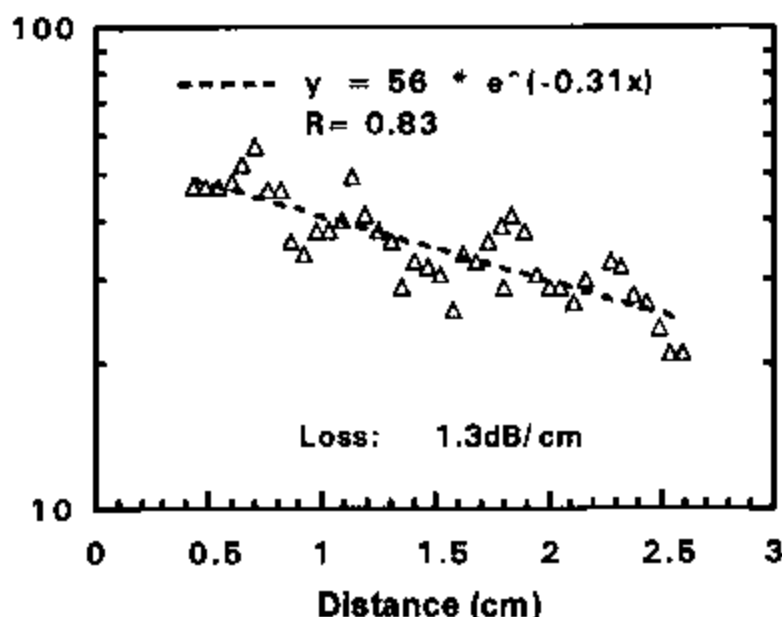


Figure 3. Optical loss measurement of a planar LD-3 polymer waveguide with NOA61 as the cladding material.

5. CONCLUSION

In conclusion, the crosslinker crystallization problem has been solved by balancing the polymer-crosslinker reaction rate and the solvent evaporation rate. The different reaction probabilities of the two ends of a crosslinker resulting from the reaction sequence are understood as the underlining mechanism. The wavy surface resulting from directly curing the NOA61 optical adhesive was solved by pre-curing. Good optical quality multilayer planar waveguides with relative low loss have been fabricated. Although this discussion is limited to LD-3 polymer and NOA61, the same principles can be applied to fabricate other crosslinked polymer films.

6. ACKNOWLEDGEMENT

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