Inverse-poling techniques in crosslinkable polymer electro-optic materials

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ABSTRACT

Domain-inverted electro-optic films have many applications in photonic devices such as high-speed electro-optic switches and quasi-phase-matched second-harmonic generators. For example, inverted domains allow a uniform electrode structure to be used in a reversed-$\Delta\beta$ directional coupler. Since corona poling is not applicable to create inversely poled structures in a crosslinkable polymer, direct-contact poling and liquid-contact poling are investigated. In unidirectional poling, liquid-contact poling allows poling electric fields higher than 250 V/μm to be applied, which is comparable to electric-field strengths in corona poling but much higher than those in direct-contact poling. For domain-inversion, the results also show that liquid-contact poling allows much higher poling electric fields to be applied than in direct-contact poling

Key words: liquid contact, poling, nonlinear polymer, electro-optic

1. HIGH-TEMPERATURE LIQUID-CONTACT POLING

1.1. Introduction

A typical electro-optical (EO) crystal such as LiNbO$_3$ has the required noncentrosymmetric structure for second-order nonlinear optics. However, the required noncentrosymmetric structure in a polymer is produced artificially. The commonly used method to align chromophores in polymeric materials into a noncentrosymmetric order is through the application of an external electric field. In order to prevent the relaxation of the chromophores after poling, polymers with high glass-transition temperatures (Tg) and polymers that are chemically crosslinkable have been used.[1,2,3,4] Polyimide is a typical high Tg material,[2,3] but the optical losses and processability remain unreported.[2] Much higher

stability can be achieved by crosslinking both ends of a nonlinear-optical (NLO) chromophore into a polymer network. In recent years, many reports using this method to develop highly stable NLO polymers have appeared.[4,5,6] For example, a thermally crosslinked NLO polymer with a poly(methyl methacrylate) backbone (commercial name: LD-3) has shown stable EO properties up to 125°C for over 1250 hours.[7]

To date, two common methods of electric-field poling are contact poling and corona poling. In contact poling, a strong electric field is applied to the cladded NLO polymer film by two parallel electrodes. These poling electrodes cover large areas and provide a path of high lateral conductivity. Such an arrangement frequently generates a localized destructive current at positions of pinhole defects. A single defect created during film processing may lead to a catastrophic short circuit and thus destruction of the device. As a result, contact poling in most cases can only be performed at a field strength much lower than that where dielectric breakdown of the NLO polymer film occurs.[8]

In corona poling, high electric field is produced by the charge deposited on the film surface through the corona discharge process. A poling electric field close to dielectric breakdown can be obtained.[9] The larger poling fields allowed by corona poling activate larger nonlinearities than those achieved using contact poling. However, surface damage is a major concern for corona poling.[8] An experimental technique using a protective layer to overcome the damage problem was reported to be effective in a side-chain polymer system.[8] For the more stable crosslinked systems, however, the surface damage problem becomes more severe due to the long poling time, such that even a protective layer is not effective. In poling crosslinkable NLO polymers, the poling electric field has to be on for the whole crosslinking process to prevent the relaxation of the chromophores back to a random orientation as before crosslinking. For most reported polymers, this process takes from half an hour to more than two hours.[4,5,6] Because of the much longer poling time, the protective layer is unable to prevent the surface damage from extending into the polymer film. We observe in our experiment that pinholes first develop in the protective layer during corona poling and then they gradually become deeper, so that they eventually penetrate into the NLO polymer film.

We report a new poling technique, which not only alleviates the surface-damage problem, but also allows a higher poling field to be applied. The experimental setup and the new poling technique are described in detail. Results for γ_{33} and other related parameters are then presented. Finally, comparisons are made between the new poling technique and the previous ones and conclusions are given.
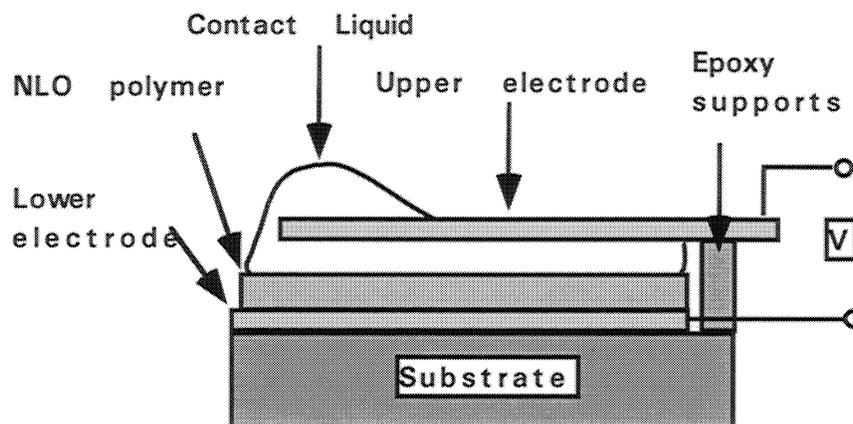
1.2. Liquid-contact poling techniques

Fig. 1. Liquid contact poling setup.

The poling setup is shown in Fig. 1. The crosslinkable NLO polymer LD-3 used in the experiment is supplied by AdTech Systems Research, Inc. Its synthesis and NLO properties can be found in previous publications.[4,7] Figure 2 shows the molecular structures of the LD-3 polymer, the crosslinker and the solvent, which were used in our experiments. Dissolved together are 100 mg of the polymer and 60 mg of the crosslinker in 1 ml of cyclopentanone. The solution is put through a 0.2 μm syringe filter and spin coated on indium-tin-oxide (ITO) films. The films are vacuum dried at room temperature. The film thickness is measured by an Alpha-Step 200 surface profiler to be 1.2 μm. The upper electrode is made of chromium which is evaporated on a glass microscope slide and patterned into round areas 0.5 cm^2 by wet etching. A gap of 10 μm between the upper electrode and the film is maintained by epoxy spacers (see Fig. 1). Special care must be taken to avoid any dust getting into the gap, which would short circuit the poling electrodes of the cell. The contact liquid, hexatriacontane, is carefully selected to satisfy the requirements imposed by the poling process. It is a solid at room temperature and melts at 75°C. When it melts, its resistivity becomes much lower and it is sucked into the gap by capillary action with no bubble formation. As a result, an electrically conductive path between the upper electrode and the polymer film is formed through the liquid layer. Most of the applied voltage to the electrodes will drop across the polymer film as long as the resistivity of the contact-liquid layer is much lower than that of the LD-3 polymer film.
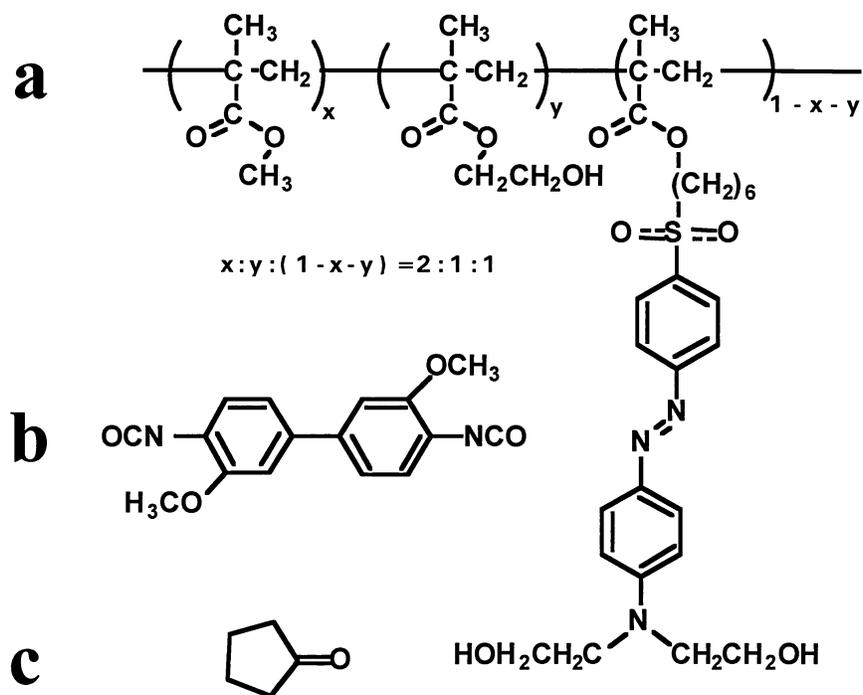
Fig. 2. Chemical structures of the LD-3 polymer solution system. (a) the LD-3 polymer. (b) the diisocyanate crosslinker. (c) the cyclopentanone solvent.
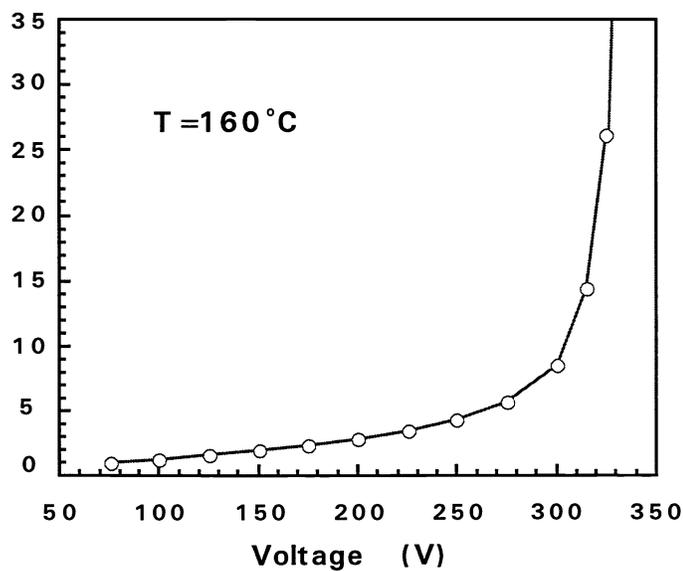

Fig. 3. Breakdown-voltage measurement of the contact liquid.

A high breakdown voltage of the contact liquid is necessary to insure that a high poling field can be applied. Fig. 3 shows the measured I-V curve at 160°C for the contact liquid. The cell used in this measurement is similar to that shown in Fig. 1, but without the polymer film. Each discrete current measurement is taken after applying a given voltage for 10 seconds. Breakdown occurs at 325 V. One can see that 300 volts can be safely applied to the 10 μm cell. If this high voltage can be dropped across the 1.2 μm NLO film, then the applied field should be 250 V/μm, which is comparable to the reported value of the corona-poling field strength.[3,8] If there is any local breakdown in the polymer film, the contact liquid can still prevent a short circuit. Although the poling current might increase, it would not be significant as long as any local breakdown is limited to very small areas. When the lower electrode is totally covered with the polymer film and the sharp edges of the upper electrode are smoothed by etching, then we observe breakdown to occur typically at only a few points.

200 | 10
 1 2   3
160 | 8
120 | 6
 80 | 4
 40 | 2
  0 | 0
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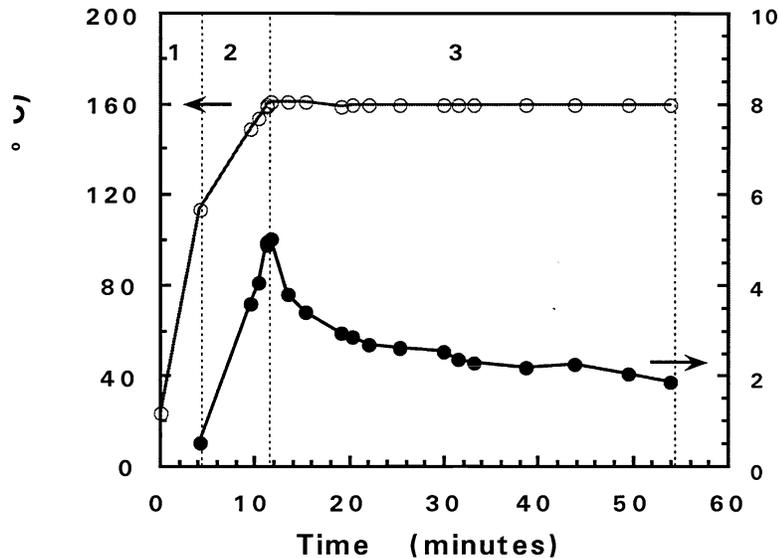   Time   (minutes)

Fig. 4. Poling process: 1. Preheating and melting of the contact liquid. 2. Poling. 3. Curing.

The experiment is carried out in an ambient environment. The heating stage consisting of a 4 inch aluminum round plate and heating wires, which allows for a rapid temperature increase. The temperature is controlled by a programmable Omega CN8500 temperature controller. Fig. 4. shows the poling process, which can be divided into three stages. In the first stage, the sample is heated to above the melting point of the contact material, which has been applied to the opening of the gap of the cell before heating. The second stage consists of electrical poling while continuously increasing the temperature of the sample. After the liquid contact is formed, a poling voltage of 300 V is applied at 114°C. During this period, most of the chromophores have not been crosslinked and are still able to rotate such that their dipoles align with the applied field. The current associated with the dipole rotation

is small, so the increase of the current is mainly due to the change in the conductivity of the materials with temperature. In the third stage, the temperature is maintained at 160°C while continuing to apply the poling voltage. At first, the current decreases quickly, but then slows. This trend is commonly observed in the poling process of crosslinkable NLO polymers. We also observe such a phenomenon in corona-poling experiments using the same material. The decrease of the poling current is due to the crosslinking process. The more the polymer is crosslinked, the higher the resistivity. In our experiment, this process is complicated by the leakage current through the epoxy spacers. After fully curing the LD-3 polymer, the heater is turned off and the sample is cooled down to 100°C within 10 minutes. The poling voltage is then turned off and the upper electrode is separated while the contact material is still in a liquid state. The fully crosslinked LD-3 polymer has a very strong resistance to solvents and abrasives. The contact material can be removed by an appropriate solvent such as Xylene. After the removal of the contact material, the polymer surface is shiny. Observed under a microscope, the films have fewer pinholes than those prepared by corona poling. A chromium electrode is deposited on the polymer afterwards by electron-beam evaporation and the γ_{33} value is measured using a reflection technique.[10,11] An electro-optic coefficient γ_{33} as high as 18 pm/V at the wavelength of 632.8 nm is obtained.

1.3. Comparison with previous poling methods

The advantages of liquid-contact poling are evident. In corona poling, a variety of chemically-reactive and physically-energetic species, such as particles ionized by the poling voltage, are present during the discharge. An exposed polymer surface may be damaged owing to polymer chain addition, chain scission, and oxidative chain degradation.[8] There is no such discharge process in the liquid-contact poling, which leads to a smoother polymer film. The previously reported γ_{33} of LD-3 is 13 pm/V at the wavelength 632.8 nm with poling conditions of 5 KV, 150°C and a 2 cm tip-to-film separation.[4,7] Under the same poling conditions, we obtain similar values of γ_{33}. The γ_{33} value is proportional to the poling electric field. We obtained γ_{33}=16 pm/V in corona poling by using the optimized poling conditions of 5 KV, 190°C and a 1.5 cm tip-to-film separation. Although improvement of γ_{33} by corona poling was obtained due to an increased poling field from the decreased tip-to-film separation, the level of surface damage actually increased. The shorter poling times made possible by a higher poling temperature, however, did lead to some improvement on the level of surface damage, but not much. The previously reported γ_{33} value[7] is deduced from second-harmonic generation, which is different from the method used here. Thus a strict comparison cannot be made, but we can still conclude that γ_{33} values higher than the previously reported value have been achieved by liquid-contact poling. Our conclusion is based on the above discussion and the consideration that the experimental error is less than 1 pm/V.

The high value of γ_{33} obtained in liquid-contact poling indicates that an equal or higher poling field has been achieved in the EO polymer than in corona poling.

This method also outperforms direct-contact poling. In direct-contact poling, a high voltage is applied across NLO films, which should be classified as insulators according to their conductivity. The conduction mechanism is no longer ohmic, but changes to being space charge limited (SCL).[12] SCL theory gives the conductivity to be $J \propto V^2 d^{-3}$, where J is the current density and d is the distance between the electrodes. The injection of charge carriers from the electrodes results in a strong electric field near the surface as predicted by theory and confirmed by experiments.[12,13] Such a nonlinear electric field distribution in the contact-poling process of NLO polymers has destructive effects because the rotation of the dipoles under the strong local electric field near the top electrodes may cause much deformation of the polymer and even of the metal electrode if it is thin. We observe in the experiments that the metal surface becomes wavy as we increase the applied voltage. The nonlinear field also makes the surface reach breakdown sooner.

Liquid contacts have been used in poling electrets,[14] but the poling is performed at room temperature and the polymers used are fully-cured ones. In this case, a lot of liquids including water can be used. For crosslinkable polymers, poling must be performed at elevated temperatures and the polymers are not fully cured, so the requirements for the contact liquid are much more stringent. The liquid should be thermally stable, non-volatile, and not dissolve or react with the polymer or the crosslinker at the poling temperature. Room temperature liquids usually are too volatile at the poling temperature (160°C). It is observed that some solid materials can be sucked into the micron size gap between the two electrodes by capillary action when they melt, because the conductivity of the materials changes dramatically at the melting point.[15] This same phenomenon has been observed in hexatriacontane. The decrease of the resistivity can be attributed to two reasons. First, the mobility increase of hexatriacontane allows easier charge transfer from one site to another. Second, impurities previously confined by the solid hexatriacontane molecules can move around when the host material liquefies. If some of the impurities have lower ionization potentials than that of the host molecules, they are more readily ionized and therefore assist the transfer of charges from one electrode to the other. The hexatriacontane used in the experiment is not ultra-pure, therefore the second conduction mechanism should be the dominant one.

2. DOMAIN-INVERTED POLING

In a crystal EO material such as LiNbO$_3$, a domain-inverted structure can be produced by rotating the crystal domains. However, this is impossible in crosslinked polymer because the

crosslinking process is irreversible. Once the NLO chromophores are crosslinked, rotating them is difficult, if not impossible. The only way to realize a domain-inverted structure is to pole a polymer film simultaneously in opposite directions. In corona poling, the electric field can only point to one direction, so corona poling is not applicable. Liquid contact poling has been applied to produce domain-inverted structures in inorganic crystals. Usually a photoresist is used to pattern the required structure and a liquid electrolyte is used to make the contact. But this scheme is not compatible with the NLO polymer poling process as described above, because neither the electrolyte nor the photoresist can work at typical poling temperatures.

The high-temperature liquid-contact poling techniques are applied to domain-inverted poling. The poling-cell structure is shown in Fig. 5. The gaps between the two electrodes change from 1 mm to 2 mm, which are made by acid etching. The polymer, planar waveguide consists of three layers: a 3 μm NOA-61 upper cladding, a 1.2 μm LD-3 polymer and a 3 μm NOA-61 bottom cladding. The liquid-layer thickness can be controlled within the range of 2 to 10 μm. The poling voltage is applied across the top two electrodes. This voltage is equally divided by the two domains. The gap between the two top electrodes is much larger than the distance between the top electrodes and the bottom electrode, so the fields in the cell point in the vertical directions as indicated in the figure, except for small areas near the edges. An electric field of 550 V has been successfully applied in poling a cell at 165°C for 55 minutes. Initially, up to 600 V was applied to this cell at which point breakdown occurred. When the poling voltage was applied again, no short circuit was found, but we reduced the voltage to 550 V to avoid breakdown again. Thus the self-curing property of the contact liquid plays a role to save the cell from being permanently destroyed by an occurrence of breakdown. To compare with direct contact poling, we have made several cells similar to that in Fig. 5. The contact liquid is replaced by the NOA-61 optical adhesive, which is a liquid and can be cured by UV light after it fills into a cell. For most cells, we apply 460 V. At this poling voltage, some cells breakdown at the beginning of the poling process, some in the middle of the poling, some near the end.
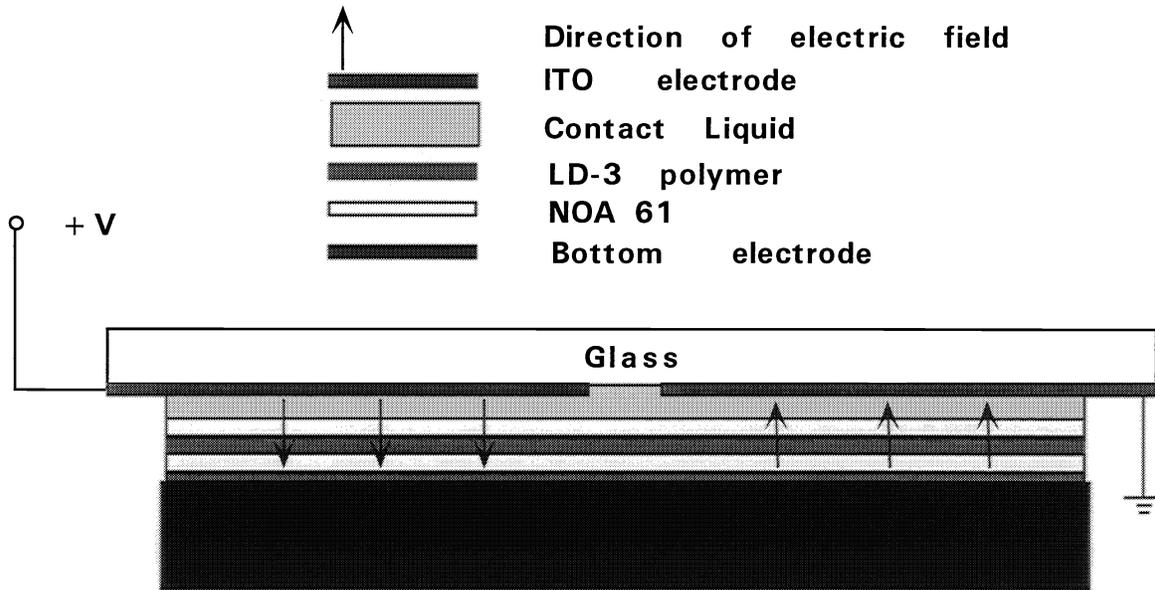
Fig. 5. Domain-inverted poling cell structure.

The domain inversion is confirmed by a measurement of the sign of the EO coefficient using an extension of the reflection technique given in Refs. 10 and 11. A 180° phase difference is observed in the modulation of the optical signal reflected by the two domains, where a lock-in amplifier is used to determine the phase difference.

3. CONCLUSIONS

We successfully used liquid-contact poling to make inverted electro-optic domains in polymer planar waveguides. We also investigated direct-contact poling to create inverted domains. Liquid-contact poling allows a higher poling voltage to be applied owing to the self-curing nature of the contact liquid; hence, it is more advantageous than direct-contact poling for achieving high EO coefficients. The key aspect of liquid-contact poling is that electric fields comparable to those in corona poling, but much higher than those in direct-contact poling, can be used. For single domains, comparable EO coefficients are achieved in liquid-contact poling as in corona poling. Thus liquid-contact poling offers the possibility to achieve EO coefficients in each domain of our domain-inverted structure that are similar in value to that obtained in a single domain by corona poling.

4. ACKNOWLEDGMENTS

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