Enhanced electro-optic coefficient of nonlinear optical polymer using liquid contact poling

Huajun Tang, John M. Taboada, Guohua Cao, Liqiang Li, and Ray T. Chen[a)]

Microelectronics Research Center, The University of Texas at Austin, Austin, Texas 78712

The value of electro-optic coefficient r_{33} of an electro-optic (EO) polymer film depends on the polarization density achieved after the electric poling process. In this letter, we report a high temperature liquid contact poling method which provides a poling field as high as 250 V/μm in LD-3 EO polymer film with less surface damages. The r_{33} value was measured to be 18 pm/V at 633 nm which is 40°/V higher than the previous reported datum. Such a high poling field and therefore larger r_{33} value are not achievable through either contact poling or corona poling. © *1997 American Institute of Physics.* [S0003-6951(97)00605-0]

Second order nonlinear optics (NLO) requires a noncentrosymmetric structure. 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 chemically crosslinkable systems have been investigated.[1–4] Polyimide is typically of a class of high Tg materials,[2,3] but the optical losses and processability remain unreported.[2] For the other class of materials, much higher stability can be achieved by crosslinking both of the ends of an NLO chromophore into the polymer networks. In recent years, many reports using this method to develop highly stable NLO polymers have appeared.[4–6] 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 h.[7]

To date, two common methods of electric field poling are the contact poling and the corona poling. In the 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 location with pinhole defects. A single defect created during the film processing may introduce a catastrophic short circuit, destroying the devices. As a result, contact poling in most cases can only be performed at a field much lower than the dielectric breakdown permitted by the NLO polymer film.[8]

In the 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 the dielectric breakdown can be obtained.[9] Larger poling fields activate larger nonlinearities compared with contact poling. However, surface damage is a major concern for corona poling.[8] An experimental technique using a protective layer to overcome the damage problems was reported to be effective in a sidechain polymer system.[8] For the more stable crosslinked systems, however, the surface damage problem becomes more severe due to the long poling time, 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 the random orientation before being crosslinked. For most reported polymers, this process takes from half an hour to more than two hours.[4–6] 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 are first developed in the protective layer during the corona poling. They gradually become deeper and deeper and eventually penetrate into the NLO polymer film.

In this letter, we report for the first time a new poling technique, that not only alleviates the surface damage problems, but also allows a higher poling field to be applied. The poling setup is shown in Fig. 1. The crosslinkable NLO polymer LD-3 used in the experiment is supplied by AdTech System Corporation. Its synthesis and NLO properties can be found in the references.[4,7] Figure 2 shows the molecular structures of LD-3 polymer, the crosslinker, and the solvent which was discovered by our group. 100 mg of the polymer and 60 mg of the crosslinker is dissolved in 1 ml cyclopentanone and then filtered by a 0.2 μm syringe filter. The solution is then spin coated on indium tin oxide (ITO) films and dried in a house vacuum. The film thickness is measured by an Alpha-step 200 surface profiler and films of 1.2 μm are obtained. The upper electrode is made of chromium which is evaporated on glass micro slides and patterned into round areas of 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 is taken to avoid any dust getting into the gap to short the cell. The contact liquid, hexatriacontane, is carefully selected to satisfy the requirements imposed by the poling process. It is in solid state at
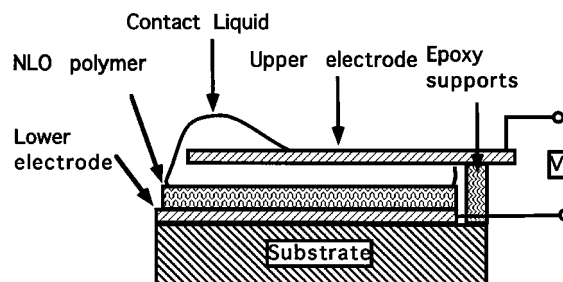

FIG. 1. Liquid contact poling setup.

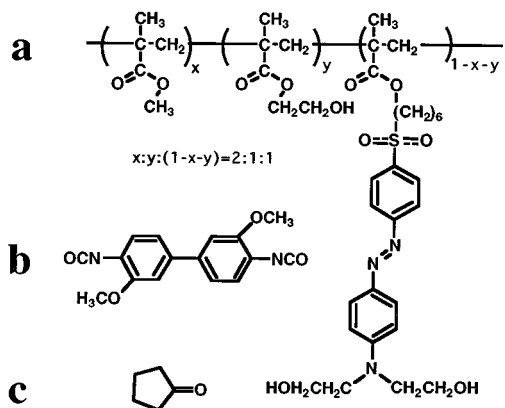[a)]Electronic mail: raychen@uts.cc.utexas.edu

FIG. 2. Chemical structures of LD-3 polymer solution system. (a) the LD-3 polymer, (b) the diisocyanate crosslinker, and (c) the cyclopentanone solvent.

FIG. 4. Poling process: (1) preheating and melting the contact liquid, (2) poling, and (3) curing.

room temperature and melts at 75 °C. When it melts, its resistivity becomes much lower and it is automatically sucked into the gap by capillary force with no bubble formation. As a result, an electrical 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.

A high breakdown voltage of the contact liquid is necessary to insure that a high poling field can be applied. Figure 3 shows the measured I–V curve at 160 °C of the contact liquid. The cell used in this measurement is similar to that shown in Fig. 1 but without the polymer film. The data of the currents are taken after applying the voltages for 10 s. The breakdown occurs at 325 V. We can see that 300 V 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 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 the local breakdown is limited to very small areas. If the lower electrode is totally covered with the polymer films and the sharp edges of the upper electrode have been smoothened by etching, most of
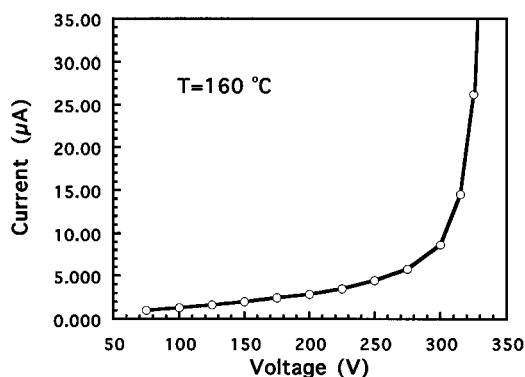

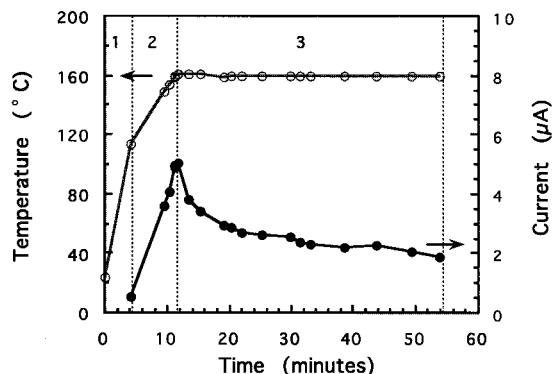FIG. 3. Breakdown voltage measurement of the contact liquid.

the time the breakdown only occurs at a few defective points as observed.

The experiment is carried out in an ambient environment. The home made heating stage consisting of a 4 in. aluminum round plate and heating wires allows rapid temperature ramp. The temperature is controlled by a programmable Omega CN8500 temperature controller. Figure 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 heating the sample up. 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 able to rotate to align their dipoles 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 of conductivity of the materials with temperature. In the third stage, the temperature is maintained at 160 °C while keeping the poling voltage on. At first, the current decreases quickly, then the decrease slows down. This trend is commonly observed in the poling process of crosslinkable NLO polymer. We also observe such a phenomenon in the 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 min. The poling voltage is then turned off and the upper electrode is separated while the contact material is still in liquid state. The fully crosslinked LD-3 polymer has very strong solvent resistance and abrasive resistance. The contact material can be removed by an appropriate solvent such as xylene. After the removal of the contact material, the polymer surface looked shiny. Observed under microscope, the films have fewer pinholes than those prepared by the corona poling. A chromium electrode is deposited on the polymer afterwards by electron beam evaporation and the r_{33} value is measured using reflection technique.[10,11] r_{33} as high as 18 pm/V at the wavelength of 633 nm is obtained.

The advantages of the liquid contact poling are evident. In the corona poling, a variety of chemically reactive and physically energetic species, such as ionized particles energized by the poling voltage, are present during the discharge. An exposed polymer surface may be damaged due to the polymer chain addition, chain scission, and oxidative chain degradation.[8] There is no such discharge process in the liquid contact poling resulting in a much smoother polymer film. The previously reported r_{33} of LD-3 is 13 pm/V at the wavelength of 633 nm with poling conditions of 5 kV, 150 °C and a 2 cm tip-film separation.[4,7] Under the same poling conditions, we obtain r_{33} values equal to or lower than that value. r_{33} value is proportional to the poling electric field. We obtained $r_{33} = 16$ pm/V in corona poling by optimizing the poling conditions using 5 kV, 190 °C, and 1.5 cm separation from the tip to the film surface. Although improvement on corona poling data of r_{33} was obtained due to an increased poling field resulting from the decrease of the tip to film separation, not much improvement on surface damage has been achieved even shorter poling times were made possible by higher poling temperatures. The high value of r_{33} obtained in liquid contact poling indicates that an equal or higher poling field has been achieved in the EO polymer when compared with corona poling.

This method also out performs the direct contact poling. In the direct contact poling, a high electric voltage is applied across the NLO films which should be classified as insulators according to the conductivity. The conducting mechanism is no longer ohmic, but changes to space charge limited (SCL) case.[12] The SCL theory gives $J \propto V^2/d^3$, where J is the current density and d is the distance between the electrodes. The injection of charge carriers from the electrodes results in strong electric field near the surface as predicted by the theory and confirmed by experiments.[12,13] Such a nonlinear electric field distribution in the contact poling process of NLO polymer has destructive effects because the rotation of the dipoles under the strong local electric field near the top electrodes may cause much deformation, even deforming 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 the breakdown sooner.

Liquid contact has 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 log of liquids including H_2O can be the choice. 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. It should be thermally stable, nonvolatile, and not dissolve or react to 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 solids can fill into the micron size gap between two electrodes by capillary force when they are melted and the conductivity changes dramatically at the melting points.[15] The 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 the other. Second, guest molecules, previously confined by the solid hexatriacontane molecules, can move around when the host material changes into a liquid. Some of these molecules have lower ionization energies than that of the host molecules, they are easier to be ionized and therefore assist the transfer of charges from one electrode to the other.

In conclusion, we have demonstrated the high temperature liquid contact poling for the first time. It offers an attractive method to pole NLO polymers other than direct contact poling and corona poling. It results in much less surface damage. Poling field of 250 V/μm and r_{33} value of 18 pm/V at 633 nm are experimentally achieved. This method is especially useful for crosslinkable polymers which require long poling times.

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