

A guest-host-system polymer with high electro-optic coefficients

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ABSTRACT

An electro-optic polymer with photolime gel and chlorophenol red dye is prepared using a newly developed mixed solvent of water and ethylene-glycol. This new solvent not only prevents the EO chromophore from re-crystallization, but also help the guest and host materials to mix well in the molecular level. As a result, high EO coefficient of 40 pm/v has been obtained with improved stability of EO effect. A new pulsed poling technique is developed, which increase the poling efficiency up to 35% compared with the traditional parallel-plate poling method.

Key words: Gelatin, polymer, poling, electro-optic coefficient

1. INTRODUCTION

Electro-optic (EO) polymers are promising materials for optical integrate circuits because polymers have some unique merits over inorganic alternatives like lithium niobate, such as large EO coefficients, flexible fabrication process, and fast material response times. High EO coefficient γ_{33} of up to many hundreds of picometer per volt is expectable with EO polymers.^[1] Thin films can be easily spin-coated with polymers, and optical component, such as waveguides, switches, and modulators, can be efficiently fabricated using the standard photo-lithography technique. Fast material response times of picoseconds can render super-high-speed EO switch and modulators. Moreover, tailoring of nonlinear optical properties and even a whole material performance is possible via chemical modifications. On the other hand, there are also still some problems associated with polymeric EO devices. For an example, EO coefficients of polymers are not stable, typically relax over time. The doped EO chromophores usually can easily get clustered or crystallized out from the host materials during film preparation. This crystallization phenomena prevent one from obtaining high loading concentration and the predicted high EO coefficients. The upper limit of this concentration is usually 10%-20% depending on different material systems.^[2] The conventional electric poling methods, include the parallel plate direct contact poling and the corona poling, are limited by the dielectric breakdown, and can only achieve the poling efficiency of 30%. Namely, the dipoles within the EO polymers can only be aligned to 30% of the fully aligned ideal situation.^[3] This low poling efficiency for polymers also prevents us from achieving the predicted high EO coefficients.

The EO polymer being reported here is synthesized with photolime gel doped with chlorophenol red dye. Polymer films are prepared with a mixed solvent of water and ethylene-glycol. The application of the organic solvent prevents the EO chromophores from crystallization, and hence increases the EO coefficient remarkably. Using this mixed solvent, films with relative high loading concentrations can be introduced without crystallization. After high-temperature poling, films prepared with this mixed solvent are very robust and less sensitive to moisture than previous films prepared using pure water. The high EO coefficients and slow relaxation speed confirm that the application of the organic solvent not only prevents the EO chromophores from crystallization, and hence increases the EO coefficient, but also help the EO chromophore molecules to mix well with the host material molecules, which enhanced the stability of the EO effect. A new poling technique, pulsed poling, is also investigated. By using a pulsed electrical field instead of a constant electrical field as in the conventional poling strategies, a relative higher poling electrical field, and thus an improved poling efficiency can be achieved.

2. PREPARATION OF POLYMER FILMS

Water has been employed as the conventional solvent for preparing photolime gel polymers in the past, because photolime gel, as the host material, is soluble in water. While most EO chromophores such as chlorophenol red are rarely soluble in water (30 mg/ml). As a result, it is hard to make EO polymers with high guest/host concentration which is the essential factor to achieve high EO coefficients. The different solubility leads to a problem that chlorophenol red is easy to get crystallized out of the host material during the film-spin-coating procedures, because the guest material clusters before the gelling of the host material. In our experiments, it has been found that this effect may take place with a ratio of chlorophenol red to gelatin of less than 10% (by weight), as shown in Fig. 1 (a). Such a low loading concentration prevent us from achieving large EO coefficients. Even with a low loading concentration, though the film's surface looks good, the EO effect might still be influenced by the micro-clustering phenomena inside the films though the clustered particles are too small to be seen. On the other hand, films prepared with pure water are sensitive to environmental moisture, and that greatly affects the EO properties of the films.

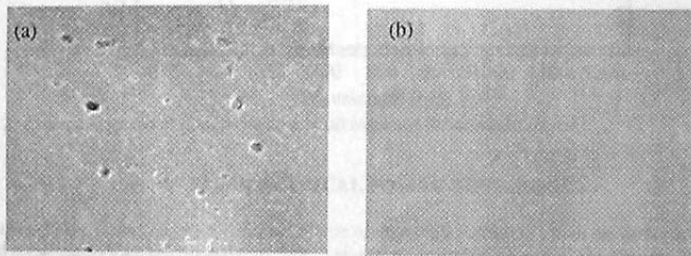


Fig. 1. Microscopic pictures of films prepared with (a) pure water as the solvent (chlorophenol/photolime gel = 10%), and (b) the new mixed solvent (chlorophenol/photolime gel = 30%).

Chlorophenol red is rarely soluble in water, but it is well soluble in most organic solvents. On the contrary, gelatin is soluble in water but not organic solvents. It is reasonable to use a mixture of water and an organic material as the solvent to make similar solubility for both chlorophenol red and photolime gel, so as to prevent the crystallization phenomena. Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) is selected in our experiments as the organic solvent because it mixes very well with water, and has a high evaporation temperature of 197°C , which is much higher than that of water. During the spin-coating procedure, the water solvent will evaporate before the evaporation of the organic solvent, therefore the photolime gel will get gelled first, and then the photolime gel molecules will hold the adjacent chromophore molecules before they getting clustered, and thus the crystallization phenomena is prevented. The detailed film preparation procedure is as following. Firstly dilute photolime gel into water and chlorophenol red into ethylene glycol respectively in a hot-bath box of 85°C . After solved completely, mix this two solutions quickly and keep stirring it in the hot-bath box for about four hours. Then spin coat films under the same temperature. The thickness of the films are controlled by the concentration of the solutions and the spin-coating speed as well as the coating temperature. Films are then dried in a vacuum oven for evaporating the remaining solvents to avoid problems like blistering or air-voids. Based on this technique, high quality gelatin films without microscopic clustering can be prepared with loading concentration of chlorophenol red to gelatin up to 35%. Figure 1 (b) shows the microscopic picture of a film prepared by this procedure. Figure 2 shows the absorption spectra of films prepared with the mixed solvent and with pure water. Compared with the films prepared with pure water, films prepared with the mixed solvent shows smaller optical loss with an increased dynamic range of wavelength in the visible region. This is due to the application of the organic solvent leads to the fact that the chromophore molecules are thoroughly bonded to the host polymer backbone, thus a very high film homogeneity is achieved and the absence of phase separation lessens the scattering losses caused by the inhomogeneous distribution of the chromophores in the host polymer matrix.

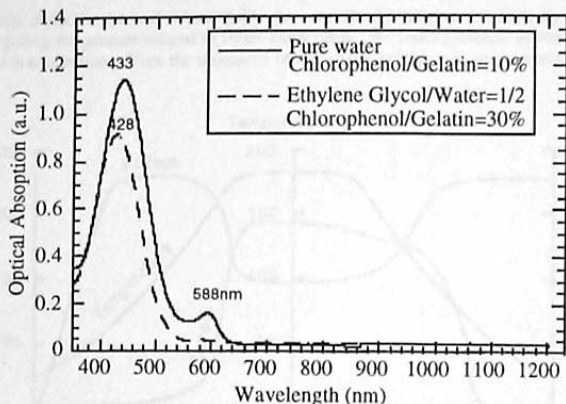


Fig. 2. Absorption spectra of films prepared with (a) water and (b) the mixed solvent.

3. PULSED ELECTRICAL POLING TECHNIQUE

Electric poling is another important factor that affects polymers' EO coefficient. Both the traditional contact poling and the pulsed poling methods are investigated here. Fig. 3 shows the schematic diagram of the computer-controlled poling stage. EO polymer is spin-coated on a glass substrate which has a coated indium tin oxide (ITO) film serving as the bottom electrode. The upper electrode is a thin film of aluminum deposited on the surface of the polymer film using electron-beam evaporator. Both the poling voltage applied onto the polymer film and the poling temperature of the stage throughout the poling process can be programmed before hand. The leaking current across the polymer film, which reveals the poling progress, is also monitored in time during the poling process. Through this computer-controlled poling setup, we can apply the highest possible voltage across the polymer film under its dielectric break-down point. This voltage is automatically adapted with the variation of the poling temperature.

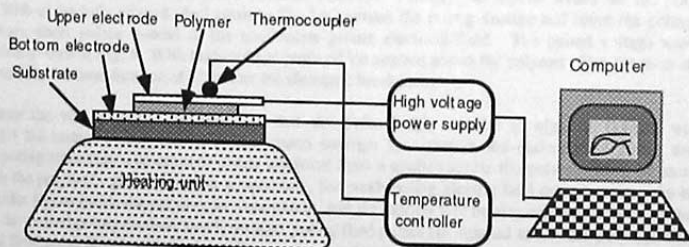


Fig. 3. Schematic diagram of the computer-controlled poling setup.

Fig. 4 shows the variation of the poling parameters in the parallel-plate direct contact poling process. A gradually increased high voltage is applied across the sample at the very beginning of the poling process. Leaking current is almost zero at this time because the dry gelatin film is a good insulator at room temperature. When the poling temperature climbs to the glass-transition temperature, 180°C for this sample, the leaking current increases rapidly. To avoid the dielectric breakdown brought on by overheating, the poling voltage is decreased automatically according to the leaking current. With the progress of the poling process, more and more chlorophenol-red molecules are aligned and crosslinked such that their

dipole moments are lines along the external electric field. As a result, the polymer conductivity decreases as the poling progresses. With the poling temperature reduced to room temperature, the leaking current decreases rapidly to zero right below the glass-transition temperature. Even the increment of the poling voltage can not compensate the leaking current a lot.

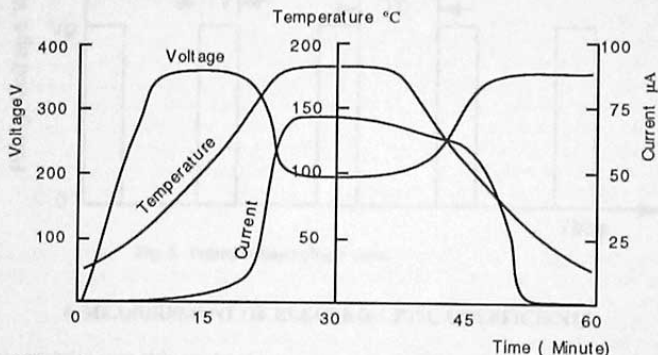


Fig. 4. Poling voltage, temperature and leaking current varying with poling time in a typical poling process.

The linear EO coefficients of an organic polymer are proportional to the poling voltage that applied across the polymer film during the poling process, because the higher the poling voltage applied across the polymer film, the larger degree the EO dipoles orientation being aligned to, the more efficient the polymer is poled.^[4] The highest poling voltage in the direct contact poling is limited by the current injection caused dielectric breakdown, which is about 200-300 v/ μm with respect to different polymers.^[2] This electrical field value is usually much lower than the dielectric breakdown value permitted by the EO polymer films. Corona poling can apply a relatively higher poling voltage across polymer films by making use of the corona discharge or a partial breakdown of air at atmospheric pressure. By exposing a polymer film to a corona discharge, poling electric fields very close to the dielectric breakdown can be obtained. Through these two conventional poling methods, only 30% of the poling efficiency can be achieved. Namely, the dipoles within the EO polymers can only be aligned to 30% of the fully aligned ideal situation.^[4] To increase the poling voltage and hence the poling efficiency, we use high voltage short pulses instead of the continuous poling electrical field. The pulsed voltage wave used here is rectangular wave shown in Fig. 5. With high-voltage pulse of V_p applied across the polymer film for time duration T_v , and then released to zero for time duration of T_0 before the dielectric breakdown.

Because the voltage pulses are short, so that the pulse height can be as high as 1kV/ μm without dielectric breakdown. So the instant poling electric field is much stronger than that in the conventional poling methods. In the conventional poling strategies, a continuous poling electrical field is applied across the polymer film, by increase the poling temperature to the polymer's glass-transition temperature, the weak poling electric field may overcome the resistance of the mutual molecular forces inside the polymer to some extent, and the dipoles will be aligned continuously to the corresponding extent. With the pulsed poling method, much stronger poling field pulses are applied across the polymer film continuously, each electrical field pulse is strong enough to disrupts the London forces to achieve a better alignment of the dipoles,^[1] the alignment effects of every electrical field pulse are accumulated to achieve the final macro alignment of the dipoles.

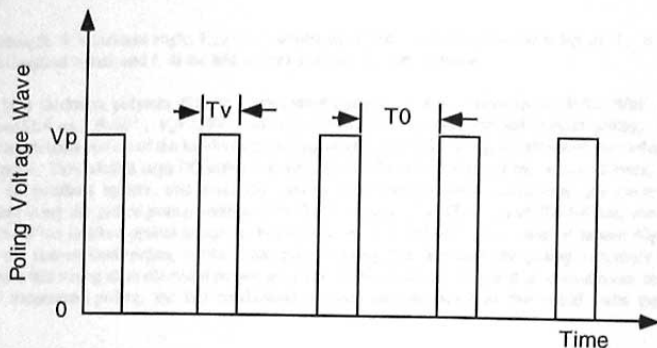


Fig. 5. Pulsed poling voltage wave.

4. MEASUREMENT OF ELECTRO-OPTIC COEFFICIENTS

The phase-retardation method is employed here to measure the EO coefficients.¹⁵ Fig. 6 shows the schematic diagram of the measurement apparatus. A sinusoidal electrical signal is used to modulate the phase difference of the p-wave and s-wave of the light that pass through the polymer film. A lock-in amplifier is used to detect the modulated portion of the light signal, or the interference intensity of the p-wave and s-wave. The EO coefficient r_{33} is then determined with the following equation:¹⁵

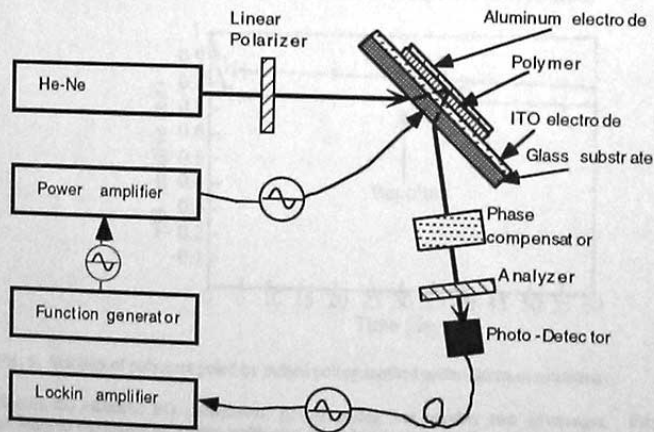


Fig. 5. Electro-optic coefficient measurement setup.

$$r_{33} = \frac{3\lambda_m}{4\pi V_m I_e n^2} \frac{(n^2 - \sin^2 \theta)^{3/2}}{(n^2 - 2\sin^2 \theta) \sin^2 \theta} \quad (1)$$

where λ is wavelength, θ is incident angle, V_m is the amplitude of the electrical modulation signal, I_m is the amplitude of the modulated AC optical signal, and I_c is the half intensity of the DC optical signal.

For a $5\mu\text{m}$ thickness polymer film of chromophore/gelatin loading concentration 35%, With the experimental conditions of $\lambda=632.8\text{ nm}$, $\theta=60^\circ$, $V_m=150\text{V}$, and $I_c=18\text{mV}$, after the conventional contact poling, we measured the amplitude of the modulated portion of the incident optical signal as $I_m=0.4\text{mV}$. So γ_{33} is calculated according to equation (1) to be around 30 pm/v . This relative large EO effect is mainly due to the involvement of the organic solvent, which improves the mixture of the guest/host system, and raises the loading concentration while eliminating the microscopic clustering phenomena. When using the pulsed poling method with $V_p=1\text{ kv}/\mu\text{m}$, $T_v=100\text{ ms}$, and $T_0=400\text{ ms}$, the amplitude of the modulated portion of the incident optical signal is measured to be $I_m=0.55\text{ mV}$. γ_{33} value of around 40pm/v is obtained. Compared with the conventional poling method, the pulsed poling has increased the poling efficiency by 35%. It is interesting that with this strong short electrical pulses, polymer films even can be poled at around room temperature. After one hour's room temperature poling, the EO coefficients are measured the same as that poled under the glass transition temperature.

Thermal stability of the EO response has been a critical issue in the practical applications of poled polymers. Polymer films prepared with the mixed solvent become much harder physically after poling. They are no longer sensitive to the environmental moisture. The glass transition temperature is above 180°C , which is well above that of other conventional EO polymers. The stability of the EO effect of polymers poled under these two conditions are slightly different. As shown in Fig. 6, films poled under glass transition temperature shows an initial fast decay to 15% within the first 5 days, followed by a slow decay, that is quite similar to other guest-host-system EO polymers[6,7]. Films poled under low temperature shows an initial fast decay to 25% within the first 5 days, followed by a slow decay, which decay a little bit faster than other guest-host-system EO polymers. On the other hand, films poled under low temperatures can be re-poled, namely, after a long time, repeating of the poling process will recover the decayed EO coefficient, as shown in Fig. 6. That is impossible for films poled under glass transition temperatures, in another word, the repeating of the poling process has not any effect on their EO properties, and there is no leaking current during the re-plying process.

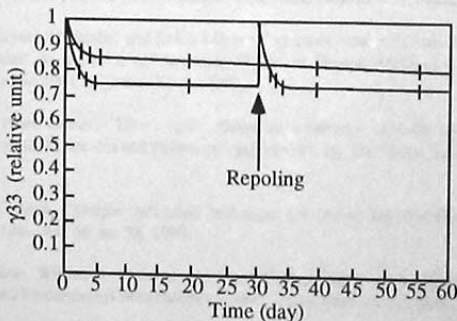


Fig. 6. Stability of polymers poled by pulsed poling method under different conditions.

Besides the enhanced EO coefficients, pulsed poling has another two advantages. Firstly, there is no high temperature induced waveguide degrading problems such as loss increment. Secondly, domain inversion on EO polymers can be fabricated with smaller gaps. As we know, today more and more EO devices such as switches and modulators are designed on domain inverted EO polymers. With pulsed poling, the short electrical pulses can be contrarily applied upon the two reversal domains with a time sequence, so that the reversal domains can be formed at the same time with smaller gaps while without high voltage potential short.

5. CONCLUDING REMARKS

A new technique of using mixed solvent to prepare guest-host-system EO polymers has been developed and proved by experiments. The involvement of the organic solvent eliminates the microscopic clustering phenomena, and thus increases the loading concentration which account for the significant increment of the EO coefficients. The organic solvent make the dye molecules thoroughly bonded to the host polymer backbone, hence two chemical entities joint together on a molecular level, which offer the EO polymer enhanced stability. A new electrical poling technique, pulsed poling, has been investigated. The short high voltage pulses enhance the conventional poling field strength, and therefore improve the poling efficiency and EO coefficients. With pulsed poling, EO polymer films can even be poled under temperatures that are much lower than the polymer's glass transition temperature. Lower temperature poling eliminates the film degrading problems which are caused by high temperature poling. Though the EO coefficients of the polymer films poled under relatively lower temperature decay a little bit fast than that of the films poled under the glass transition temperature, the former can be recovered by re-plying, which is impossible for the later.

6. ACKNOWLEDGMENT

This research is sponsored by ONR, BMDO, and AFOSR.

7. REFERENCES

- [1]. Larry R. Dalton, Aaron W. Harper, and Bruce H. Robinson, "The role of london forces in defining noncentrosymmetric order of high dipole moment-high hyperpolarizability chromophores in electrically poled polymeric thin films", *Proc. Natl. Acad. Sci. USA*. Vol. 94, pp. 4842-4847, May 1997, Chemistry.
- [2]. Chia-Chi Teng, "High-speed electro-optic modulators from nonlinear optical polymers", pp441-436 of "Nonlinear optics of organic molecules and polymers", Hari Singh Nalwa, Seizo Miyata, CRC Press, Tokyo, 1997.
- [3]. Hari Singh Nalwa, Toshiyuki Watanabe, and Seizo Miyata, "Measurement techniques for refractive index and second-order optical nonlinearities", in the book of "Nonlinear Optics of Organic Molecules and Polymers", pp89-350, by Hari Singh Nalwa, Seizo Miyata, CRC press, Tokyo, 1997.
- [4]. Christian Bosshard, and Peter Gunter, "Electro-optic effects in molecular crystals and polymers", in the book of "Nonlinear Optics of Organic Molecules and Polymers", pp391-440, by Hari Singh Nalwa, Seizo Miyata, CRC press, Tokyo, 1997.
- [5]. C. C. Teng and H. T. Man, "Simple reflection technique for measuring the electro-optic coefficient of poled polymers," *Appl. Phys. Lett.*, vol. 56, no. 18, 1990.
- [6]. Dave Gerold, Ray T. Chen, William A. Farome, and David Pelka, "Poled electro-optic photolime gel polymer doped with chlorophenol red and bromomethyl blue chromophores", *Appl. Phys. Lett.*, vol.66, no.5, pp.538-540, 1996.
- [7]. David R. Martinez and Karl Koch, Felix K. Ratsavorg and Gene O. Carlisle, "Large stable second-harmonic coefficient in an azo-dye attached polymer oriented by corona poling," *J. Appl. Phys.* vol.75, no.8, 1994.