1000 V/μm pulsed poling technique for photolime-gel electro-optic polymer with room-temperature repoling feature

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An electric pulsed-poling technique is developed for achieving high-performance electro-optic polymers. A high poling field of 1 kV/μm can be applied across a polymer thin film without experiencing breakdown. This poling technique has been applied to a guest-host nonlinear polymeric system of photolime gel and chlorophenol red with loading concentration of 30 wt %. An electro-optic coefficient up to 40 pm/V at the 632.8 nm wavelength is achieved, which is 35% higher than that obtained by using conventional poling approaches. After decay the electro-optic coefficient can be fully recovered using the same poling method at room temperature. © *1998 American Institute of Physics.* [S0003-6951(98)00526-9]

Organic electro-optic (EO) materials have been drawing great attention recently because of their unique advantages over inorganic crystals, such as flexible thin-film formation and high EO coefficients. Their EO properties can be tailored via chemical modifications. Theoretically, the EO coefficient r_{33} of organic polymers could be as high as 100 pm/V,[1] but r_{33} values achieved thus far in experiments are much below the theoretical prediction. One of the major reasons is the low electric-poling efficiency that is proportional to the poling field strength during the poling process. The higher the poling electric field across the polymer film during the poling process, the larger degree the dipoles in the polymeric matrix are aligned, resulting in a larger EO coefficient.

The two conventional electric poling techniques are corona poling and metal-contact poling. The highest field for the metal-contact poling is limited by the localized leakage current which creates thermal sources across the poling electrodes. As a result, a catastrophic breakdown often takes place before the dielectric breakdown.[2,3] It has been found that electrical field strength in the range of 200–300 V/μm can be achieved using this method.[2–4] This electrical field value is usually much lower than the dielectric breakdown value ($\sim$500 V/μm) permitted by the EO polymer films.[2,3] With corona poling, a relatively higher poling field can be employed.[2,5] By exposing a polymer film to a corona discharge, poling electric fields very close to the dielectric breakdown can be obtained. The poling efficiency ranges from 0% to 100% depending on the degree of orientation of the dipoles. Only 30% of the poling efficiency can be achieved through these two conventional poling methods.[6–8]

To increase the poling field, and hence the poling efficiency, we employ a pulsed electric field instead of the continuous poling field as used in the conventional approaches. The diagram showing the pulsed electric-poling field as a function of time is shown in Fig. 1. A high-voltage electric field pulse (E_p=1000 V/μm) is applied across the polymer film for a short time duration T_v, and then released to zero for a relatively long time duration of T_0. Because each high-voltage pulse is so short, ranging from 50 to 100 ms, very

little current is injected through the polymer film under the poling process. Electric poling field values as high as 1 kV/μm have been achieved without the breakdown commonly observed in both contact and corona polings. Since the poling electric field is much higher than the dielectric breakdown field of polymers, the electric dipoles can be well-aligned along the external poling field. Such a strong electric poling field improves the poling efficiency and increases the EO coefficients.

For conventional poling approaches, a continuous poling electrical field is employed during the poling process while heating the polymer film to its glass-transition temperature. In the pulsed poling process, one can obtain a poling field much stronger than that in the conventional poling methods without breakdown. The electrical pulses are strong enough to disrupt the mutual molecular forces within the film. The alignment effects of each pulse during the poling process are accumulated to the final alignment of the dipoles.

Figure 2 show the schematic diagram of the computer-controlled poling setup. The EO polymer, made out of photolime gel and chlorophenol red,[9,10] is spin coated on a glass substrate which is coated with indium–tin–oxide (ITO) film as the bottom electrode. The upper electrode is a thin film of
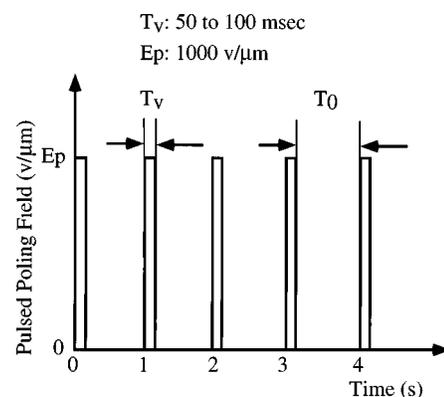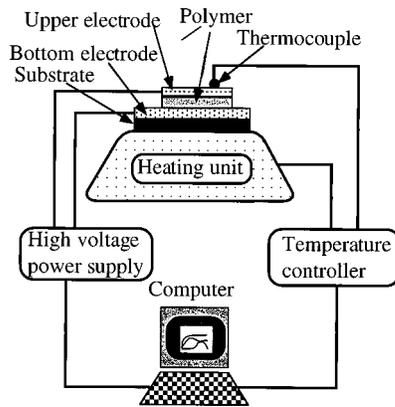

FIG. 1. Details of pulsed electrical poling field.

FIG. 2. Schematic diagram of the computer-controlled electric-poling setup.

FIG. 3. Stability of polymers under pulsed and continuous poling conditions.

aluminum deposited on the surface of the polymer. Both the poling voltage and the poling temperature throughout the poling process can be programmed and controlled by the computer. The leakage current across the polymer film is also monitored in time through the computer during the poling process.

A guest-host polymer of chlorophenol red doped photolime gel with loading concentration of 30% (wt) is synthesized with a mixed solvent which helps the guest and host material mix well in the molecular level and eliminates the recrystallization or the microscopic clustering phenomenon.[9,10] After poling, the reflection geometry is adopted to measure the EO coefficient r_{33} at a wavelength of 632.8 nm.[11] A sinusoidal electrical signal is used to modulate the phase difference of the p and s wave of the light passing 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 and s wave. The EO coefficient r_{33} is then determined by the following equation:[11,12]

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2\theta)^{1/2}}{\sin^2\theta}, \qquad (1)$$

where λ is wavelength, n is the refractive index, θ is the 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. Using conventional contact poling with a continuous poling field strength of 250 V/μm at the glass transition temperature of 180 °C, an EO coefficient, r_{33}, value of 30 pm/V is obtained. The pulsed poling technique with $E_p = 1000$ V/μm, $T_v = 100$ ms, $T_0 = 900$ ms, gives an EO coefficient, r_{33}, value of 40 pm/V. The R–C time constant of the poling cell is measured to be less than 1 μs, which is much smaller than the poling-pulse duration. Compared with the conventional poling method, the pulsed poling has increased the poling efficiency by 35%.

It is interesting to note that such a high-voltage pulsed poling can even be conducted at room temperature for the photolime-gel EO polymer film. After the room-temperature pulsed poling, the EO coefficients are measured the same as that poled at the glass–transition temperature. We have investigated the magnitude and the stability of the EO effect of polymers poled under different conditions. The result is in Fig. 3. Films poled at polymer's glass–transition temperature using the traditional continuous electric field show an initial
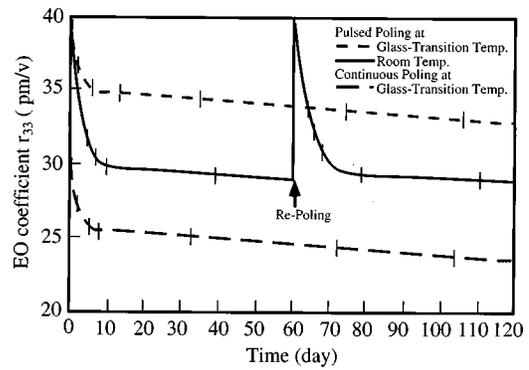
fast decay to 85% within the first five days, followed by a slow decay. Films poled at the glass–transition temperature (180 °C) using pulsed electric field show a similar decay trend, except the EO coefficient is improved. Films poled under room temperature using pulsed electric field show an initial fast decay to 75% within the first five days, followed by a slow decay.

Another exclusive characteristic of the photolime-gel-based EO polymer is that the films poled under room temperature can be repoled. As shown in Fig. 3, repetition of the poling process long after poling will fully recover the decayed EO coefficient, which is not feasible for films poled at elevated temperatures. The room-temperature repoling process can thus maintain the large EO coefficient over a long time scale. This is crucial for making practical polymer-based EO devices. Since the repoling process is performed at room temperature, it has no side effect on such optical properties as film-surface damage and oxidation and optical-loss enhancement.

In summary, we report the electric poling of photolime-gel based EO polymer films using high voltage pulses. An electric field of 1 kV/μm is applied. This new technique enhances the poling field strength, and therefore improves the poling efficiency and EO coefficients. With pulsed poling, photolime-gel-based EO polymer films can even be poled and repoled at room temperature. The EO coefficient can be fully recovered after room-temperature repoling. An r_{33} value as high as 40 pm/V is achieved at 632.8 nm.

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