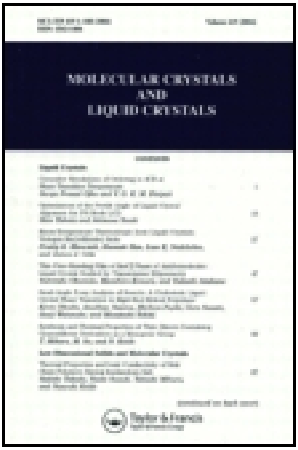

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Electro-Optical Measurements of Ferroelectric Copolymers of Vinylidene Fluoride and Trifluoroethylene

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Electro-Optical Measurements of Ferroelectric Copolymers of Vinylidene Fluoride and Trifluoroethylene

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Electro-optical measurements of ferroelectric copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) with VDF molar contents of 72 mol% and 50 mol% have been studied. Through the study of the relaxation dynamics of the EO coefficient for the P(VDF/TrFE) copolymer, it was found that the poling process improve temporal stability of P(VDF/TrFE) 50/50 mol% poled at room temperature and 72/28 mol% copolymer poled at near T_c.

Keywords: P(VDF/TrFE) copolymer; electro-optic; relaxation

INTRODUCTION

Recently, poled polymers are important elements in the field of nonlinear optics, as they show temporal stability of second-order nonlinear optical (NLO) effects. The NLO properties of polymeric materials have been attracting a great deal of interest[1], especially for their potential application in photonic systems. In order for second order NLO processes to propagate in such systems, they must lack the inversion symmetry (be noncentrosymmetric). The technique most widely used to create noncentrosymmetry in a polymer have been the electric poling process. Copolymers of vinylidene fluoride and trifluoroethylene (VDF/TrFE) have been of great interest because of their piezoelectric and pyroelectric properties and the existence of an observable ferroelectric to paraelectric transition[2]. In this letter, we report temporal stability and poling process of the poled P(VDF/TrFE) copolymer, which makes use of the ellipsometric electro-optical measurement.

EXPERIMENTAL

In the preparation of samples, thin films of the different molar ratios of VDF and TrFE copolymer were spin coated onto an indium tin oxide (ITO) coated glass substrate. The counterelectrode is implemented when an approximately 25 nm thick layer of Al is thermally evaporated onto the polymer. We used a 632.8 nm He-Ne laser as a light source. In order that the parallel (p-wave) and perpendicular (s-wave) components of the optical field are equal in amplitude, a laser beam is incident on the back of the glass substrate at an angle of 45°. It propagates through the substrate, the ITO, the polymer layer, and is then reflected back out into the air by the top Al electrode. The phase shift between the p- and the s-polarized component of the reflected light was monitored using Babinet-Soleil compensator, an analyzer, and into a detector. The modulation in the beam is measured using a lock-in amplifier.

RESULTS AND DISCUSSION

The electro-optic (EO) coefficients of the poled samples were measured modulation (10 Hz) as a function of applied electric field using a simple reflection technique[3] at room tempeature. The EO coefficient, r_{33}, of the poled film was calculated using the following equation:

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

where V_m is the modulation voltage, θ is the incident angle, and

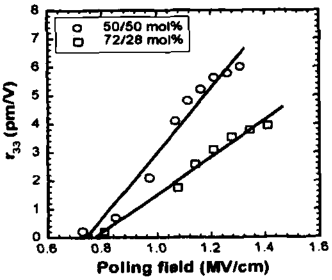

FIGURE 1 Electro-optic coefficients r_{33} as a function of applied electric field

I_m and I_c are the modulation intensity and the dc intensity component of the modulated output beam, respectively. The results are presented in Fig.1, a linear dependence of the EO coefficient on the applied electric field is obtained for the films with VDF/TrFE molar ratios of 72/28 and 50/50. After the polymer films were kept at the desired poling temperature under an electric poling field (1 MV/cm), it were then cooled to room temperature to "frozen in" the alignment and the field was turned off. The relaxation results of normalized EO coefficient for P(VDF/TrFE) copolymers with VDF molar contents of 72 mol% and 50 mol% are shown in Fig. 2.

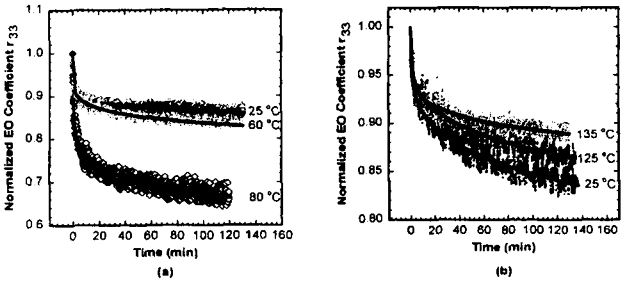

FIGURE 2 Relaxation of normalized electro-optic coefficients for (a) 50/50 and (b) 72/28 mol% P(VDF/TrFE) copolymers

The relaxation curves are typically empirically fitted to the Kohlrausch-William-Watts (KWW) stretched exponential function[4]:

$$\Phi(t) = e^{-(t/\tau)^{\beta}} \tag{2}$$

In this equation, τ is the average relaxation time constant, while β is the stretch parameter which describes the widths of the relaxation time constant distribution. We found that temporal stability of the EO coefficient from the 50/50 mol% copolymer poled at room temperature and 72/28 mol% copolymer poled at near $T_c(= 131.1\ ^\circ C)$ were lager than that of the films poled at near $T_c(= 65.5\ ^\circ C)$ and at room temperature, respectively. Then the relaxation time τ for 50 mol% and 72/28 mol% copolymers were 3.3×10^9 and 2.6×10^7 minutes, respectively.

CONCLUSIONS

A linear dependence of the EO coefficient on the applied electric field is obtained for the films with VDF/TrFE molar ratios of 72/28 and 50/50. It was found that the poling process improve temporal stability of P(VDF/TrFE) 50/50 mol% poled at room temperature and 72/28 mol% copolymer poled at near T_c.

Acknowledgements

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