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Second-Order Nonlinear Optical Active Polymethacrylate and Polyester Containing a Methylsulfonylbenzothiazole Azo Chromophore

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We synthesized the second-order nonlinear optical (NLO) copolymers for studying the effect of temperature on the temporal stability of the electro-optic effect. Heterocyclic azo chromophore was synthesized to be anchored to methacrylate and naphthalate polymer backbone. The decaying behavior of the electro-optic response was traced at different temperatures. The rates of relaxation were considered based on the difference in the polymer structure.

Keywords: heterocyclic chromophore; electro-optic; molecular relaxation

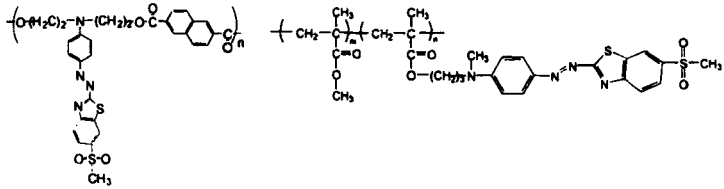
INTRODUCTION

Poled polymeric systems have drawn remarkable interests in recent years as promising candidates for application in electro-optic and photonic devices. In an attempt to investigate the dipolar relaxation after poling, we designed and synthesized two polymers.

Polynaphthalate is composed of a relatively long repeating unit with a short side chain group. Polymethacrylate consists of a relatively short repeating group with a long side chain group. Using two copolymers, we report the results of the isothermal relaxation of the E/O response of poled films.[1-3]

EXPERIMENTAL

The synthesis of two polymers will be described elsewhere. The structures of polymers were illustrated in Figure 1. Polymethacrylate and polynaphthalate were dissolved in tetrachloroethane/ methylenechloride and dimethylacetamide/ tetrahydrofuran respectively, with a 10-15% proportion in weight and the solution was filtered before spin coating with a 0.2 μm filter.



(a) (b)

FIGURE 1 Structures of polymers used in this study; (a) polynaphthalate; (b) polymethacrylate.

***In-situ* measurement of electro-optic effect:** We measured the linear E/O signal (I_m/I_c) of the samples by way of reflection technique [1-4]. The linear electro-optic coefficient, "r_{33}" of the poled polymer film was calculated by the following equation. The r_{33} value is directly proportional to I_m/I_c in equation (1).[1-3]

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

where n is the refractive index of the sample and I_m is the amplitude of electro-optic modulation. V_m is the a.c. voltage applied to the sample and I_c is the intensity of incident light where phase retardation is 90° between TE and TM mode.

RESULTS AND DISCUSSION

Polynaphthalate was prepared with naphthalene dicarboxylic acid (NDA) and chromophoric diol compound *via* Mitsunobu reaction. The glass transition temperatures of polynaphthalate and polymethacrylate were found 118°C and 105°C respectively.

In order to investigate the isothermal relaxation of the E/O response quantitatively, we selected a reduced temperature (T_{red}). The reduced temperature (T_{red}) was calculated dividing the measuring temperature, T (K) by the glass transition temperature, T_g (K). We recorded the data for the isothermal decay using two polymers. The decay curves were fitted to the Kohlrausch-Williams-Watts(KWW) stretched exponential function. We calculated the relaxation time τ, the average relaxation time $<\tau>$, and the stretching parameter resulting from the above curve fitting.[1]

First, we showed the decay curves of the E/O signal at T_g in both polymers. The rate of the relaxation in polymethacrylate is clearly observed to be smaller than that in polynaphthalate (see Figure 2). In Figure 3, the relationship between the average time constant, $<\tau>$ and the reduced temperature (T_{red}) were illustrated. In this comparison, we could find that the rates of relaxation in polymethacrylate is much smaller than those in polynaphthalate below T_g. It is attributed to the

structural difference in two polymers. In polynaphthalate, the polar NLO chromophore is tethered to the long repeating unit. On the while, the same chromophore was bound to the short main chain unit in polymethacrylate. Therefore, the chromophore in polymethacrylate is more sterically hindered so that randomization of the reoriented molecules can be retarded.

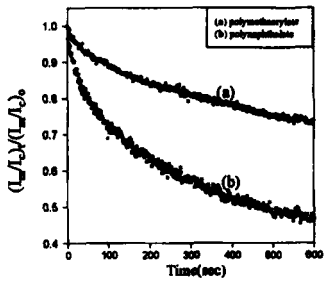


FIGURE 2 Decaying curves of the E/O signal at T_g.

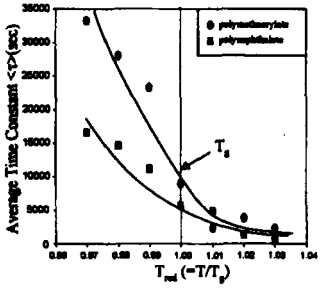


FIGURE 3 Relationship between <τ> and T_{red}.

In short, the relaxation of E/O effect is strongly dependent on the steric hindrance of the polar side chain below the glass transition temperature.

Acknowledgment

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