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The temperature dependence of second harmonic generation efficiency have been studied to investigate the poling and relaxation dynamics of polyamic acid carrying two end-on attached chromophores of DR1 and DANS. We interpreted the experimental results with the free volume model and thermal orientation fluctuation of structural components such as the nonlinear optical chromophores and main chains.

Key words: SHG; poling; relaxation; polyimide; DR; DANS

INTRODUCTION

Organic materials have been spotlighted as promising candidates for various applications such as optical data storage, optical modulator, harmonic generator, optical parametric oscillation, and surface treatment of liquid crystal display cell, etc.[1,2] During the past few years, there has been great interest in orienting polar chromophores, doped or functionalized in polymer host. However, these materials have some problems with regard to the temporal stability of aligned samples. Particularly, the aligned elements relax back to random orientation through thermal relaxation. To improve this temporal stability, polyimide has been utilized as polymer host.[3] Also, polyimide has been utilized as an alignment layer for the liquid crystal display.[4] For the nonlinear optical application or the pretilt of liquid crystal molecules, it is important to align the polyimide by the electrical poling or the optical poling.

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In this paper, we report the alignment of chromophore in the polyimide by corona poling. To understand the mechanism of alignment as well as that of relaxation, we measured the temperature dependence of the second harmonic generation (SHG), and investigated the dynamics of the poling and relaxation processes

EXPERIMENTAL

Sample preparation. Polyamic acid carrying two end-on attached chromophores (DR1 and DDANS) was synthesized for this experiment(DDANS-DR(PAA) in Figure 1). This amic acid form can be transformed into polyimide through the heat treatment near the glass transition temperature(DDANS-DR(PI) in Figure 1). The glass transition temperature is estimated to be 179°C from differential scanning calorimetry. In the preparation of the film, DMF was employed as the solvent. The solution was spin-coated on the glass plate(1200 rpm) and the precursor film was heat-treated at 110°C for 18h to remove the residual solvent.

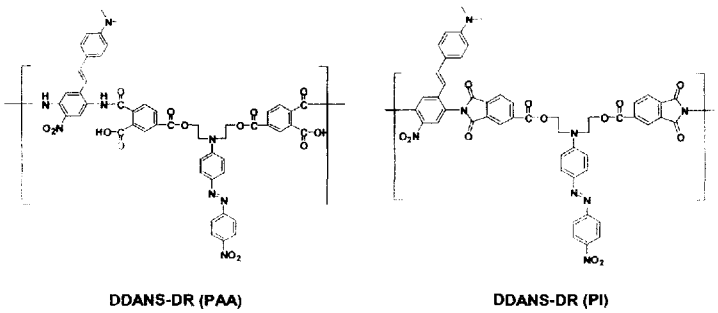

FIGURE 1. Chemical structures of the polyamic acid(PAA) and the polyimide(PI) carrying DDANS and DR1 chromophores.

Corona poling and measurement of the second harmonic generation. For the electrical alignment of the chromophore dipoles, we used corona poling method. The poling voltage of 4.0 kV was applied evenly on the sample film. The distance between tungsten tip and ITO electrode was 1.0 cm. The second harmonic generation experiment was performed with a *p*-wave at the fundamental frequency of a Q-switched Nd:YAG laser operating at 10 Hz. The SHG power was measured in the temperature region between room temperature and glass transition temperature.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the SH intensity as a function of the temperature at which the sample was poled. In the temperature region away from the glass transition temperature, the SH intensity is increased when the temperature increased from 50°C to 100°C. This behavior can be explained with free volume concept. It is expected that as the temperature is increased, in addition to enhanced thermal mobility of structural components, free volume surrounding the chromophore and mainchain is increased and then the NLO chromophores and mainchains can be more easily aligned due to reduction of steric hindrance. Meanwhile, near the glass transition temperature, the SH intensity is seen to decrease when the temperature is increased from 100°C to 180°C. This can be ascribed that thermal orientation fluctuations of NLO chromophores and mainchains are large enough to override their alignments from the electrical poling. Next, we decreased the temperature after poling at 175°C for 1h. SH signal is increased for the cooling process from 175 to 125°C, but it is decreased for the cooling process from 125 to 50°C. The remnant of SH signal at 50°C after repeated heating and cooling processes shows that sample was partially poled. If we select the proper condition for heat treatment, we will increase the remnant. The shift of the SH intensity versus temperature curve on cooling is speculated to occur from the free volume decrease as a result of the imidization during poling.

Figure 3 shows poling dynamics at 60 and 135°C. We fitted the experimental data to the double exponential function. The fast and slow time constants can be considered to represent for the pendant chromophore and mainchain alignments, respectively. At 60°C, polyimide mainchains were slowly aligned after the pendant chromophore alignments. Meanwhile, the time profile of SH signal at 135°C is indicative of polyimide mainchain relaxation due to the thermal orientation fluctuation.

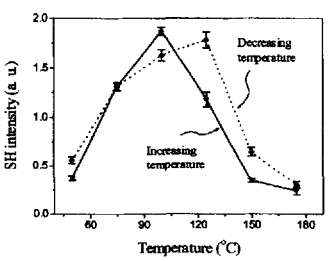

FIGURE 2. SH intensity as a function of the temperature at which sample was poled.

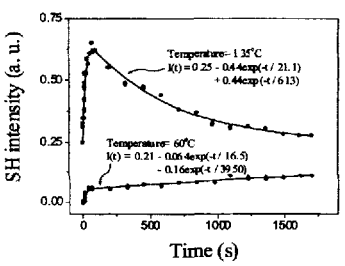

FIGURE 3. Dynamics of the SH signals at 60°C and 135°C

In conclusion, we have measured *in situ* the dynamics of the poling and relaxation processes using the optical second harmonic generation method. The results were interpreted with the free volume model and thermal oriental fluctuation of structural components such as the nonlinear optical chromophores and main chains.

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