A real-time poling approach for preparing second-order nonlinear optical polymer thin films

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Abstract

A new real-time poling approach for preparing second-order nonlinear optical (NLO) polymer thin films is presented. The presented method may be conveniently applied to many polymer thin film systems without going through the complicated conventional synthesis and poling procedures. This method, which is proven in this work to be feasible experimentally, is done by simultaneously co-depositing a NLO active dye, disperse red 1 and two polyamide thin film forming monomers on a gold electrodes pre-patterned glass substrate while concurrently applying an electrical field for poling. A second harmonic generation (SHG) signal is detected from the resultant thin films at a very low poling field ranging from 0.01 to 0.1 MV/cm which increases in intensity as the poling field increases. © 1997 Elsevier Science S.A.

Keywords: Polymer thin films; Second harmonic generation (SHG)

1. Introduction

The great electrooptic application of organic second-order nonlinear optical (NLO) materials has triggered tremendous research efforts in searching for the most applicable material synthesis and processing systems [1–12]. The primary requirement is to have sound NLO properties surviving the peak processing temperature and lasting for a sufficiently long time span in use. Although the peak processing temperature encountered varies with different fabrications or may decrease in the future process and although the lifetimes required are different for various end-use purposes, it is always desirable to have the NLO materials highly stable at raised temperatures. Coupled with some other stringent requirements, not many systems or materials can possibly succeed.

Hence, it is the purpose of this study to present a new approach that may enable many polymeric materials, in-cluding high-glass transition ones, to be a feasible matrix and many NLO-active dyes to be the desired dopants for making numerous adaptable NLO thin films. This can be done by simultaneously co-depositing a NLO-active chromophore and polymer thin film forming monomer(s), while concurrently applying a poling field. The current approach has been proved successfully via real-time poling vapor co-deposition in preparing a dye-doped polyamic acid (PAA) thin film, which exhibits second harmonic generation (SHG) characteristics fairly well.

The process involves simultaneously co-depositing the desired NLO molecules and the polymer film forming monomers on a substrate on which an electrical field is concurrently applied for poling. The NLO dye molecule used here is disperse red 1 (DR-1) and the polymer thin film forming monomers are dianhydride, pyromellitic dian-hydride (PMDA) and diamine, 4,4'-diaminodiphenyl ether (ODA). These two monomers are used to form a PAA thin film, which can become a high glass transition polyamide (PI) after curing. In the following sections, we will show the corresponding theoretical calculation regarding the possibility of accomplishing a real-time poling process, and reveal the experimental procedures and results concerning the NLO characteristics of the resultant thin films.

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2. Experimental

The NLO polymer thin films were prepared by simultaneously co-depositing 0.025 g DR-1 molecules and 0.2 g each of the monomers on a glass substrate using thermal evaporation (Fig. 1). The deposition process began in a vacuum of 5×10^{-5} mbar and the resultant thin films were 0.7 ± 0.1 μm thick.

The glass substrate was first pre-patterned with pairs of gold (Au) electrodes, 0.3 μm thick and with spacings of 100, 200, 500, and 1000 μm for poling, as illustrated in Fig. 1. An electrical voltage of 1500 V was applied through the paired electrodes concurrently during the deposition process.

Thermal curing was carried out in a vacuum after the deposition process. Substrate temperature was raised to 150°C at a ramp rate of 3°C/min and held for 30 min. Meanwhile, the poling field was applied throughout the curing process and turned off after it was cooling down to below 40°C.

The SHG, which occurred from the resultant specimens, was measured in order to study the effects of the poling and decay of the poled order. The SHG measurements were performed using a Q-switch Nd:Yag laser ($\lambda = 1064$ nm) with a Y-cut quartz crystal reference ($d_{11} = 0.5$ pm/V). The incident laser beam, with a power of about 2.7 mW, was targeted at the spacing between the electrodes and the SHG signal (532 nm) was measured after it had passed through the sample.
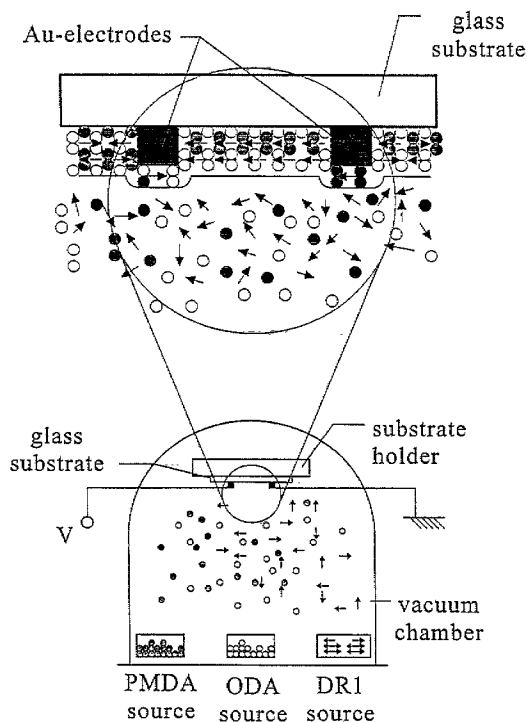

Fig. 1. Schematic diagram of the real-time poling vapor deposition polymerization system for preparing dye-doped second-order NLO polymer thin films.

3. Results and discussion

Theoretically, the poling time, t_p, required for a static NLO molecule at an angle θ with respect to the poling field has been derived to be [1]:

$$t_p = \frac{\pi}{2} \sqrt{\frac{ma^2}{\mu E}} \left\{ 1 + \left(\frac{1}{2}\right)^2 k^2 + \left(\frac{1 \times 3}{2 \times 4}\right)^2 k^4 \right.$$
$$\left. + \left(\frac{1 \times 3 \times 5}{2 \times 4 \times 6}\right)^2 k^6 + \ldots \right\} \tag{1}$$

where m is the molecular mass, a is half of the charge separation distance, μ is the dipole moment of the NLO molecule, E is the poling field strength and $k = \sin(\theta/2)$. For example, the calculated poling time required to rotate a NLO molecule at 175°, with respect to the desired orientation, is from 1.9×10^{-9} to 6.1×10^{-10} s for a poling field ranging from of 0.01 to 0.1 MV/cm. Such a poling time should be sufficient to rotate more than 95% of the NLO molecules to the desired orientation.

In practice, however, the evaporating NLO molecules are in a dynamic state. The time required for a 180° out-of-phase molecule to rotate to the desired poling direction is estimated to be 2.2×10^{-10} s. This is even shorter than that required in the static state.

In order to efficiently orient the NLO molecules, the poling time required for these molecules must not only be short; it has to be even shorter than its travelling time in the poling zone as well. The length of the poling zone assumed to be equal to the 0.3-μm thickness of the electrodes enables the molecules to travel the distance at 1.7×10^{-9} s before depositing on the substrate [2]. As the poling time required is shorter than the travelling time, it therefore allows the NLO molecules to be poled in real time.

The above calculations have demonstrated the possibility of real-time poling of the process. However, the effects of thermal rotational motion and mechanical damping of the NLO molecule are not included in the calculation model. These two factors are crucial in determining the final poling order of the dye molecules in the resultant thin

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[1] First, the NLO molecule is assumed to have a dipole moment μ, mass m and charge group centers distance $2a$. The moment of inertia of the molecule is assumed to be ma^2. The equation of motion for a polar molecule in a uniform poling field is $ma^2(d^2\theta / dt^2) = \vec{\mu} \times \vec{E} = - \mu E \sin\theta$. Accordingly, for a NLO molecule at angle θ, the poling time, t_p, can be solved as [13]. $t_p = \pi/2\sqrt{ma^2/\mu E} \{1 + (1/2)^2 k^2 + (1 \times 3/2 \times 4)^2 k^4 + (1 \times 3 \times 5/2 \times 4 \times 6)^2 k^6 + \ldots\}$. In the present system, DR-1 molecule has a molecular mass of 314 g/mol, dipole moment 8.72 Debye [14], and $2a$ 14.5 Å.

[2] The traveling time of the NLO molecules is estimated by dividing the length of the poling zone with the velocity of the molecules. The poling length is 0.3 μm. The velocity of the molecule is assumed to be equal to $1.732 \sqrt{KT/m}$, where K is the Botzmann's constant and T the evaporation temperature of DR-1 (423 K).
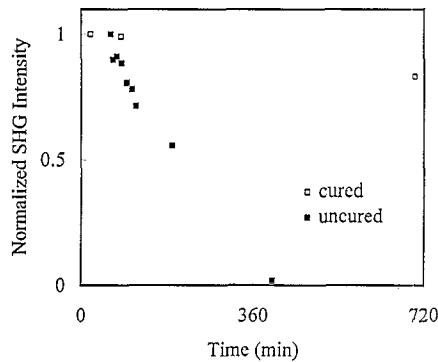
Fig. 2. Relaxation characteristics of the SHG intensity for the resultant polymer thin films before and after curing.

films. To better realize the entire poling process, it is suggested that the two factors be taken into account in future theoretical studies.

Fig. 2 shows the SHG intensity decay curves for the poled PMDA-ODA-DR1 films at room temperature. For the uncured film, the SHG intensity decreased with time, and vanished after 6 h. In contrast, the cured film possessed much better stability. Its SHG intensity remained at 88% of its original intensity after 12 h. The curing process does improve the film stability.

Fig. 3 shows the SHG coefficients as a function of the poling field for the resultant dye-doped polymer thin films. All the poled regions of the thin films yielded a SHG signal, regardless of the strength of the poling field. This verifies that the NLO molecules can be poled in real time using the present approach. Moreover, the SHG coefficients increased with the increasing strength of the poling field, suggesting that thermal fluctuation of the NLO molecules can be better restrained in the presence of a stronger electrical field.

Thermal stability of the resultant thin films has also been examined. Their SHG signal decreases as the temperature increases, as shown in Fig. 4a. The uncured film does not show a SHG signal at above 140°C, while the cured film still shows a significant SHG signal.
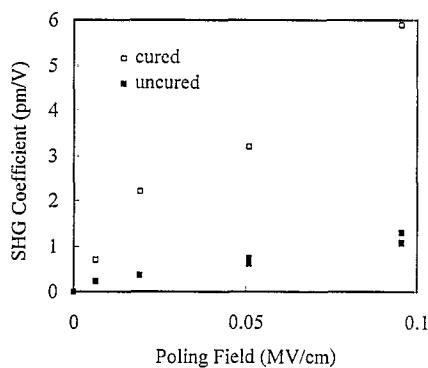
Fig. 4b shows the temporal stability of the films at

Fig. 3. SHG coefficient d_{33} as a function of poling field for the resultant thin films, where subscript 3 denotes the direction along the poling field.
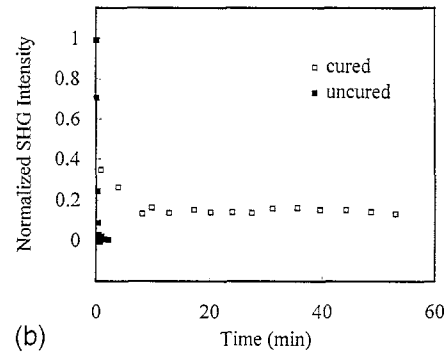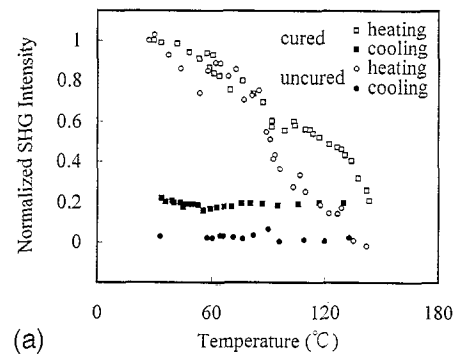

(a)

(b)

Fig. 4. Thermal stability of the resultant thin films (a) SHG intensity versus temperature and (b) temporal stability at 140°C.

140°C. For the uncured film, its SHG intensity decays to zero within 50 s. For the cured sample, its SHG intensity first drops by 85% in the initial heating stage, then its SHG intensity remains unchanged for a long period of time. The thermal stability of the NLO thin films can be greatly improved by the curing process.

When the curing temperature is raised to 200°C, only a very weak signal can be detected. This may be attributed to the degradation of the DR1 molecule since its azo-group cannot sustain high temperature by nature [15].

The work by Wu et al. [5] reveals that thermal stability strongly depends on the curing temperature; i.e., the film cured at higher temperatures exhibits higher thermal stability in their SHG characteristics. The authors think that more thermally stable NLO thin films can be obtained by using the presented approach if more thermally stable NLO active chromophores are introduced or other curing methods, e.g. chemical imidization, are employed. These are currently under investigation.

4. Conclusion

A new real-time poling approach for preparing second-order NLO polymer thin films is presented. Second-order NLO thin films of guest-host type have been successfully obtained by simultaneously co-depositing a NLO active dye and two polyamide film-forming monomers by thermal evaporation while concurrently applying a poling field.

The resultant thin films remain stable at 140°C after curing at 150°C for 30 min.

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