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Side radical influence on the nonlinear optical properties and thermal stability of poled polymer films

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Films of polyetherketone doped with the chromophores Disperse Red 1 (DR1) and Disperse Red 13 (DR13) were prepared by spin-coating method. By the *in situ* Second-harmonic Generation (SHG) signal intensity measurement, the optimal poling temperatures were obtained. For the investigated polyetherketone polymer doped with DR1 (DR1/PEK-c) and polyetherketone polymer doped with DR13 (DR13/PEK-c) films, the optimal poling temperatures were 150°C and 140°C, respectively. Under the optimal poling conditions, the high second-order nonlinear optical coefficient $\chi_{33}^{(2)} = 11.02$ pm/V has been obtained for the DR1/PEK-c; and for DR13/PEK-c at the same conditions the coefficient is 17.9 pm/V. The SHG signal intensity DR1/PEK-c could maintain more than 80% of its initial value when the temperature was under 100°C, and the SHG signal intensity of the DR13/PEK-c could maintain more than 80% of its initial value when the temperature was under 135°C.

1. Introduction

The increased interest in organic nonlinear-optical materials [1–3] for communications and information processing has lead to the synthesis and development of various classes of asymmetric π-conjugated chromophores [4, 5] that incorporate into polymers with some desirable nonlinear-optical response. Hitherto, much effort was spent on obtaining large second-order nonlinear susceptibility and long-term stability on the guest-host polymeric film or system of the nonlinear optical (NLO) molecules covalently bonded to the polymer backbone [5–7]. In this paper, the effect of different side groups on the NLO properties and thermal stability of the poled polymer films was investigated using Disperse Red 1 (DR1) and Disperse Red 13 (DR13). The optical properties of the traditional chromophores DR1 and DR13 doped into a high glass transition temperature (T_g) host polymer polyetherketone (PEK-c) were investigated by *in situ* second-harmonic generation (SHG) measurement and UV-visible absorption measurement. Optimal poling temperatures were determined by using a well controlled corona poling profile with *in situ* SHG signal intensity profile with the poling temperature increasing. After the corona poling temperature was optimized by the poling profiles, the polymer films were poled by corona-onset poling at elevated temperature (COPET). The corona poling setup includes a grid voltage making the surface-charge distribution uniform. The temperature stability of the poled polymer films was measured by probing the SHG signal intensity with increase temperature.

2. Experimental

2.1. Preparation of the sample films

Polyetherketone (Commercial product) is a highly transparent host polymer [8], and its T_g is 228°C. Its structure is shown in Fig. 1c. The investigated chromophores DR1 and DR13 are shown in Fig. 1a and b respectively, their difference is that the dye DR13 has a side radical Cl on the 2' position on the benzene ring. Dyes and polyetherketone were separately dissolved in 1,2-dichloroethane; when the dyes and polymer were dissolved in 1,2-dichloroethane, the two solutions were mixed together. The pre-mixed solutions were then filtered through a syringe with 0.5 μm filter attached in order to remove the undissolved impurities. Films were made by spin-coating the solutions onto indium-tin oxide (ITO) glass substrates to form thin films, in which the doped concentraton of the dye is 20% solid by weight in the two polymer systems; solution viscosities and spinning speeds were adjusted to produce films that were typically 1–2 μm. Then the films were heat treated at 80°C to remove the residual solvent.

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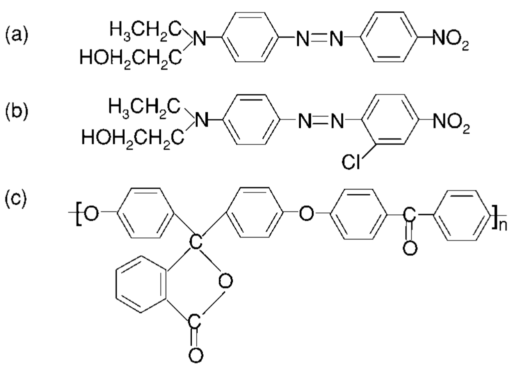


Figure 1 (a) Structure of Disperse Red 1 (b) Structure of Disperse Red 13 (c) The general structure of polyetherketone.

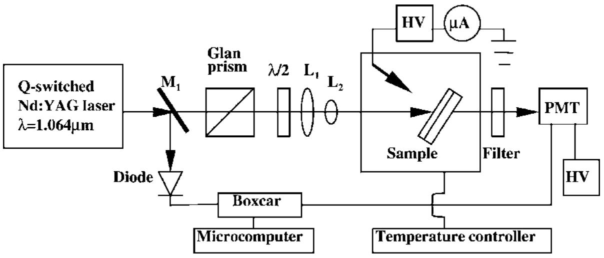


Figure 2 Schematic drawing of the experimental set-up for *in situ* SHG signal intensity measurement.

2.2. Determination of the poling temperature

Fig. 2 is a schematic drawing of the experimental set-up for *in situ* SHG signal intensity measurement. The polarized beam of a Q-switched Nd-YAG laser ($\lambda = 1.064\ \mu$m) was focused onto the sample with an angle of incidence 45°. A tungsten needle was located about 15 mm above the sample. The fundamental wave was blocked by high-pass filters and a 532 nm-interference filter. The SHG signal was detected by a photomultiplier tube then amplified and averaged in a boxcar integrator, and the boxcar output was registered by a microcomputer.

The optimal poling temperatures of the poled polymer films were determined by a well controlled corona poling profile with *in situ* SHG signal intensity profile with the poling temperature increasing.

2.3. Poling

Fig. 3 shows the corona poling setup, the grid is parallel to the surface of the poled polymer film. The distances between the needle and the grid, and between the grid and the surface of the film are 50 mm and 4 mm, respectively. A voltage of +10 kV was applied to the needle electrode. A bias voltage of +750 V applied to the grid was used for making the surface-charge distribution uniform. The polymer films were poled by a well-controlled corona poling set-up. The poling processes were carried out below their glass transition temperature for 20 minutes, and then cooled to room temperature while maintaining the needle and grid voltages.

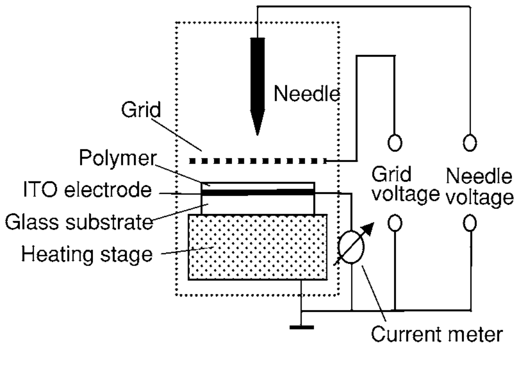


Figure 3 The corona poling set-up.

2.4. Linear absorption

The absorption spectra of the films were measured on a U-3500 UV-visible spectrophotometer, which could cover the 190–3200 nm range with sufficient dynamic range to measure absorbances as large as 9.999.

3. Results and discussion

Fig. 4 shows the *in situ* SHG signal intensity profile when the poling temperature was increased from room temperature (the temperature rising rate is 5°C/min). When the temperature was below 135°C, the SHG signal intensity was very small except for a small peaks at about 65°C (DR13) and 85°C (DR1) that are associated with the β transition of the polymer systems. When the temperature in the narrow range from 135°C to 145°C for DR13/PEK-c and 140°C to 155°C for DR1/PEK-c, the SHG signal intensity increased rapidly, for more dye molecules in the polymer were oriented along the electric field direction due to the greater mobility of the polymer at these temperatures. But the SHG signal intensity decreased quickly when the temperature was above the temperature that can be regarded as a critical temperature. The main reason to explain these decreases of the SHG signal intensity when the temperature is beyond the critical temperature is that dye molecules in the polymer sublimate[9] and oxidize at this temperature; a dramatic rise of the conductivity of the polymer can occur at the critical temperature, and results in the decrease of the effective electric field strength in the polymer film. So the optimal temperature of these polymer films could be determined as about 140°C (DR13) and 155°C, (DR1), respectively. At the same time the second-order nonlinear coefficients could be obtained, and they were 11.02 pm/V and 17.9 pm/V, respectively.

Fig. 5 shows absorption spectra of the poled and unpoled polyetherketone films doped with disperse red dyes. From Fig. 5 the maximum absorption peak was the same for the two polymer systems. Their orientational parameters were not the same. The orientational order parameter ϕ of the chromophore molecules in the

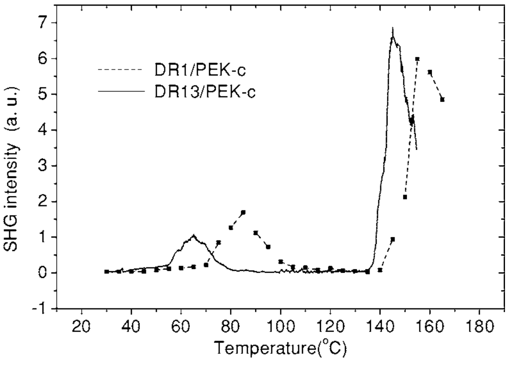
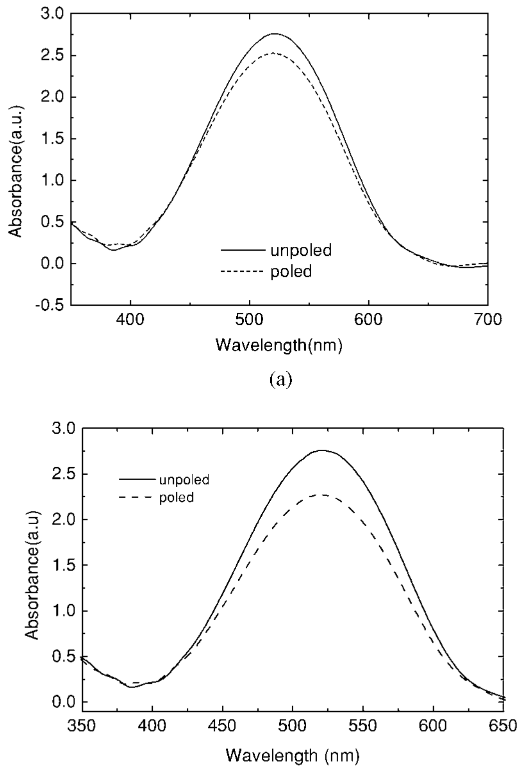


Figure 4 The *in situ* SHG signal intensity profile versus temperature.



(a)

(b)

Figure 5 (a) The absorption spectra of the DR13/PEK-c (b) The absorption spectra of the DR1/PEK-c.

polymer system was determined by the change of the absorpance between the poled and unpoled thin films according to the following relationship [10]:

$$\phi = 1 - \frac{A_\perp}{A_0}$$

where $A_\perp$ is the absorbency of the poled thin film, A_0 is the absorbency of the unpoled thin films, shown as Fig. 5, ϕ is 0.09. From Fig. 5b the orientational order parameter ϕ for the same conditions of the DR1/PEK-c was 0.18 under this poling condition, the change in ϕ may be caused by the Cl on the acceptor benzene ring.

In order to determine the thermal stability of the two polymer systems, the SHG signal intensity was measured with the temperature increasing at a rate of 5°C/min by the experimental setup for *in situ* SHG signal intensity measurement. The *in situ* measurement results of the nonlinear optical response for the poled polymer films as a function of temperature were shown in Fig. 6.

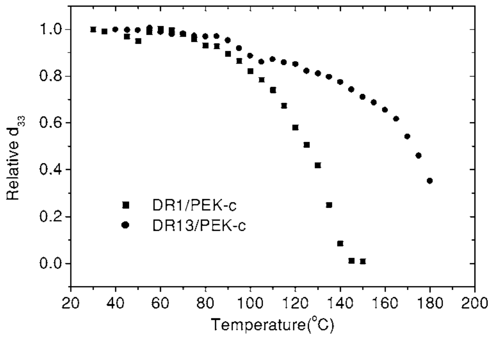


Figure 6 The decay of the SHG signal intensity for the poled polymer films.

The two polymer systems showed good thermal stability as follows: the SHG signal intensity showed a very small decay at temperatures below 80°C, and maintained approximately 80% of its initial value at 135°C for DR13/PEK-c and 100°C for DR1/PEK-c system; and approximately 50% of its initial value at 175°C for DR13/PEK-c system and 125°C for the DR1/PEK-c polymer system. The difference in behavior between the two poled polymer systems is because of the Cl on the 2' position of the DR13.

4. Conclusions

Using the *in situ* SHG signal intensity measurement, the optimal poling temperature can be obtained. For DR1/PEK-c and DR13/PEK-c polymer films, the optimal poling temperatures are 150°C and 140°C, respectively. Under this optimal poling temperature, the high second-order nonlinear optical coefficient $\chi_{33}^{(2)} = 11.02$ pm/V has been obtained for the polyetherketone polymer doped with 20% by weight DR1; and for DR13 at the same condition is 17.9 pm/V. The thermal stability of the DR13/PEK-c guest-host polymer system is better than that of DR1/PEK-c, The latter's SHG signal intensity can maintain more than 80% of its initial value for temperatures under 100°C, and the SHG signal intensity of the DR13/PEK-c can maintain more than 80% of its initial value for temperatures under 135°C, this because of the Cl on the DR13 chromophore.

Acknowledgements

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