Thermally Stable Guest–Host Polyetherketone Poled Polymer for Electro-Optical Applications *

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The high glass transition temperature polymer polyetherketone doped with disperse red 13 (DR13/PEK-c) has been prepared by the spin-coating method. Through in situ second-harmonic generation, the corona poling temperature was optimized by measuring the temperature dependence of the in situ *second-harmonic generation signal intensity under the poling electric field. The linear electro-optic coefficients of the poled polymer films have been determined at 632.8 nm by using a simple interferometric technique. The polymer system was measured after 13 000 h, and found that it remained at 80% of its initial value.*

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The development of thin-film polymer materials that are suitable for the fabrication of high-speed integrated optical devices is a major focus of research in nonlinear optics at present.[1−7] The advantages of nonlinear optical polymers over the currently used inorganic crystals include large nonlinear optical response, large laser damage threshold, low dielectric constant, and especially the ease and low cost of fabrication and compatibility with microelectronic processes.[8,9] Among these nonlinear optical polymeric systems, the guest–host polymer system does not require chemical attachment of chromophore to the host polymer, which can be fabricated at a cost lower than any other systems, such as side-chain, cross-linked and main chain polymers. Generally speaking, the guest–host system has two disadvantages: the decay of the nonlinear optical properties is fast and the chromophore concentration in the polymer system is low. Recently, we have demonstrated an approach to overcome these disadvantages by using a high glass transition temperature (T_g) host polymer polyetherketone (PEK-c) and a traditional chromophore disperse red 13 (DR13). They mixed very well. After the corona poling condition was optimized by the poling profiles, the polymer films were poled by corona-onset poling at elevated temperature (COPET). The corona poling set-up includes a grid voltage making the surface-charge distribution uniform. The linear electro-optic (EO) coefficients of the poled polymer films were determined at $\lambda = 632.8$ nm by using a simple interferometric technique. The thermal stability of the polymer system was demonstrated by the time dependence of the piezoelectricity of the poled polymer. The sample was measured again after 13 000 h, and the result shows that a drop to 80% of its original value has been found.

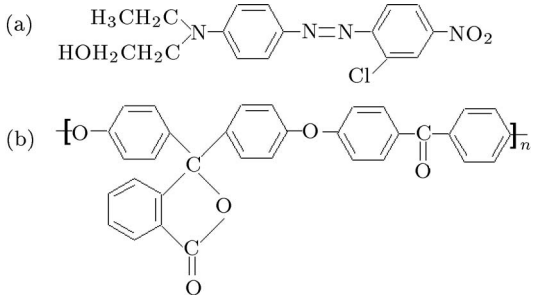


Fig. 1. (a) Molecular structure of disperse red 13 (DR13) chromophore and (b) general structure of the polymer PEK-c host.

The molecular structure of DR13 is shown as Fig. 1(a). The host polymer PEK-c is a highly transparent polymer with a high glass transition temperature ($T_g \sim 228°C$). The structure is shown in Fig. 1(b). PEK-c is an ideal host polymer for device fabrication because it is mechanically strong, and is easily processed into low optical loss thin films. DR13 and PEK-c were dissolved in 1,2-dichlorethane, and then the solutions were filtered through a syringe with a 0.45 μm filter attached to remove the undissolved impurities after two days. The final polymer solutions can easily be spin-coated on to the indium–tin oxide (ITO) glass substrates to form thin films in which the doped concentration of DR13 in per cent solid by weight is 20% in the polymer system. Then the films were kept in an oven at 80°C for 10 h to ensure removal of the residual solvent. The polymer film thickness and the refractive index were measured to be 1.056 μm and 1.754, respectively, using a Model 2010 Prism Coupler (Metricon) at 0.6328 μm. The working principle is similar to the prism coupler method.

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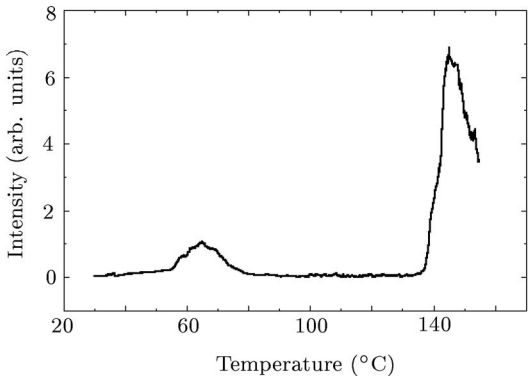


Fig. 2. *In situ* second-harmonic generation signal intensity profile versus poling temperature of the DR13/PEK-c polymer films.

The optimal poling temperature of the investigated polymer DR13/PEK-c films was obtained by means of well-controlled corona poling profile with *in situ* second-harmonic signal intensity probed at an increasing poling temperature.[11] Figure 2 shows the *in situ* second-harmonic signal intensity profile when the poling temperature was increased from room temperature at a rate of 5°C per minute. The *in situ* second-harmonic profile shown in Fig. 2 is a reproducible result obtained for several samples. When the temperature is below 135°C, the second-harmonic signal intensity is very small except for the small peak at about 65°C that is associated with the β transition of the polymer system. We have demonstrated why the second-harmonic intensity appears as a peak at about 65°C and decays when the temperature is above 65°C for the PEK-c polymer system.[10] When the temperature is in the narrow range from 135 to 145°C, the second-harmonic signal intensity increases rapidly because more chromophore molecules in the polymer film are oriented along the electric field direction due to the greater mobility of the polymer at this temperature. The second-harmonic signal intensity decreases quickly when the temperature is above 145°C, which can be regarded as a critical poling temperature. The main reason, which can explain this decrease of the second-harmonic signal intensity at a temperature beyond the critical poling point, is that the chromophores in the guest–host polymer system sublimate and aggregate (or crystallize) at this temperature.[11] A dramatic rise of the conductivity of the polymer film can occur at this temperature,[13] and can result in the decrease of the effective electric field strength in the polymer film. Thus, the optimal poling temperature for this polymer film can be determined to be about 140°C. According to the optimal poling condition, the poling process was carefully designed and carried out. A poling set-up as shown schematically in Fig. 3 was used. A voltage of $+8 \sim +10$ kV was applied to the needle electrode. A grid with a bias voltage of +800 V was used for making the surface-charge distribution uniform. After poling for about 400 s at 140°C, the sample was cooled to room temperature while keeping the needle voltage and grid voltage unchanged.

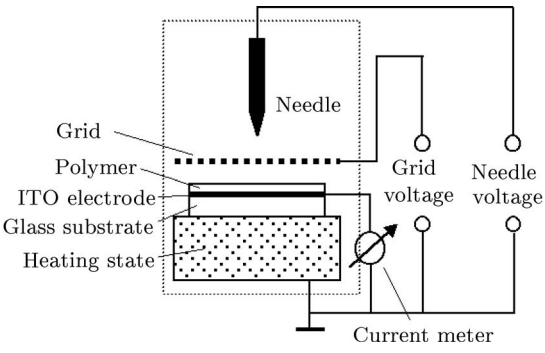


Fig. 3. Set-up for the corona poling of polymer films. The samples are mounted on a heating stage, and the current through the polymer sample is determined by an amperemeter.

The linear EO coefficients of the poled polymer films can be determined at the wavelength of 632.8 nm by using a new simple interferometric technique.[12] In order to measure the linear EO coefficients, a thin film of aluminium on the top of the polymer layer was fabricated by thermal evaporation. The measured value of the EO coefficients γ_{13} is 7.07 pm/V for the investigated poled polymer DR13/PEK-c thin films. When the poling electric field is relatively low and the orientational order of the chromophores in the polymer films and the anisotropy of the poled polymer films are relatively small. The relationship between γ_{33} and γ_{13} can be approximately regarded as $\gamma_{33} \approx 3\gamma_{13}$.[13–16] Thus, the EO coefficients $\gamma_{33} = 21.2$ pm/V can be obtained for the investigated poled polymer DR13/PEK-c thin films.

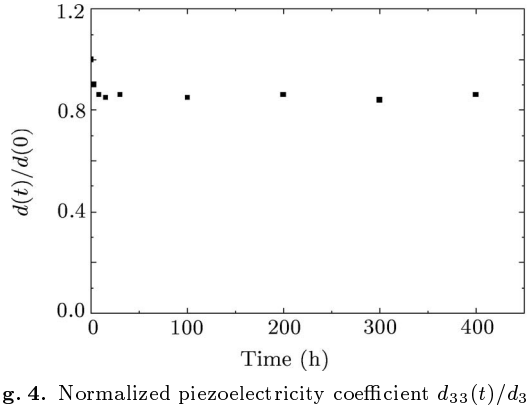


Fig. 4. Normalized piezoelectricity coefficient $d_{33}(t)/d_{33}(0)$ of the poled polymer films at 80°C for 400 h.

Because the polymeric films poled normal to the surface (z-direction) have ∞ mm symmetry with the uniaxis in the z-direction, the piezoelectric coefficient of the poled polymer films depends on the order parameter of the chromophores in the poled polymer films. The decay of the orientational alignment of the

chromophores was determined by probing the piezoelectric coefficient of the poled polymer in an oven at 80°C for over 400 h. Figure 4 shows the time dependence of the normalized piezoelectric coefficient of the poled polymer films at 80°C. The result shows an initial drop to 86% of its original value in 8 h, and then it remains unchanged for the rest of the time. The samples were placed at room temperature, after 13 000 h. They were measured again using the same method, which shows that the linear EO coefficient γ_{33} remains at 80% of its original value.

The guest–host polymer DR13/PEK-c thin films have been prepared by the spin-coating method. The corona poling condition has been optimized by the poling profiles with the *in situ* second-harmonic signal intensity probing. After the polymer films were poled by using the well-controlled COPET, the linear EO coefficient $\gamma_{13} = 7.07\,\mathrm{pm/V}$ of the poled polymer films has been determined at $\lambda = 632.8\,\mathrm{nm}$ by using a new simple interferometric technique. The thermal stability of the polymer system after poling for 400 h was demonstrated by the time dependence of the piezoelectricity of the poled polymer. The polymer system of DR13/PEK-c was re-measured by the same method after 13 000 h and it was found to remain at 80% of its original value.

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