

# polymer communications

## Novel second-order nonlinear optical polymeric composites

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A novel NLO chromophore with a five-membered heteromatics was synthesized. The chromophore was dispersed into two high- $T_g$  polymers, PEK-C and PES-C. Then they were spin coated onto ITO glass and were poled by employing a corona poling technique. The relaxation behaviour of poled films was studied by using UV-Vis spectra. Good temporal stability was found for all the samples. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: nonlinear optical; polymer composite; temporal stability)

### Introduction

Recent advances in optical communications have created intense interest in nonlinear optical materials. Poled organic polymers are considered as the most potential nonlinear optical materials because of the easy processability<sup>1</sup>. Among various material requirements, the most notable ones are high temporal stability, large electro-optical coefficients ( $r_{33}$ ) and low optical loss. The key problem existing in poled polymeric systems was the relaxation of the electric field-induced non-centrosymmetric alignment indispensable for second-order nonlinear optical properties. It has been proved that polymers with high glass transition temperature ( $T_g$ ) can enhance the stability of poled structures<sup>2-4</sup>. Here we dispersed a novel nonlinear optical chromophore into two kinds of high- $T_g$  polymers, PEK-C and PES-C (Figure 1). PEK-C and PES-C have good optical clarity and their dielectric constants are very low. All above proved that PEK-C and PES-C were good polymer matrices for nonlinear optical chromophores. The second-order NLO response depends on the density of electron and the extent of intramolecular charge-transfer in the chromophore (donor-acceptor system). So we introduced the easily delocalisable conjugating units such as electron-rich furan ring into the D-A system. We hope the electro-optical coefficient will be

improved. In addition, there are a few hydrogenous atoms on the heterocyclic ring, which may reduce the optical absorption.

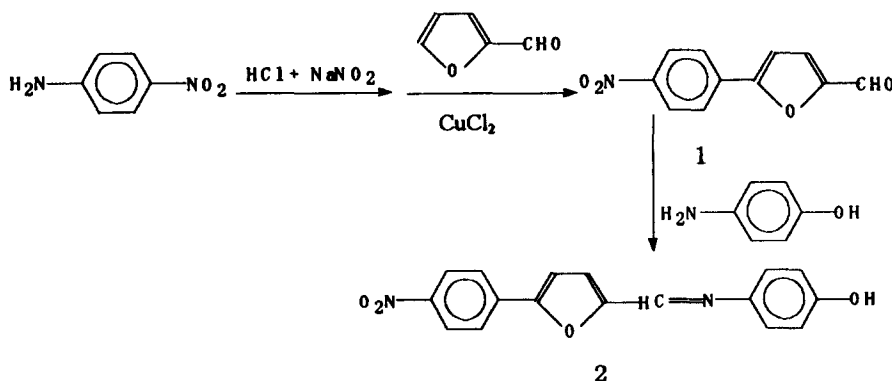
### Experimental

The chromophore was synthesised as shown in Scheme 1.

**Compound 1.** Compound 1 was synthesised according to the literature<sup>5</sup> and some steps were modified. Nitroaniline (9.0 g) and 5.0 g sodium nitrite were stirred into a paste with a little water, and added to 20 ml concentrated hydrochloric acid and 20 g crushed ice while stirring. Sodium carbonate was added until the pH value of the solution was 3–4. Furfuraldehyde (7 ml in 50 ml acetone) was added. While maintaining the temperature at 20–30°C, 3 g copper chloride hydrous solution was added dropwise. Stirring was continued for another 4 h, followed by water evaporation, filtering, and then recrystallisation with acetone. Yield, 13.3 g yellow crystal; m.p., 203–204°C.

I.r. ( $\text{cm}^{-1}$ ): 1516.9, 1344.0 ( $-\text{NO}_2$ ); 1685.2 ( $\text{CH}=\text{O}$ ); 1105.9 ( $\text{C}-\text{O}$ ).

Analysis calculated for  $\text{C}_{11}\text{H}_7\text{NO}_4$ : C, 60.83; H, 3.20; N, 6.45%. Found: C, 60.95; H, 2.97; N, 6.91%.



Scheme 1

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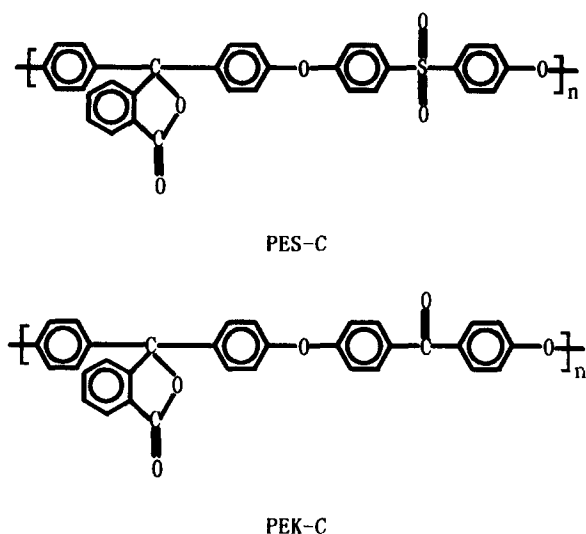


Figure 1 Structure of PES-C and PEK-C

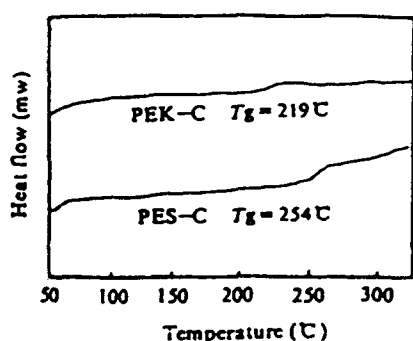


Figure 2 The d.s.c. spectra of PEK-C and PES-C

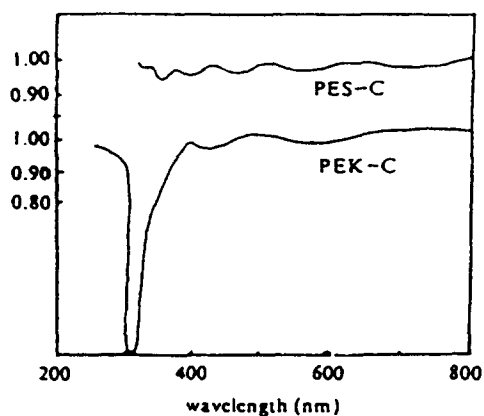


Figure 3 The transparency of PEK-C and PES-C

**Compound 2.** 4-Hydroxyaniline (2.18 g) and 4.34 g compound 1 were refluxed for 3 h. They were cooled overnight, filtered and recrystallised with ethanol. Yield, 6.6 g; m.p., 220–223°C.

I.r. ( $\text{cm}^{-1}$ ): 3436.6 (O–H); 1621.3 (N=CH); 1512.2, 1329.8 ( $\text{NO}_2$ ); 1105.9 (C–O).

Analysis calculated for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_4$ : C, 66.20; H, 3.89; N, 9.09%. Found: C, 64.55; H, 4.06; N, 9.14%.

$^1\text{H}$  n.m.r. (acetone- $d_6$ , ppm):  $\delta$  8.37 (s, CH=N); 7.5–8.2 (m, H on benzene ring); 6.8–7.1 (2d, H on furan ring).

PEK-C and PES-C were synthesised by our laboratory<sup>6,7</sup>. PEK-C (or PES-C) was dissolved in THF. Compound 2

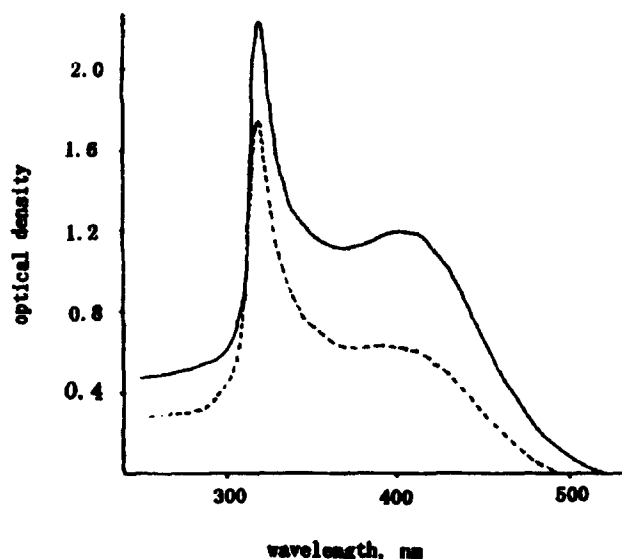


Figure 4 The UV-Vis spectra of the poled (---) and the unpoled (—) films

(10% weight ratio of PEK-C) was added. The solution was filtered and spin-coated onto the ITO glass. The slides were dried under vacuum at room temperature for 12 h to remove the residual solvent.

Corona-poling with a needle top electrode was employed to pole the polymer film. The film was poled under a 10-kV electric field at 210°C for 30 min, then cooled to room temperature while the electric field was kept on.

### Results and discussion

Since the polymers with high glass transition temperature have less free volume, the motion of the nonlinear optical chromophore becomes very difficult. Thus, the stability of the alignment is improved. PEK-C and PES-C have very high glass transition temperature. Figure 2 shows their d.s.c. spectra. As is known, nonlinear optical materials must have good optical clarity. From Figure 3 we find that PEK-C has only one strong absorption peak at 310 nm and has a good optical transparency in a very large scale. PES-C has several very weak absorption peaks and proves to be transparent. PEK-C and PES-C can dissolve in THF and their dielectric constants are very low. All the above features proved that PEK-C and PES-C are good polymer matrices for nonlinear optical chromophores.

The UV-Vis spectra of the poled and the unpoled films are shown in Figure 4. We found that the maximum absorption wavelength was very small (only about 401 nm), while the value for the commonly used Dispersed Red 1 was 460 nm. That is to say, the NLO material we synthesized shows great value in frequency doubling applications.

From Figure 4 we also found the maximum absorption peak of the poled film to be reduced. As is known, the poled order parameter can be expressed by the following equation:

$$\Phi = 1 - A_2/A_1$$

where  $A_1$  is the absorbance of the unpoled polymer films and  $A_2$  is the absorbance of the poled polymer films.

We also used UV-Vis spectra to study the relaxation behaviour of the poled polymer films. These are shown in Figure 5. From Figure 5 we found that the NLO polymers with high  $T_g$  had good stability at 100°C.

Other measurements are in progress.

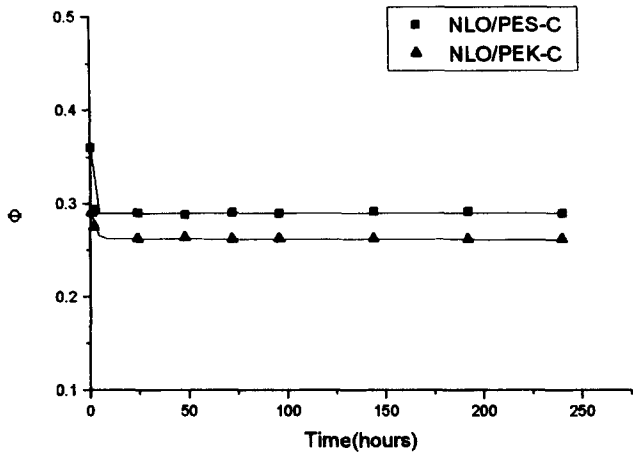


Figure 5 The relaxation behaviour of the poled polymers: (A) NLO/PEK-S; (B) NLO/PEK-C

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