Materials Science-Poland, 37(4), 2019, pp. 541-546
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/msp-2019-0055

Structure and performance optimization of phenol polyphosphazene grafted by 2,4-dinitroaniline containing small nonlinear optical molecules

YING ZHANG[1,*], YOU LI[1,2]

[1]Harbin University of Science and Technology, Harbin 150080, China
[2]Harbin Research Institute of Electrical Instruments 150028, Harbin, China

Electro-optic (EO) polymers, possessing high EO coefficient and low dielectric constant, are considered to be a new generation of nonlinear optical materials that have great application prospect in photo-communication, information storage, and data processing. The host-guest structure of EO polymers is the most typical one in this field. However, the phase separation during polarization between the host polymer and the guest nonlinear optical molecule (NLO) limits potential applications of the material. To solve the problem, a new synthetic method was designed in this paper. First, 2,4-dinitroaniline was grafted to phenol polyphosphazene by chemical method for polar improvement of the main chain. Then, another small NLO molecule was mixed into the polymer by physical method for further improvement of EO coefficient. The preparation process was studied and the structure of the product was characterized. The effects of different NLO mixing proportions and different polarizing temperatures on EO coefficient were investigated in details. Orientation stability of the sample was tested. Experimental results show that our products possess not only high EO coefficient but also good phase stability, which makes them good candidates for the application in information technology.

Keywords: *phenol polyphosphazene; EO polymer; 2, 4-dinitroaniline; NLO; information technology*

1. Introduction

Compared with inorganic crystal, electro-optic (EO) polymers possess higher EO coefficient and lower dielectric constant. The molecular structure of this kind of material is diverse and the response speed is rapid. It is considered to be a new generation of NLO material that has great application prospect in photo-communication, information storage, data processing, image reconstruction and so on [1–3]. The host-guest structure of EO polymers is the most typical one in this field. Researches all over the world are working on simple technique enabling easy manufacturing of these compounds. However, there is a serious phase incompatibility problem between the host polymer and the guest EO molecule [4–6]. Phase separation, leading to the instability and EO properties degradation, often happens during the polarization process, which limits further applications of the materials [7, 8].

In order to solve the problem, a new molecular structure of EO polymer has been designed and introduced in this paper. The polymer material was prepared by a combination of chemical and physical methods. First, 2,4-dinitroaniline was grafted to phenol polyphosphazene by chemical method for polar improvement of the main chain. Then, another small NLO molecules were mixed into the polymer by physical method for further improvement of EO properties. Here, ethyl 4-(dimethylamino) benzoate (EDB) and 4-6-alkoxy-4'-cyano-biphenyl (6OCB) were selected as NLO molecules. The structure of the polymer is shown in Fig. 1. Preparation method of the material was investigated in detail and the structure of the product was characterized. The effects of different NLO molecules, mixing proportion and polarizing temperature on EO coefficient were analyzed. The relationship between molecular species, phase stability and relaxation characters was obtained.

---

[*] E-mail: songmingxin@126.com

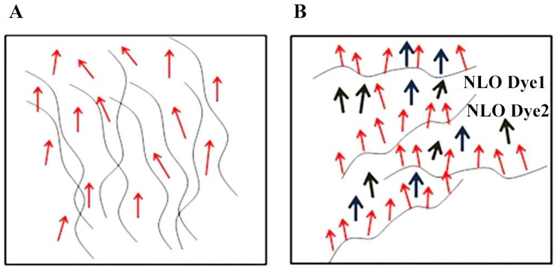
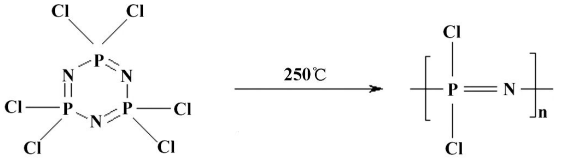


Fig. 1. Structure of the polymer.

2. Experimental

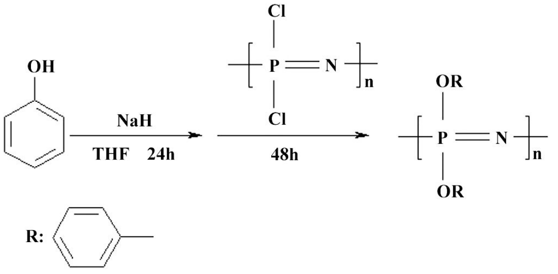
2.1. Preparation of polydichlorophosphazene

Polydichlorophosphazene can be obtained by ring-opening polymerization of hexachlorocyclotriphosphazene at 250° in a muffle furnace. The chemical reaction is given by:



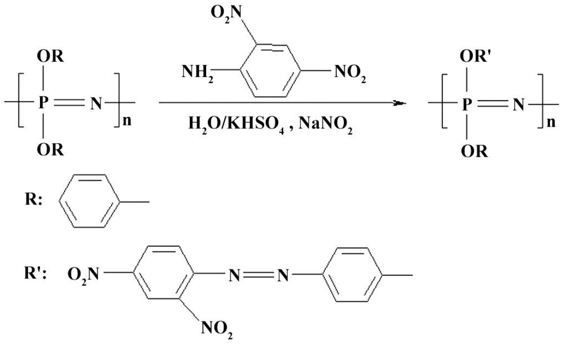
2.2. Synthesis of phenol polyphosphazene

Phenol polyphosphazene can be obtained by nucleophilic substitution of 0.4 g polydichlorophosphazene and 0.4 g of phenol in THF solution with the volume of 40 mL. The chemical reaction is given by:



2.3. Preparation of phenol polyphosphazene grafted by 2,4-dinitroaniline

Phenol polyphosphazene grafted by 2,4-dinitroaniline can be obtained by mixing 0.2 g of dry phenol polyphosphazene, 0.1 g of 2,4-dinitroaniline, 0.2 g of potassium bisulfate, 0.2 g of sodium nitrite and 10 mL of distilled water through microwave method. The power of the microwave was 400 W and the reaction time was 10 min. The chemical reaction is given by:



2.4. UV-Vis absorption spectrum

UV-Visible (UV-Vis) absorption spectrum investigation was carried out with a photometer (UV757CRT), and the result is shown in Fig. 2. The only peak that appeared at 441 nm is the absorption peak of –N=N–, which is caused by n → π* transition.

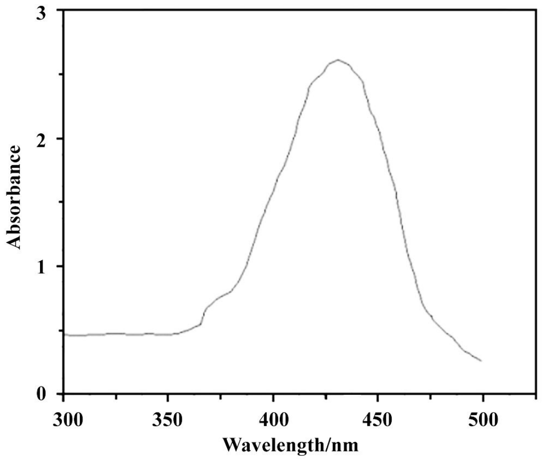


Fig. 2. UV-Vis absorption spectrum of phenol polyphosphazene grafted by 2,4-dinitroaniline.

2.5. Infrared absorption spectrum

Infrared (IR) absorption study was carried out with a spectrograph (EQUINOX55), and the IR absorption spectrum is shown in Fig. 3. It can be seen that the characteristic absorption peaks of $–NO_2–$ appear at 1521 cm^{-1} and 1339 cm^{-1}. The peaks of –P–O–C– are obtained at 1049 cm^{-1} and 927 cm^{-1}. The vibration absorption peak of –P=N– appears at 1195 cm^{-1} and the characteristic absorption peak of –N=N– appears at 1595 cm^{-1}. The peak obtained at 855 cm^{-1} is the p-disubstituted peak of benzene ring. The C–H stretching vibration absorption peak appears at 3080 cm^{-1} and stretching vibration absorption peak of C=C appears at 1450 cm^{-1}. The characteristic absorption peak of benzene ring appears at 730 cm^{-1}. All the results indicate that the phenol polyphosphazene grafted by 2,4-dinitroaniline was synthesized successfully.

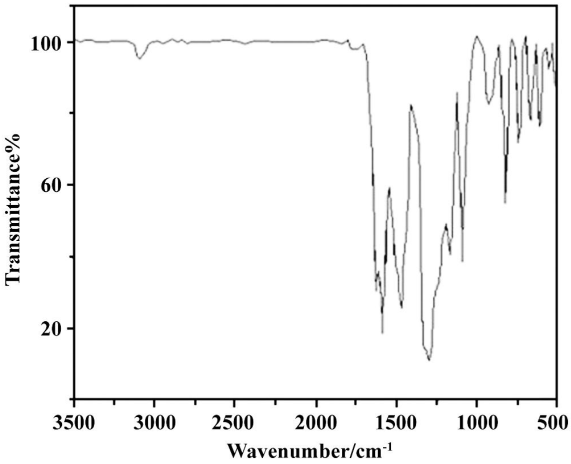


Fig. 3. IR absorption spectrum of phenol polyphosphazene grafted by 2,4-dinitroaniline.

2.6. Simple reflection method

EO coefficients of the products were tested through a simple reflection method [9, 10], the schematic diagram of which is shown in Fig. 4.

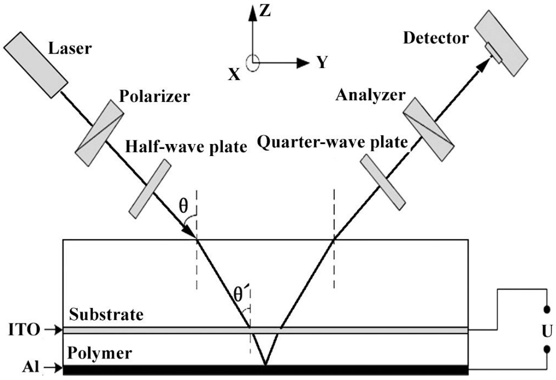


Fig. 4. Schematic diagram of simple reflection method.

After propagating through a polarizer and half-wave plate, the incident light enters the glass substrate at the incidence angle of θ. The incident light is reflected at the surfaces of the glass substrate and aluminum electrode. Then, the incident light approaches the polymer surface at the incidence angle of θ'. Double refraction occurs between the polarized light p and s in the polymer. After propagating through the analyzer and quarter-wave plate, the emergent light goes into the detector. In the cross-polarization system, the light intensity can be given by:

$$I_{out} = 2I_c \sin^2 \frac{\phi_{sp}}{2} \tag{1}$$

where 2Ic stands for the maximum value of the light intensity, and φ_{sp} stands for the phase difference. Now, EO coefficient can be calculated provided that the change of the light intensity could be obtained. Assuming $\gamma 33 = 3\gamma 31$, EO coefficient can be given by:

$$\gamma 33 = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \cdot \frac{\left(n^2 - \sin^2\theta\right)^{3/2}}{\left(n^2 - 2\sin^2\theta\right)\sin^2\theta} \tag{2}$$

where V_m is the maximum value of the voltage and I_m is the electric current. λ stands for the wavelength and n for the refractive index.

3. Results and discussion

3.1. Effect of different NLO mixing proportiona on EO coefficient

For the further improvement of EO properties of polydichlorophosphazene, small NLO molecules were mixed with phenol polyphosphazene grafted by 2,4-dinitroaniline through physical methods. Here, EDB and 6OCB were selected, and the molecular formula of them are shown in Fig. 5.

Ten groups of samples with different EDB mixing proportions of 1 wt.% to 10 wt.% with 1 wt.%

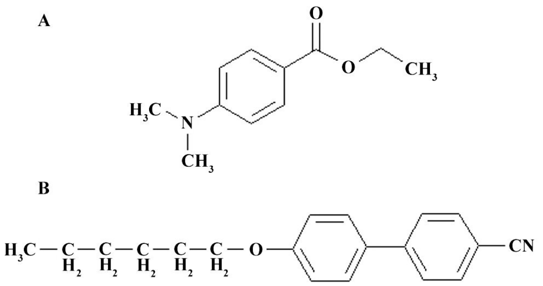


Fig. 5. Molecular formula of (A) EDB and (B) 6OCB.

increment were prepared. Another ten groups of samples were prepared with different 6OCB mixing proportions of 1 wt.% to 10 wt.% with 1 wt.% increment. EO coefficients of the samples were tested by a simple reflection method. The test results are shown in Fig. 6.

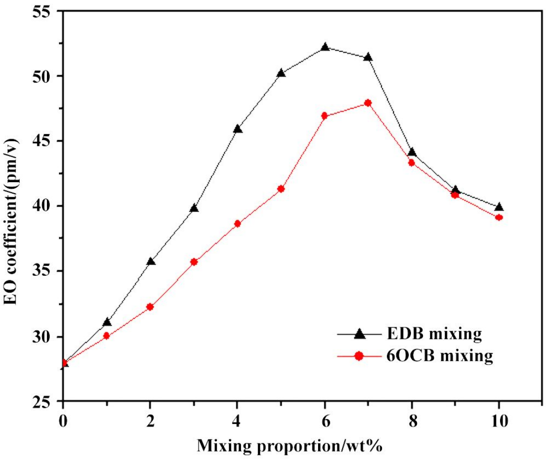


Fig. 6. Effect of NLO molecules on EO coefficient.

For both EDB and 6OCB mixing proportions, it can be seen that EO coefficient increases as the mixing proportion increases, reaches the peak around 6 wt.% to 7 wt.% mixing proportion and then decreases when the content of EDB and 6OCB increases further. We can conclude that after reaching the critical value, the glass transition temperature falls dramatically with the rising NLO molecules content, which leads to phase separation during the poling process. The NLO molecules precipitated from the polymer reduced the transparency of the sample, which caused a decrease in EO coefficient. From the plots, some other important information can be obtained, as well. For EDB mixing, the maximum value of EO coefficient is 52.2 pm/V with the mixing proportion of 6 wt.% while it is 47.9 pm/V for 6OCB with the mixing proportion of 7 wt.%. Compared with their initial values, the enhancement of EO coefficient is 85.8 % and 70.5 %, respectively.

3.2. Effect of polarizing temperature on EO coefficient

Disordered chromophore groups rearrange themselves along the field direction, and this process is commonly defined as polarization [11]. Moreover, polarization should occur near the glass transition temperature of the polymer. The glass transition temperature has been tested by a differential scanning calorimeter (DSC). For EDB mixing, the glass transition temperature is 80 °C, while it is 81 °C for 6OCB mixing. The schematic illustration of the polarization is shown in Fig. 7.

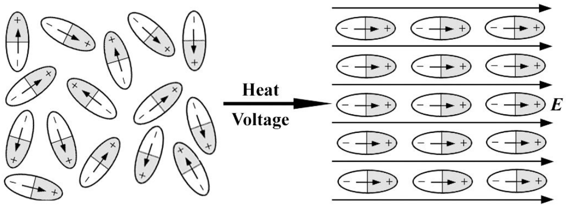


Fig. 7. Schematic illustration of polarization.

Corona discharge method with the voltage of 9 kV and the current of 40 mA was used for sample polarization. The effect of polarizing temperature on EO coefficient is depicted in Fig. 8 and Fig. 9. It can be seen that EO coefficient of the sample at 75 °C polarizing temperature increases faster than that at 65 °C polarizing temperature for both EDB mixing and 6OCB mixing.

3.3. Optimal sample morphology

Fig. 10 and Fig. 11 show the SEM photographs of the samples with optimal mixing proportions. The sample composed of 94 wt.% polymer and 6 wt.% EDB is marked as sample one, while the sample composed of 93 wt.% polymer and 7 wt.% 6OCB is marked as sample two. It can be seen that both EDB and 6OCB are distributed evenly inside

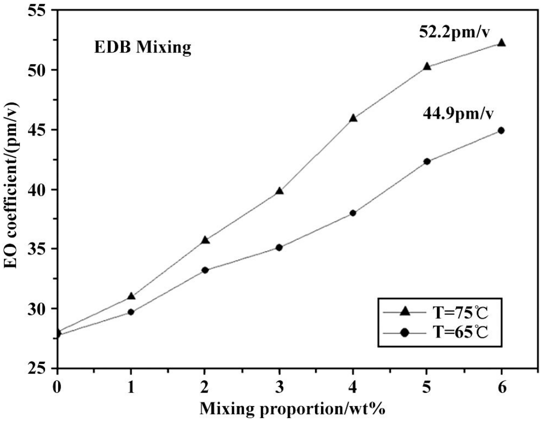


Fig. 8. EO coefficient at different polarizing temperatures for EDB mixing.

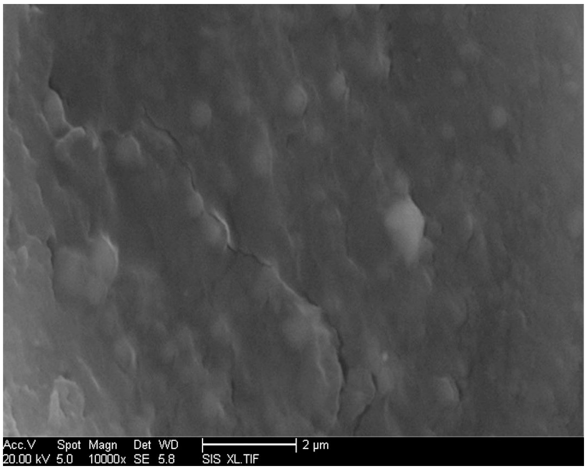


Fig. 10. SEM of sample one.

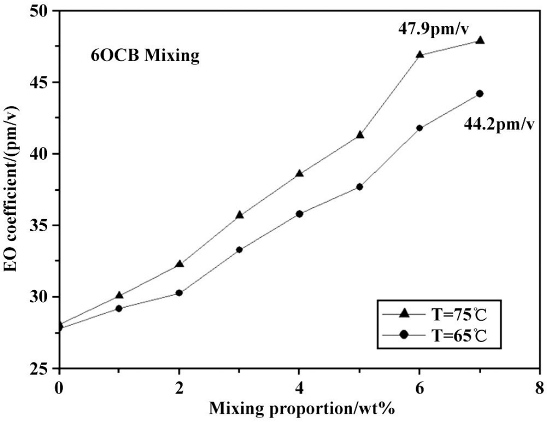


Fig. 9. EO coefficient at different polarizing temperatures for 6OCB mixing.

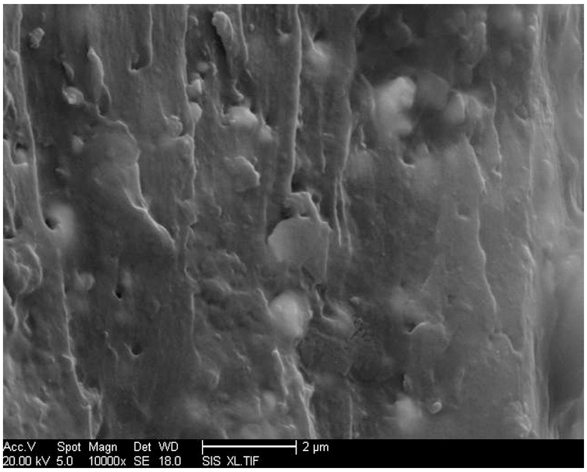


Fig. 11. SEM of sample two.

the polymer. There are no precipitates and phase separation in the SEM images, which indicates that our product possesses good phase stability.

3.4. Orientation stability testing

After polarization, dielectric relaxation happens to chromophore groups. Thus, the second-order nonlinearity of the polymer decreases as relaxation begins [12]. The two samples were placed for 600 h at room temperature and their EO coefficients were tested every 50 h. Fig. 12 shows the testing result. It can be seen that EO coefficients drop to 77 % and 75 % of their initial values, respectively.

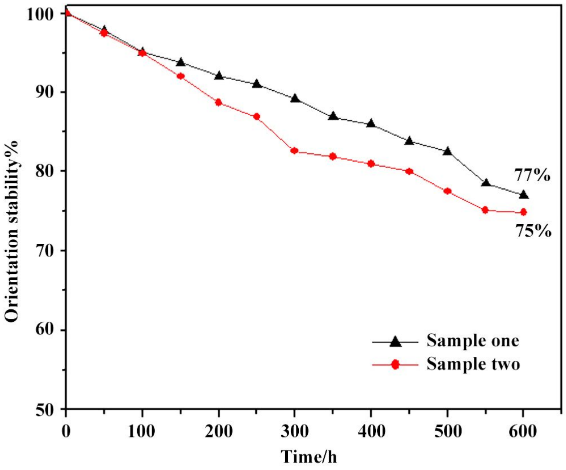


Fig. 12. Orientation stability testing result.

4. Conclusions

Phenol polyphosphazene grafted by 2,4-dinitroaniline was synthesized and characterized successfully. Small NLO molecules mixing can improve the EO coefficient effectively. For EDB mixing at 6 wt.%, the enhancement of EO coefficient was 85.8 % while for 6OCB mixing at 7 wt.%, the improvement of EO coefficient was 70.5 %. In addition, polarizing temperature has also affected the EO coefficient. After keeping at room temperature for 600 h, EO coefficients of the samples with optimal mixing proportion dropped to 77 % and 75 % of their initial values, respectively. It means that our products possess excellent EO properties although dielectric relaxation still exists. Our results show that EDB mixing enhances EO coefficient more than 6OCB mixing. However, both the samples, possessing not only high EO coefficient but also good phase stability, can be good candidates for the application in information technology.

Acknowledgements

This work was supported by the Natural Science Foundation of Heilongjiang Province (E201445), and the Innovative Talents Project of Harbin (2016RAQXJ025).

References

[1] GORKOVENKO A.I., PLEKHANOV A.I., SIMANCHUK A.E., YAKIMANSKIY A.V., *J. Appl. Phys.*, 116 (2014), 223104.

[2] LIU J.L., WANG L., ZHEN Z., *Colloid Polym. Sci.*, 290 (2012), 1215.

[3] ISSAM A.M., HARIS M., *J. Inorg. Organomet. P.*, 19 (2009), 454.

[4] LI R., XIE J., PANG M., *Mater. Lett.*, 67 (2012), 103.

[5] ZHANG Y., QIU C.J., LI Y., ZHANG W.L., WANG X., *Mater. Sci.-Poland*, 32 (2014), 402.

[6] MIN J.C., SANG K.L., JIN J.I., DONG H.C., DALTON L.R., *Thin Solid Films*, 515 (2006), 2303.

[7] ZHANG Y., LI Y., WANG X., QIU C.J., *Mater. Lett.*, 136 (2014), 449.

[8] QUINTANA J.A., BOJ J.A., VILLALVILLA J.M., ORTIZ J., FERNANDEZ-LAZARO J., SASTRE-SANTOS A., DIAZ-GARCIA M.A., *Appl. Phys. Lett.*, 87 (2005), 261111.

[9] YAMADE T., OTOMO A., *Opt. Express*, 21 (2013), 29240.

[10] YOU J.C., MI S.K., JU-YEON L., *Mol. Cryst. Liq. Cryst.*, 539 (2011), 102.

[11] MCKENNA E.M., LIN A.S., 2007. *J. Opt. Soc. Am. B*, 24 (2007), 2888.

[12] YU W.W., FU H.K., ZHANG D.Z., DU M., ZHENG Q., *Acta Polym. Sin.*, 9 (2013), 1212.

Received 2016-11-10
Accepted 2019-04-23