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Enhanced electro-optic property of host-guest polyphosphazene thin film and its application

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ABSTRACT

A new synthetic method by doping two kinds of chromophoric groups into polyphosphazene was reported in this paper. One kind of the chromophoric group (phenol nitro azobenzene) was grafted to the polymer by chemical method for polar improvement of the main chain, and the product was phenol polyphosphazene grafted by paranitroaniline. Then another small nonlinear optical molecule (NOL) was mixed into the polymer by physical method for further improvement of EO property. Here ethyl 4-(dimethylamino) benzoate (EDB) and 4-6-alkoxy-4′-cyano-biphenyl (6OCB) were selected respectively. The effect on EO coefficient by different mixing proportion was investigated and the test of the sample orientation stability was performed. Experimental results show that the material possesses not only high EO coefficient but also fine phase stability. The enhancement of EO property by EDB mixing is more obvious than that by 6OCB and the maximum value of EO coefficient can be 52.2 pm/v. Finally, the polymer thin films were used to detect terahertz (THz) radiation. It is found that the detecting efficiency and the spectrum sensitivity are enhanced largely compared with conventional inorganic crystal.

1. Introduction

EO polymer, especially host-guest one, has been a researching focus for its unique EO property in recent years [1–4]. This kind of material shows higher EO coefficient, greater photoconductivity, lower dielectric constant and better controllability [5–7]. However, the phase separation between the host and guest was a serious problem all the time which limited the enhancement of electro-optic property.

A synthetic method to solve the problem by doping two kinds of chromophoric groups into polyphosphazene was reported in this paper. One kind of the chromophoric group (phenol nitro azobenzene) was grafted to the polymer by chemical method for polar improvement of the main chain, and the product was the side chain electro-optic (EO) polymer phenol polyphosphazene grafted by paranitroaniline. UV–visible absorption spectrum and infrared absorption spectrum were utilized for structure characterization. Then another small NOL was mixed into the side chain polymer by physical method for further improvement of EO property. Here, two kinds of NOL, EDB and 6OCB, were selected respectively. EO coefficient was tested by the simple reflection technique and the test of the sample orientation stability is performed [8,9]. Experimental results show that the material possesses not only high EO coefficient but also fine phase stability. The effects on EO coefficient by different kinds of NOL and different mixing proportions were investigated in great details. Finally, thin films of our products and conventional inorganic crystal were prepared to detect THz radiation. The time domain waveform and the frequency spectrum of THz wave were obtained. Compared with ZnTe crystal, changes of the detecting efficiency and the spectrum sensitivity were analyzed and discussed.

2. Experimental procedures

Phenol polyphosphazene grafted by paranitroaniline was synthesized by dry phenol polyphosphazene, paranitroaniline, potassium bisulfate, sodium nitrite and distilled water under condition of the microwave heating method [10]. The power of the microwave was 400 W and the reaction time was 10 min. The highest productivity was 78.9% and EO coefficient of the product is 28.1 pm/v. UV–vis absorption spectrum was tested by photometer (UV757CRT) and infrared (IR) absorption spectrum was tested by spectrograph (EQUINOX55). Based on phenol polyphosphazene grafted by paranitroaniline, ten groups of samples were prepared

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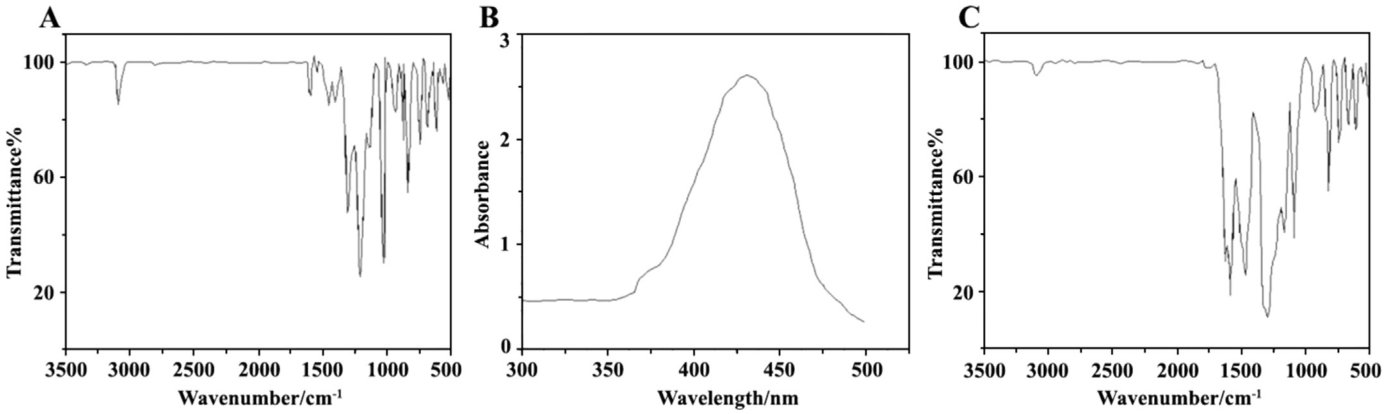

Fig. 1. (A) IR spectrum of phenol polyphosphazene. (B) UV–vis and (C) IR spectrum of phenol polyphosphazene grafted by paranitroaniline.

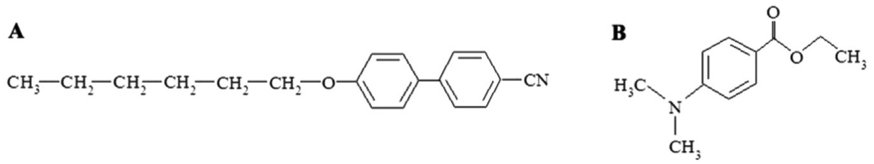

Fig. 2. (A) The molecular formulas of 6OCB and (B) EDB.

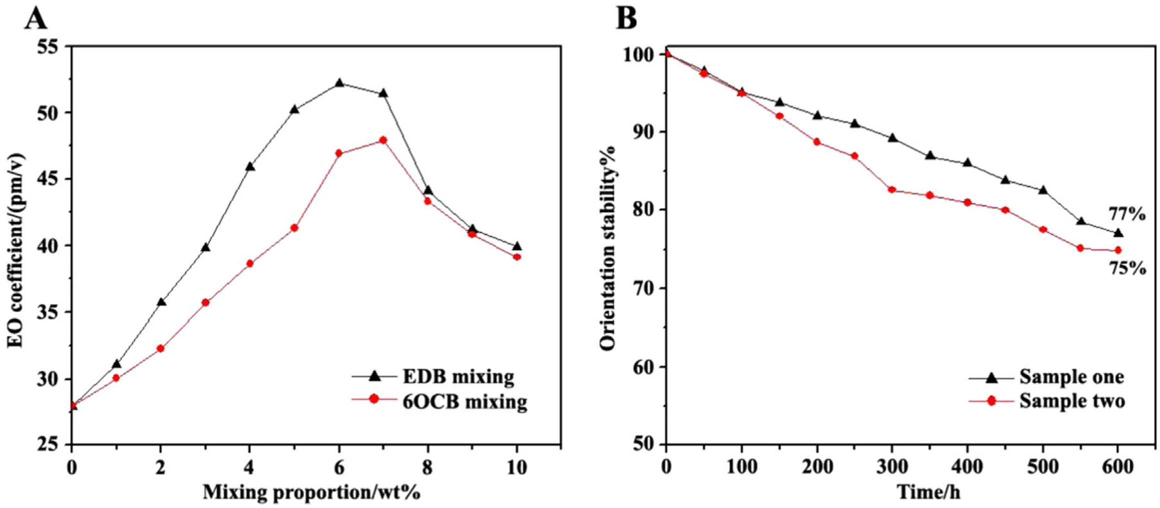

Fig. 3. (A) Effect on EO coefficient by different mixing proportion. (B) Orientation stability testing result. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with different EDB mixing proportion of 1–10 wt%. Also, another ten groups of samples were prepared with different 6OCB mixing proportion of 1–10 wt%. EO coefficients were tested by simple reflection method respectively. In order to test the orientation stability, two samples with optimal mixing proportion were placed for 600 h at room temperature and EO coefficients were tested every 50 h.

Next, the samples with optimal mixing proportion were selected to form polymer thin films by spin-coating method. The tetrahydrofuran (C_4H_8O) was selected as solvent and the rotational speed was 3000 r/min. Every 30 s, a thin film with the thickness of several microns could be obtained. After drying for 12 h, the film was poled by corona poling technique with the voltage of 9 kV, the current of 40 μA and the temperature of 65 °C.

In our experiments, the excitation of THz wave was based on optical rectification principle, and the detection of THz wave proceeded by free space electro-optic sampling technique. Furthermore, our product was used to detect THz wave instead of ZnTe crystal while the excitation of THz wave was unchanged.

3. Results and discussion

Fig. 1(A) shows the IR spectrum of phenol polyphosphazene, while Fig. 1(C) is that of phenol polyphosphazene grafted by paranitroaniline. It can be seen that the vibration absorption peek of P=N appears at 1195 cm^{-1}. The characteristic absorption peeks of P–O–C appear at 1050 cm^{-1} and 927 cm^{-1}, while the ones of P–N appear at 1320 cm^{-1} and 752 cm^{-1}. The C–H stretching vibration absorption peek appears at 3080 cm^{-1} and the p-disubstituted peek of benzene appears at 855 cm^{-1}. The peeks obtained at 1600 cm^{-1} and 1450 cm^{-1} are the characteristic absorption peeks of C=C. Fig.1(B) shows the UV–vis spectrum of phenol polyphosphazene grafted by paranitroaniline. The only peek obtained between 400 nm and 450 nm is the absorption peek of azo group caused by n-π^* transition. All the results indicate that phenol polyphosphazene grafted by paranitroaniline is synthesized successfully.

The molecular formulas of EDB and 6OCB are shown in Fig. 2. The effect on EO coefficient by different NOL mixing proportion is