Electro-optic Coefficient Measurement of the Double Electro-Optic Molecules Polymer based on Terahertz Application

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Abstract

In the terahertz (THz) science research field, electro-optic (EO) polymer possesses many superior characters compared with mineral crystal. Two kinds of the side group EO polymer, polyphosphazene with plmaol grained by 2, 4-dinitroaniline and polyphenylacrylate containing p-nitro bisazo group, are synthesized and characterized. For higher EO coefficient, the double EO molecules polymer thin films are prepared by mixing a small nonlinear optical (NLO) molecule into the side group EO polymer. The principles of preparation are given and the EO coefficients are tested. The effect on the EO coefficients by different mixing proportion and different poling temperature are analyzed in details. Experiments results show that the double EO molecules polymer has fine stability, higher EO coefficient and can be easily processed. This kind of material has the potential to be widely applied in the emission and detection of THz radiation.

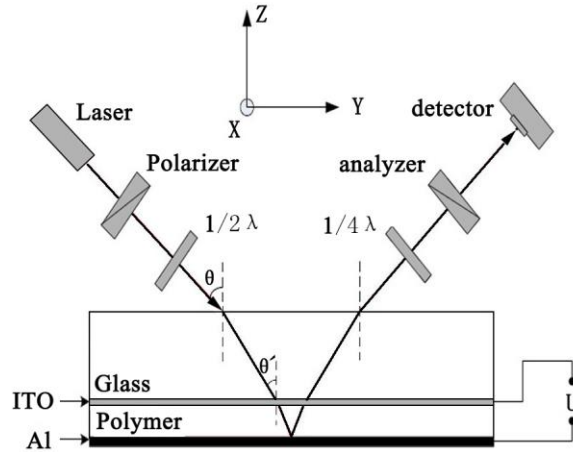*Keywords: THz science; mineral crystal; double EO molecules polymer; EO coefficient*

1. Introduction

EO polymer has been the research focus in THz science field nowadays. Compared with mineral crystal, EO polymer possesses many superior characters. This kind of material is very stable against temperature, oil, radiation, solvents and so on [1, 2]. Meanwhile, EO polymer has fast response time，good plasticity, simple device fabrication and good mechanical property. The most important thing is that this polymer possesses higher EO coefficient than other mineral crystal materials. Due to these unique functional properties, EO polymer have been developed and utilized in biomedicine, liquid crystals, aerospace, power electronics, energy storage and generation, membrane science, elastomers, surface science, photoelectric functional materials, military manufacturing and biomedical science [3, 4, 5].

Although the EO coefficient of the EO polymer has been improved, it is still not enough to meet the requirement of scientific research. Two kinds of the side group EO polymer, polyphosphazene with plmaol grained by 2, 4-dinitroaniline and polyphenylacrylate containing p-nitro bisazo group, are synthesized and characterized [6, 7]. The UV-visible absorption spectrum and the IR spectrum are obtained. The EO coefficients are tested by the simple reflection technique. For higher EO coefficient, the double EO molecules polymer thin films are prepared by mixing a small nonlinear optical (NLO) molecule into the side group EO polymer. The EO coefficients are tested.

2. Simple Reflection method

Under the influence of electro-optic effect, the phase delay of the linearly polarized light happens. The interference of p light and s light can reflect the EO coefficient of the polymer. This method is named the simple reflection technique [8]. The schematic of the method is shown in Fig.1.

Figure 1 The Schematic of the Method

Incident light is converted to the linearly polarized light under the action of the polarizer. Than the linearly polarized light reaches the glass surface with the incidence angle of θ and refracts twice at the glass surface and the ITO respectively. Next, the light reaches the surface of the polymer with the incidence angle of θ'. Under the influence of electro-optic effect, birefringence effect of the p light and s light happen that is reflected by the Al electrode. Than the p light and s light propagate though the 1/4 slide, and refract with each other at the analyzer. The results are tested by the detector and the lock-in amplifier.

The light intensity at the detector is given by:

$$I_{out} = 2 I_c \sin^2 \frac{\varphi_{sp}}{2}$$ (1)

$2I_C$ is the maximum value of the output light intensity, and φ_{sp} is the phase displacement. Suppose $\gamma_{33} \approx 3\gamma_{31}$, than the coefficient can be given by:
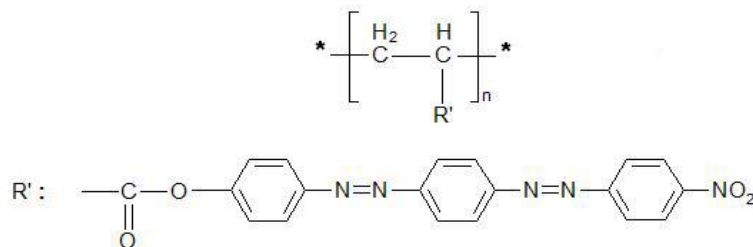
$$\gamma_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \cdot \frac{\left(n^2 - \sin^2\theta\right)^{3/2}}{\left(n^2 - 2\sin^2\theta\right)\sin^2\theta}$$ (2)

The λ is the wavelength of the laser and n is the refractive index of the polymer. The V_m is the peak value of the voltage and I_{mo} is the light intensity.
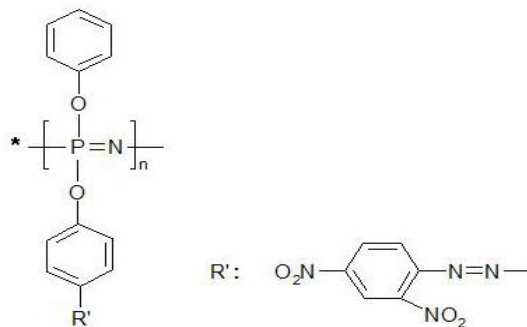
3. Side Group EO Polymer

3.1. Synthesis of the Material

The diazonium salt solvent was made from p-nitro azo aniline, NaNO2, hydrochloric acid, and water. The polyacrylic acid benzyl ester, THF, NaOH, distilled water, sodium dodecyl benzene sulfonate are stirred together to form the yellow solvent. Than the yellow solution react with the diazonium salt solution with the temperature of 0-4℃ and the PH value of 5-7. The polyphenylacrylate containing p-nitro bisazo group can be obtained by drying the reaction product. The molecular formula is shown in Figure 2.

Figure 2 The Molecular Formula of the Polyphenylacrylate Containing p-nitro Bisazo Group

The phenol polyphosphazene, 2, 4-dinitroaniline, sodium nitrite, potassium bisulfate and distilled water are placed together to react for a period of time. Than the polyphosphazene with plmaol grained by 2, 4-dinitroaniline can be obtained by washing and drying the dark red reaction product. The molecular formula is shown in Fig.3.
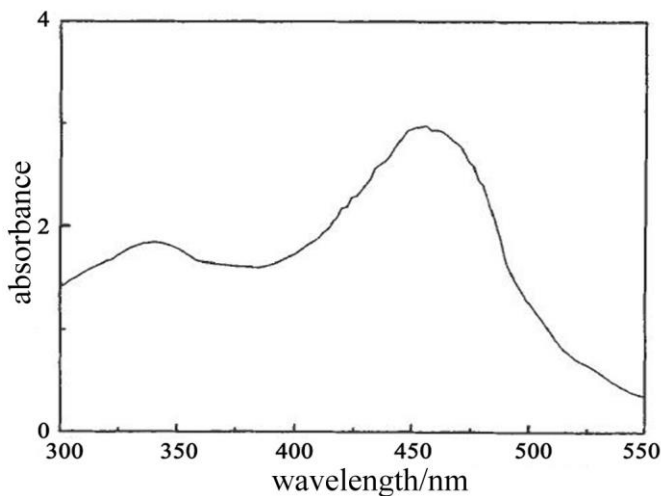

Figure 3 The Molecular Formula of the Polyphosphazene with plmaol Grained by 2, 4-dinitroaniline
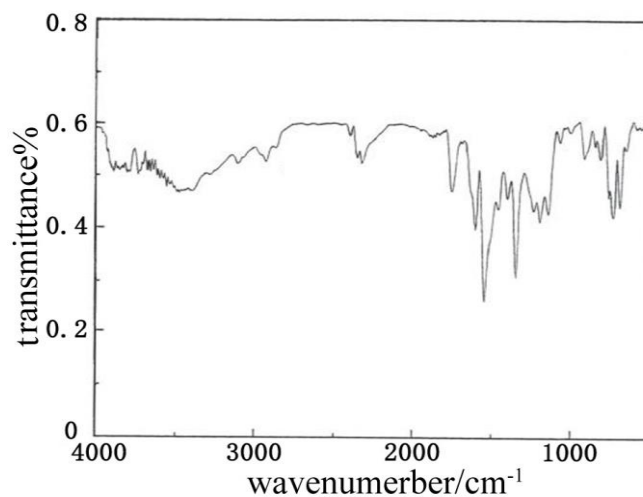
3.2. Structure Characterization

The UV-visible absorption spectrum of the polyphenylacrylate containing p-nitro bisazo group is shown in Fig.4. The peak appeared at 425 nm to 475 nm is the absorption peak of azo group, which are the result of the n-π* transition. The result indicates that the azo group has been grafted to the main chain successfully. The IR spectrum of the polyphenylacrylate containing p-nitro bisazo group is shown in Fig.5. The peaks obtained at 1330cm-1 and 1588 cm-1 are the characteristic absorption peaks of the C-O and N=N. The absorption peak of the

benzene p-substituted appears at 845cm-1. These absorption peaks observed indicate that the reaction product is the polyphenylacrylate containing p-nitro bisazo group really.
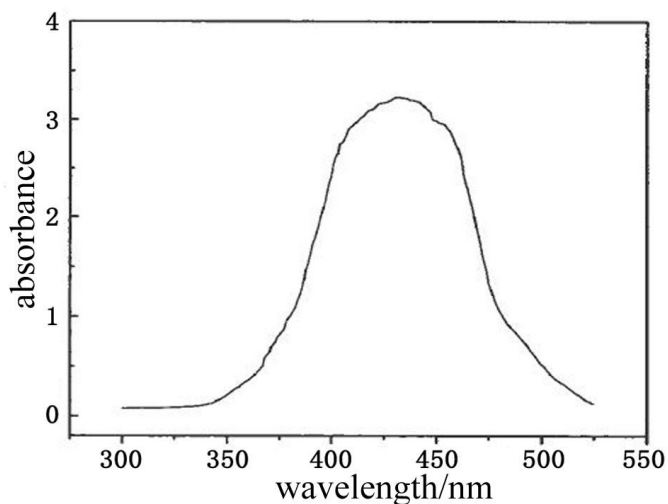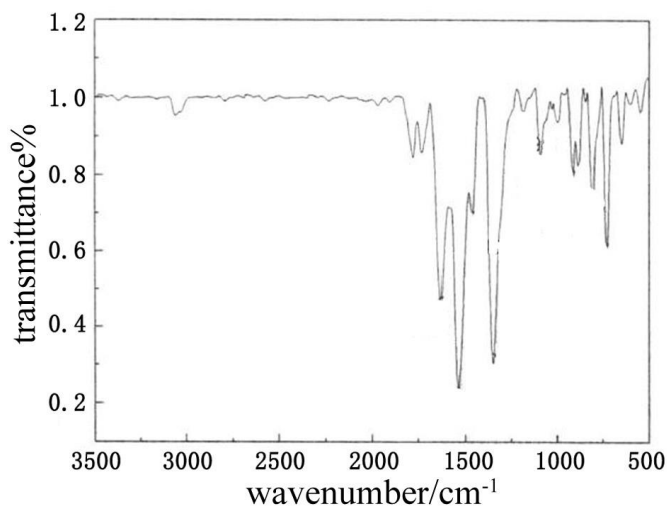

Figure 4 UV-visible Absorption Spectrum

Figure 5 The IR Spectrum

The UV-visible absorption spectrum of the polyphosphazene with plmaol grained by 2, 4-dinitroaniline is shown in Fig.6. The peak appeared at 400 nm to 475 nm is the absorption peak of azo group (N=N), which are the result of the n-π* transition. This indicates that the azo group has been grafted to the phenol polyphosphazene successfully. The IR spectrum of the polyphosphazene with plmaol grained by 2, 4-dinitroaniline is shown in Fig.7. The peaks obtained at 1050cm-1 and 927 cm-1 are the characteristic absorption peaks of the P-O-C. The peaks obtained at 1195cm-1 and 1450 cm-1 are the stretch absorption peaks of the P=N and C=C. The benzene p-substituted peak appears at 855 cm-1 and the benzene characteristic absorption peak appears at 731 cm-1. These results observed indicate that the reaction product is the polyphosphazene with plmaol grained by 2, 4-dinitroaniline really.

Figure 6 UV-Visible Absorption Spectrum

Figure 7. The IR Spectrum

3.3. Measurement of the EO Coefficient

The EO coefficients of the two side group EO polymers are tested by simple reflection method. The EO coefficient of the polyphenylacrylate containing p-nitro bisazo group is 12.36 pm/V and the EO coefficient of the polyphosphazene with plmaol grained by 2, 4-dinitroaniline is 13.64 pm/V.

4. Double EO Molecules Polymer

4.1. Physical Mixture of the Small EO molecule

Based on the side group EO polymer, double electro- optic molecules polymer can be obtained through small EO molecule physical doping for higher EO coefficient. Ethyl 4-dimethylaminobenzoate (EDB) has been chosen as a small EO molecule for the experiment to improve the EO coefficient. The molecular formula of EDB is shown in Figure 8.
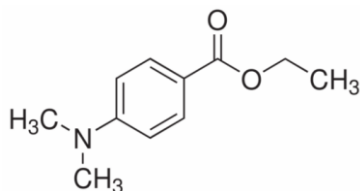
Figure 8 The Molecular Formula of EDB

4.2. The Effect on the EO Coefficients by Different Mixing Proportion

In order to know the effect on the EO coefficients by different mixing proportion, nine groups of EDB with different qualities are mixed into the two kinds of the double EO molecules polymers respectively. The polyphenylacrylate containing p-nitro bisazo group is chosen as sample A and the polyphosphazene with plmaol grained by 2, 4-dinitroaniline is chosen as sample B. The qualities of EDB are 2wt%、3wt%、4wt%、5wt%、6wt%、7wt% 、8wt%、9wt%、10wt%. Than the EO coefficients of all the samples are tested. The results are shown in Fig.9.
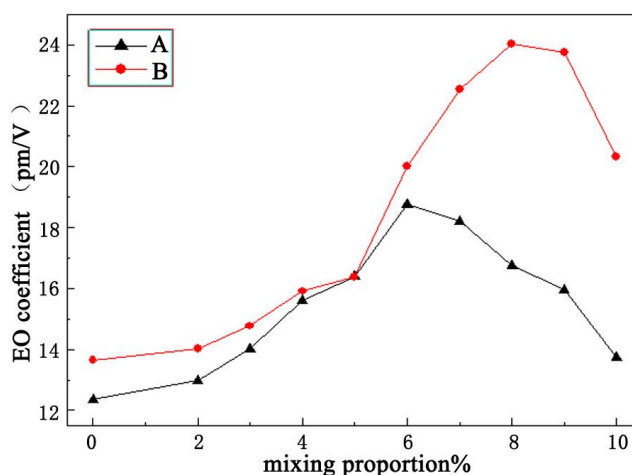

Figure 9 The Effect on the EO Coefficients by Different Mixing Proportion

For the polyphenylacrylate containing p-nitro bisazo group, the EO coefficient increases as the mixing proportion becomes larger. When the mixing proportion is 8wt%, the EO coefficient reaches its maximum value. Then the EO coefficient decreases as the mixing proportion becomes larger. The variation tendency of the polyphosphazene with plmaol grained by 2, 4-dinitroaniline is the same as the polyphenylacrylate containing p-nitro bisazo group. The only difference is that the EO coefficient reaches its maximum value when the mixing proportion is 6wt%. All the experimental results show that physical mixture of the small EO molecule can indeed improve the EO coefficient, although the effects are different for different materials. The decrease of the EO coefficient is due to the high mixing proportion, which leads to the dropping of the glass transition temperature.

4.3. The effect on the EO coefficients by different poling temperature

Poling is that the chromophores in the EO polymer orient according to the direction of the external economy electric field [9, 10]. In order to know the effect on the EO coefficients by different poling temperature, the EO coefficients of the two samples with suitable mixing proportion are tested respectively. The poling temperatures are 65℃ and 75℃. The results are shown in Fig.10 and Fig.11.
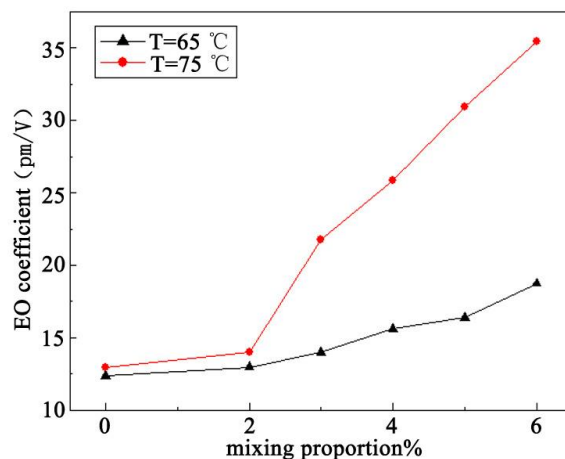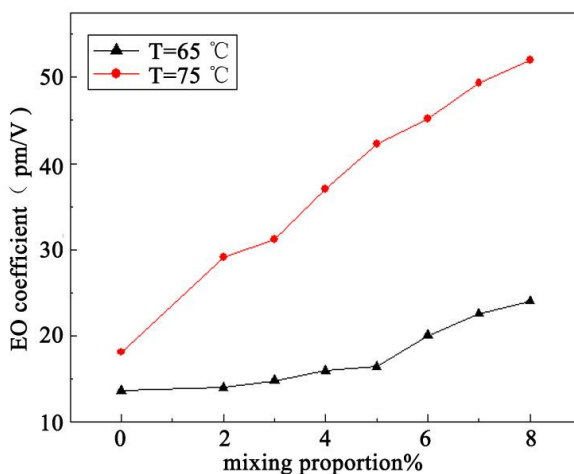

Figure 10 The Result for Sample A

Figure 11 The Result for Sample B

5. Conclusions

The experimental results show that the EO coefficients can be improved by small EO molecule physical doping, while the maximum values are got at different mixing proportions for different polymers. For the polyphenylacrylate containing p-nitro bisazo group, the EO coefficient is improved by 51.7%. For the polyphosphazene with plmaol grained by 2, 4-dinitroaniline, the EO coefficient is improved by 76.1%. Especially, the maximum value for the polyphosphazene with plmaol grained by 2, 4-dinitroaniline can be 24.02 pm/V. In addition, the poling temperature can affect the EO coefficients too. The EO coefficient

increases as the poling temperature becomes larger. The poling temperature must be around the glass transition temperature, the closer the batter.

In conclusion, the double EO molecules polymer has fine stability, higher EO coefficient and can be easily processed. This kind of material has the potential to be widely applied in the emission and detection of THz radiation.

Acknowledgements

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