Materials Letters 154 (2015) 51–54

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

# Synthesis and characterization of polymethyl methacrylate with double electro-optic molecules thin film and its application

Zhang Ying [a,*], Li You [a,b]

[a] State Key Laboratory Breeding Base of Dielectric Engineering, Harbin University of Science and Technology, Harbin 150080, China
[b] Harbin Research Institute of Electrical Instruments, Harbin 150028, China

ARTICLE INFO

*Article history:*
Received 7 March 2015
Accepted 15 April 2015
Available online 22 April 2015

*Keywords:*
PMMA
Double EO molecules
Polymers
EO coefficient
Thin films
Terahertz

ABSTRACT

Polymethyl methacrylate (PMMA) with double electro-optic (EO) molecules was synthesized. One kind of chromophoric groups, hydroxyethyl carbazole, reacted with PMMA by a chemical method to form poly (methacrylic acid ethyl carbazole ester). Another small nonlinear optical molecule (NOL), 4–6-alkoxy-4′-cyano-biphenyl (6OCB), was mixed into the polymers by a physical method to further improve EO properties. The structure of the material was characterized and the effect on EO coefficient of different mixing proportions was investigated. Photoconductive properties and the orientation stability were studied. Experimental results showed that the enhanced EO coefficient was 44.8 pm/V when the mixing proportion was 20 wt%. Thermally stimulated discharge current (TSDC) testing curves were obtained, which confirmed the existence of two depolarization processes. Thin films formed by this polymer material were used to detect terahertz (THz) radiation. The detecting efficiency and the spectrum sensitivity were enhanced largely compared with ZnTe crystal. It can be concluded that this polymer material is a very good candidate for THz application.



## 1. Introduction

EO materials are very crucial in the process of THz excitation and detection. During the past decades, THz technology has been widely utilized in the researching of communication, medical diagnosis and so on. Nowadays, the fast development calls for new materials possessing better EO properties. Compared with conventional inorganic crystals, EO polymers have many superior characters, which has been the research focus of most excellent scholars [1–4].

PMMA is one kind of functional polymers showing better EO properties, dielectric properties and mechanical properties. It is considered to be a good candidate for THz research [5,6]. In order to further improve its EO coefficient and phase stability, a method by doping two kinds of chromophores to PMMA is reported in this paper. One kind of chromophoric group, hydroxyethyl carbazole, reacted with PMMA by a chemical method to form poly(methacrylic acid ethyl carbazole ester). The structure of the product was characterized by UV–visible (UV–vis) absorption spectrum and infrared (IR) absorption spectrum. Another small nonlinear optical molecule, 4–6-alkoxy-4′-cyano-biphenyl (6OCB), was mixed into the polymers by a physical method to further improve EO properties. The effect on EO coefficient of different mixing proportions was analyzed in details. Depolarization process was sketched and characteristic parameters were tested by the TSDC method. Photoconductive properties were studied and the test of orientation stability was performed. Finally, thin films of PMMA with double EO molecules, with a suitable 6OCB mixing proportion of 20 wt%, were prepared to detect THz radiation. Compared with the detection results of ZnTe crystals [7,8], changes of the detection efficiency and the spectrum sensitivity were analyzed and discussed.

## 2. Experimental procedures

Poly(methacrylic acid ethyl carbazole ester) was synthesized by PMMA and hydroxyethyl carbazole by a esterification method. P-toluenesulfonic acid was selected as catalyst. The reaction temperature was 110 °C and the reaction time was 10 h [9]. The molecular formula of the product is shown in Fig. 1. The highest productivity is 83.7% and intrinsic EO coefficient is 12.3 pm/V. UV–vis absorption spectrum was tested by spectrometry photometer (UV-2550, Japan) and IR absorption spectrum was tested by Fourier transform spectrograph (IS10, USA). Then, 6OCB of different qualities were mixed into our product. The change of EO coefficient was investigated. Under the glass transition temperature condition, the sample with 20 wt% mixing proportion was placed for 600 h and EO coefficients were tested every 50 h.

* Corresponding author. Tel.: +86 451 86390143.
*E-mail address:* zhangying_yoyo@126.com (Z. Ying).

http://dx.doi.org/10.1016/j.matlet.2015.04.071
0167-577X/

Next, thin films formed by the product with 20 wt% mixing proportion were prepared by a spin-coating method. Tetrahydrofuran (THF) was selected as solvent. The rotational speed was 3000 r/min and the spin time was 50 s. After drying for 24 h, thin films with the thickness of several microns were obtained. Then, films were poled by corona poling technique with the voltage of 9 kV and the current of 45 μA. Depolarization process was sketched and characteristic parameters were tested by the TSDC method. Also, photoconductive properties were studied.

Finally, the polymer thin films were used to detect THz radiation instead of ZnTe crystal. Optical signals were converted to electrical signals by a differential detector and the results were tested by a lock-in amplifier.

## 3. Results and discussion

UV–vis absorption spectrum is shown in Fig. 2(A). The peeks appeared at 328 nm and 341 nm are the absorption peeks of carbazole groups, which are caused by $\pi$–$\pi^*$ transition. The peeks obtained at 249 nm and 295 nm are the absorption peeks of benzene ring, which are caused by n–$\pi^*$ transition. Fig.2(B) is the IR absorption spectrum. It can be seen that the stretching vibration absorption peeks of C–H, $-CH_3$ and C═O appear at 3050 $cm^{-1}$, 2940 $cm^{-1}$ and 1722 $cm^{-1}$ respectively. The peek obtained at 1600 $cm^{-1}$ is the characteristic vibration absorption peek of benzene ring, which overlaps the vibration absorption peek of C═C. The peeks appear at 1450 $cm^{-1}$, 1326 $cm^{-1}$ and 1135 $cm^{-1}$ are the stretching vibration peeks of $-CH_2$-, C–N and C–O. All the results above indicate that poly(methacrylic acid ethyl carbazole ester) is synthesized successfully.

The effect on EO coefficient of different 6OCB mixing proportions is shown in Fig.3(A). It can be seen that EO coefficient increases as the mixing proportion becomes larger, and reaches its maximum value of 44.8 pm/V at the mixing proportion of 20 wt%. When the mixing proportion is larger than 20 wt%, EO coefficient will be near saturation value. It can be concluded that when the mixing proportion is too high, the phase separation occurs during the poling process. The functional groups precipitated from the polymer lower the transparency of the sample, which leads to the saturation of EO coefficient. Here, it is important to note that vibrational contributions of the chromophore to EO coefficient are not considered temporarily [10]. Fig.3(B) shows the orientation stability testing result. We can see that EO coefficient drops to 71.3% of its initial value, which follows the dielectric relaxation law of the Kohlarush–Willians–Watt equation.

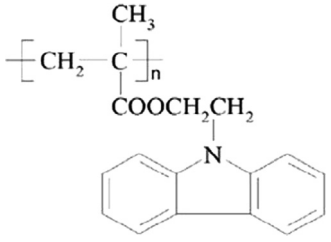


**Fig. 1.** Molecular formula of the polymer.

Fig.3(C) shows the photoconductivity of the polymer. It can be seen that the photoconductivity increases as the field intensity becomes larger, while the optical power density remains unchanged. It is the improvement of carrier mobility, caused by the enhancement of extra field, that leads to the increase of the conductivity. Also, we can see that the photoconductivity increases as the optical power density becomes larger, while the field intensity remains unchanged. It is because that the enhancement of optical power density leads to the increase of carrier concentration. The TSDC testing result is shown in Fig.3(D). The double peeks of the green dotted curve indicate that there must be two depolarization processes for PMMA with double EO molecules. We separate the curve into dissociation curve 1 and dissociation curve 2 by whole calculation method. The yellow dotted curve is the depolarization curve of poly(methacrylic acid ethyl carbazole ester), which is almost the same as dissociation curve 2. So it can be concluded that the double peeks of the green dotted curve stands for the two depolarization processes of the two EO molecules. One is carbazole group, the other is 6OCB. It can be calculated that the activation energy of carbazole group is 0.7 eV, and the relaxation time is $1.0*10^{-7}$ s. Similarly, the activation energy of 6OCB is 1.2 eV, and the relaxation time is $2.0*10^{-9}$ s.

Fig.4(A) and (B) shows the SEM photograph and the EDX test result of the polymer thin film. It can be seen that 6OCB is distributed evenly in the polymer matrix. There is no precipitation and phase separation phenomena, which indicates that our product possesses fine phase stability. Time domain waveform and frequency spectrum of THz radiation are shown in Fig.4(C) and (D). The full curve stands for testing result of PMMA with double EO molecules and the dotted curve for ZnTe crystal. We can see that the time domain width of terahertz wave is about 1 ps, the center frequency is about 1 THz and the spectral range is about 3 THz. As we all know, the amplitude of the waveform is usually named 'detecting efficiency' and the amplitude of the center frequency is named 'spectrum sensitivity'. Compared with ZnTe crystal, the detecting efficiency of our product is enhanced by 27.5% and the spectrum sensitivity is enhanced by 64%. The oscillations between 2 and 4 THz at the end of the curve are caused by the detecting light reflections between the top and bottom surface of the thin film, which is not the intrinsic feature of the polymer material.

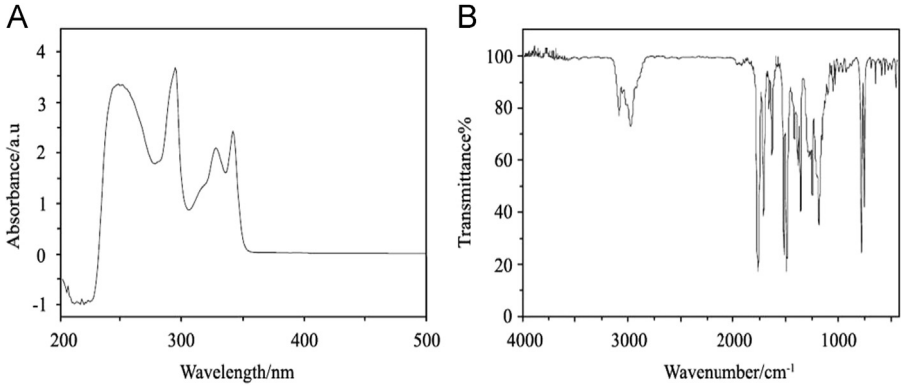


**Fig. 2.** (A) UV–vis spectrum and (B) IR spectrum.