Invited Paper

The New Terahertz Radiation and Detection Source Based on Organic Electro-Optic Poling Polymer

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Abstract: Due to the unique properties of terahertz waves, terahertz technology has been used in biomedicine, food inspection, environmental monitoring, security counter-terrorism and other fields concerning national economic and social development. High power broadband terahertz radiation and detection source material is needed to solve related problems urgently as the base of terahertz technology. This paper proposed to use a new kind of terahertz radiation and detection source material——simple processing electro-optic (EO) poling polymers with big nonlinear coefficient and thermal stability, which can replace the inorganic crystal by optical rectification effect for radiation and strong EO activity for detection. Through the research of polymeric EO performance, we designed and fabricated series of chromophores and polymers with different properties. By adjusting the type and concentration of chromophores, the combination of chromophores with polymer and the polarization process, we can obtain a high EO activity, high thermal stability and low dielectric constant polymer materials. We also use some advanced technology and theory to study the various factors affecting terahertz radiation efficiency.

Keywords: Terahertz radiation and detection, Electro-optic poling polymer, Electro-optic activity, Organic materials.

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1. Introduction

THz radiation is usually refers to an electromagnetic wave of the wavelength in the 0.03 *mm*-3 *mm* (0.1 *THz*-10 *THz*) range, and it is the band located between the microwave and infrared light in the electromagnetic spectrum (the junction region of the electronics and optics). In recent years, the research of THz science and technology has widespread for its unique properties. THz technology can be used in the time domain spectroscopy (gas phase spectroscopy study [1], the solution dynamics and charge transfer [2], identification of a compound structure [3], extracting important information from the DNA, drug analysis and other biomedical field [4]) and imaging technology. [5] (in vivo imaging, environmental monitoring and security anti-terrorism, etc. [6]) THz science and technology will play an important role in promoting the national economy and social development and be closely related with people's lives and social progress.

Over the last decade, many scientists are carrying out studies of THz radiation source by increase frequency from electronics method or by decrease frequency from optical method, ultra-short laser pulse excitation is found can generate broadband THz radiation pulse by two ways: photoconductive excitation mechanism [7] and optical rectification effect [8]. The broadband THz radiation source can be used for time-domain spectroscopy imaging systems and precision time-resolved spectroscopy application, the method of optical rectification effect is widely used for the wider bandwidth output for many kinds of radiation source materials. Recently, most of the radiation source materials are the inorganic EO crystals in optical rectification effect [9-10], but there is little study on organic crystals in this area for the harsh growing conditions [11-12]. Actually, as a radiation source material, the generation of THz wave by EO polymer is also based on optical rectification effect. In recent years, the application of EO poling polymer on the THz radiation and detection has become an international research hotspot. As early as 2002, Alexander and Hayden's research [13] had verified that the EO polymer is much better than ZnTe inorganic crystals or organic DAST crystal considering the efficiency of THz wave radiation and detection efficiency, and they also proved that with the same thickness, EO polymer (DAPC) has the radiation efficiency 10 *times* that of ZnTe and 5 *times* that of DAST. By improving the chemical structure of the chromophores, another EO polymer system (CFAPC) can obtain hundreds of times of THz radiation intensity than the ZnTe [14]. The polymer materials produced by the University of Washington got 15 *THz* wide band gap-free THz spectroscopy by unremitting efforts in 2008 [15], while Mr. Rahman [16] from the U.S. application of photonics research company also published an article to point out that waveguide devices with dendritic molecule of the EO polymer materials as efficient terahertz emission source is an ideal choice.

Because the synthesis of these active compounds is still relatively difficult without foundation inland, the EO polymer can meet the requirement of THz radiation and detection is rare. This paper shows optical property, electronic property, and high EO activity of the poling polymer materials including the active chromophores and the polymer matrix. The key technology based on our preliminary work which affects the EO performance is also discussed. We originally expound the factors which can affect high power and broadband terahertz output for this poling polymer. The research will provide the related basis for exploring the new terahertz radiation and detection source.

2. Experimental methods

2.1 Material and methods

The Simple Reflection Method (SRM) at 1310 *nm* was used to measure the E-O coefficient (r_{33}) [17]. According to our instrument, the error on r_{33} measurement was less than ±10%. The refractive index of the film was measured with a prism coupler (Metricon, model-2010) instrument at the wavelength of 1310 *nm*. The UV-vis property was performed on Hitachi U2001 photo spectrometer.

2.2 Experimental process

The EO polymer material contains the active chromophores (host part) and the polymer matrix (guest part), and the chromophore is the source of EO activity. Figure 1 shows the designed Chromophore 1 and 2 with a novel electron donor from the molecular point of view and the synthesis of two chromophores refers to our published literatures [18-19]. Relative to the traditional aniline donor, the new julolidine donor has the stronger electron-donating ability and greater steric hindrance, thus the interactions between dipole molecules is weaker and the EO polymer system has higher poling efficiency and larger EO activity (EO coefficient is higher). Compared to the Chromophore 1, Chromophore 2 with the thiophene and long carbon chain as steric and electron-donating groups is more complex, and the EO activity is much higher.

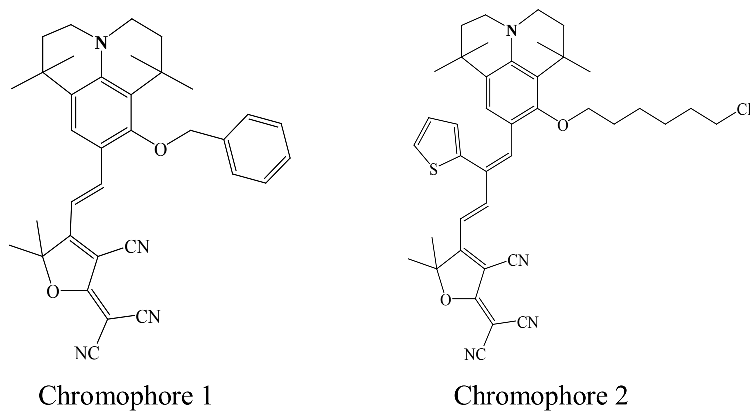

Fig. 1 The chemical structure of chromophore 1 and chromophore 2

EO polymer material has very good design flexibility, depending on the application requirements through different ways of preparing high EO coefficient polymer, such as host-guest doping, side chain, main chain, and cross-linking. Using chromophore molecular hyperpolarizability and the interaction between chromophores and the polymer, we study the mechanism of EO molecular orientation, seek to get high macroscopic EO activity, and explore the chromophore molecules in which polymer system easily align (poling process). Good film forming and easy processing have obvious advantages. It is much simpler and cheaper for the poling polymer than the cultivation of high-quality single-crystal to improve THz bandwidth. More commonly, polymer matrix includes modified poly (methyl methacrylate), polystyrene, polycarbonate (APC) and polyimide system. In our work we used polymer polycarbonate with good light and heat stability, in which polarization efficiency of chromophores was higher than other polymer film.

2.3 Poling and EO coefficient (r_{33}) measurements

To study the EO property derived from the chromophores, guest–host polymers were prepared by formulating chromophores 1 and 2 into amorphous polycarbonate (APC) using dibromomethane as the solvent (Polymer 1 and Polymer 2) with 40 *wt*.% concentration of chromophores. The resulting solutions were filtered through a 0.22 *mm* Teflon membrane filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 40 ℃ to remove the residual solvent. The poling process was carried out using corona method at a temperature of about 10 ℃ above the Tg of the polymer [20]. The r_{33} values were measured using Teng-Man simple reflection technique at the wavelength of 1310 *nm*.

3. Results and discussion

Table 1 shows the properties of the organic EO polymer materials. The UV-Vis absorption property of the synthesized chromophores was measured to explore the different π-conjugated systems in the chromophores. Chromophore 2 has the bigger π-conjugated system than Chromophore 1 because there are the thiophene and long carbon chain with electron-donating ability in the conjugated system. Therefore, EO coefficient of the Chromophore 2 is almost 10 *times* that of the Chromophore 1 in view of the big conjugated system and steric effect. The refractive index and dielectric constant was also measured, because the two parameters are relative with the THz properties. The refractive index n (1.60) of the poling polymer is close to $\sqrt{\varepsilon}$ (1.73), so the coherence length may be very long between laser pulse and THz wave.

Tab. 1 The properties of the EO poling polymer

Sample	λ_{max} in chloroform	EO coefficient (r_{33})	Refractive index n	Dielectric constant ε
Polymer 1	617 *nm*	36 *pm/V*	1.59	2.9
Polymer 2	702 *nm*	337 *pm/V*	1.60	3.0

Based on the physical mechanism of the optical rectification effect, we need to study the phase matching in terahertz radiation process. When the group velocity of the laser pulse is equal to the phase velocity of the terahertz wave, the optical rectification process could meet the phase matching condition. Since the optical rectification effect is a second-order nonlinear process, the radioactive THz electric field is proportional to the second-order nonlinear polarization. For the inorganic crystals, the maximum terahertz radiation efficiency strongly dependent on the the crystal direction and the polarization direction of the incident light can be calculated, while the electro-optical polymer material is only related with the polarization direction of incident light. Figure 2 shows the experimental apparatus. Through the polarizer to change the polarization direction of incident light, we can gain the maximum power THz waves from the detector. The electro-optic sampling based on the electro-optic effect was used for the detect THz wave. The EO coefficient of polymer materials is higher, the sensitivity of detector is better. The coherent detecting method is widely used because it can detect wide-frequency and high-accuracy THz wave.

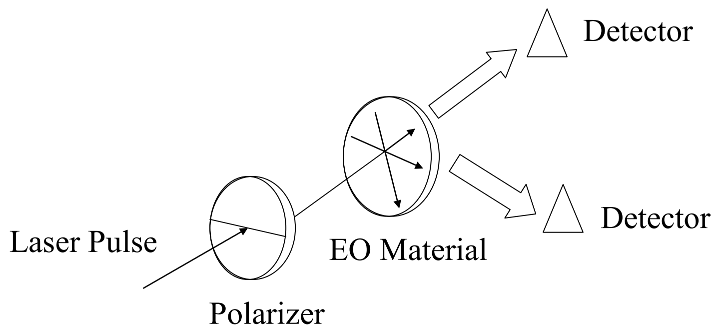

Fig. 2 The principle of the optical rectification effect for EO materials

By the mechanism of the optical rectification effect, the amplitude intensity and frequency distribution of terahertz wave are decided in the characteristics of the laser pulse and the nonlinear materials, such as the intensity and pulse width of the laser pulse, the second order nonlinear coefficient of the materials (electro-optic coefficient), the damage threshold and phase matching and so on. EO materials are the key components of optical rectification THz electromagnetic waves, and EO coefficient and phase matching are important factors that may affect the terahertz radiation efficiency. Here we propose electro-optic polymer as a new THz radiation and detection source, because organic nonlinear crystals have many advantages compared to the inorganic crystals. Firstly, EO polymer is made using simple spin-coating instead of demanding single crystal growth conditions (especially for organic crystals), and the poling polymer can be adjusted through the flexible design, which means significant savings in cost and time. Secondly, EO coefficient of the poling polymer is large and can continue to increase with the research progress. The current r_{33} can be up to several hundred pm/V (theoretical value 1000 *pm/V* or more while inorganic crystals ZnTe is only 4 *pm/V*). Thirdly, electro-optic polymer dielectric constant is relatively small (2~4), and the coherence length in the high and low frequency ranges is relatively long, so it can obtain very wide THz spectrum (from 0 to several tens of THz, while that of inorganic crystals is only 0~3 *THz*). Finally, polymer has no phonon absorption band gap and it is easy to get a flat, continuous THz spectrum.

For the use of detecting THz wave, on account of electron cloud move, the response time is very quick, counted to femtosecond. Because of the small dielectric constant of EO polymer, EO polymer can detect the wide frequency of the THz wave. Therefore, the THz device using EO polymer can be very small and has very low drive voltage and high sensitivity.

We doped the synthetic Chromophores 1 and 2 in the polymer APC and tested electro-optic coefficient. All the properties of the materials in THz were concluded in Table 2. It can be seen that by changing the structure of the chromophore, electro-optic coefficient of Chromophore 2 increases by nearly 10 *times* of Chromophore 1, so this material is very suitable for the study of terahertz radiation and detection.

Tab. 2 The properties of the organic and inorganic EO materials about THz

Sample	Processing	EO coefficient	The width of THz	THz spectrum
Polymer 1	simple	36 *pm/V*	0~several tens of THz	Continuous spectrum
Polymer 2	simple	337 *pm/V*	0~several tens of THz	Continuous spectrum
Crystal DAST	very hard	53 *pm/V*	0~several tens of THz	Phonon absorption gap 2.5 *THz*
Crystal ZnTe	mature	4 *pm/V*	0~3 *THz*	Phonon absorption gap 5.3 *THz*

Electro-optic poling polymer materials using as tunable terahertz radiation and detection source is the focus of this paper. However, how to get the best ratio to give full play to the superior performance of the polymer still remains a problem, although researchers have studied electro-optic polymers for potential applications in terahertz science and technology for years.

4. Conclusions

EO poling polymer is a class of THz radiation and detection source materials with high research value because of the high electro-optic coefficient, long coherence length, low dielectric constant, no phonon absorption band gap, flexible design and ability to get a quick response, wide frequencies and flat continuous THz spectra. Organic EO polymer with good processing can be used to fabricate new devices for applications in the field of terahertz. The research of electro-optic polymer can explore a new type of THz radiation and detection source with high strength and broad band but without phonon band gap. The detailed experimental results of EO poling polymer on THz wave will come soon.

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