

Optical properties of NAEC-PMMA nonlinear polymeric thin film

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Novel guest nonlinear optical (NLO) chromophore molecules (4'-nitrobenzene)-3-azo-9-ethylcarbazole (NAEC) were doped in poly (methyl methacrylate) (PMMA) host with a concentration of approximately 15% by weight. For a useful macroscopic electro-optic (EO) effect, these NLO molecules NAEC were arranged in a noncentrosymmetric structure in the host polymer by corona-onset poling at elevated temperature (COPET). For applying NAEC-PMMA polymer in optical devices such as EO switch, its optical properties have been investigated. The UV/Visible absorption spectra for the unpoled and poled polymer film were determined. The refractive index of the film was also determined from measurements of the coupling angles with the reflective intensity at 632.8 nm wavelength. Using the simple reflection technique, the EO coefficient γ_{33} value was measured as 60 pm/V at 632.8 nm wavelength. The second-order nonlinear coefficient d_{33} was characterized by the second-harmonic-generation (SHG) experimental setup and the calculated d_{33} value reached 18.4 pm/V at 1064 nm wavelength. The relation between the second-order nonlinear coefficients d_{33} and d_{13} for the poled polymer film was also discussed in detail and the ratio d_{33}/d_{13} value was obtained as 3.3.

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1. Introduction

At present, information communication needs great capacity and high speed. Using optics in electronic devices can increase the capacity and speed. However, this is limited because too few good nonlinear optical (NLO) materials are available. For the realization of optoelectronics, materials must possess not only a useful second-order susceptibility $\chi^{(2)}$ but also attributes such as ease of preparation, ease of fabricating into electro-optic (EO) devices, and stability. Compared with traditional inorganic materials, organic polymer materials, on the other hand, offer a great number of advantages including a large variety of molecular structures with large optical nonlinearities and the capability for designing other desirable properties such as the possible large EO coefficient, the potential ability to

integrate easily with other materials, the potential for low cost [1–3]. Polymer materials have attractive mechanical and electronic properties that facilitate their use in the practical devices and have been regarded as the key materials for all-optical communication.

Among the NLO polymer systems, the guest-host system does not require a guest chromophore to attach chemically to a host polymer, so that it can be easily fabricated at a lower cost [4]. In this paper, we will demonstrate a novel guest-host polymer system and investigate its optical properties.

2. Experiments and measurements

2.1. Film preparation

The guest chromophore molecules (4'-nitrobenzene)-3-azo-9-ethylcarbazole (NAEC) were doped in poly

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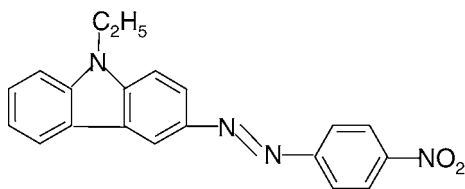


Figure 1 Molecular structure of novel chromophore NAEC.

(methyl methacrylate) (PMMA) host with a concentration of approximately 15% by weight. The chemical structure of molecule NAEC is shown in Fig. 1.

NAEC is a novel highly conjugated molecule based on substituted carbazole ramification, which can act as an extremely worthy second-order NLO chromophore [5, 6]. Its molecular ground-state dipole moment μ is 8.57D (an electron-proton pair with a separation of 10 nm gives a dipole moment of 4.8D). 1,2-dichloroethane was used as the solvent and the polymer was dissolved in it. The solution was first filtered through a 0.2 μm filter to remove the undissolved particle impurities, then spun coated onto indium tin oxide (ITO)-coated glass substrates, and finally baked at 80°C in an oven to remove all the solvent. Residual solvent is known to lower the glass transition temperature [7] and affect the orientational relaxation behavior of the polymer [8].

2.2. Film characterization and poling

Calorimetric study was performed with the Perkin-Elmer DSC-2C thermal analysis system to determine the glass transition temperature T_g . Differential scanning calorimetry (DSC) scan for NAEC-PMMA is shown in Fig. 2, which illustrates $T_g \cong 92^\circ\text{C}$.

The film was corona-onset poled at elevated temperature (COPET) [9, 10]. Compared with other poling techniques, COPET technique produces a significant increase in the long-term and long-range orientational order, second-harmonic properties and internal electric field ($E > 100 \text{ MV/m}$) [11]. The experimental setup for COPET is schematically shown in Fig. 3.

A sharp tungsten needle with diameter of 3 mm was positioned 19 mm above the polymer film and a d.c. voltage of +12 kV or so was applied to it. A grid located 5 mm above the film with a voltage of +800 V was used to make the film surface-charge to distribute uniformly. After poling for 600 s at 90°C just below T_g , the film was cooled down to the room temperature while keeping the needle and grid voltage on.

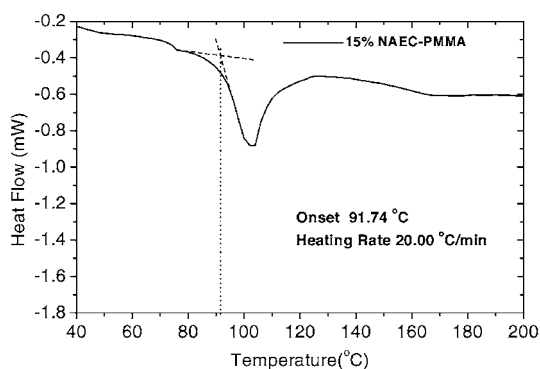


Figure 2 Heat flow of NAEC-PMMA polymer film vs temperature.

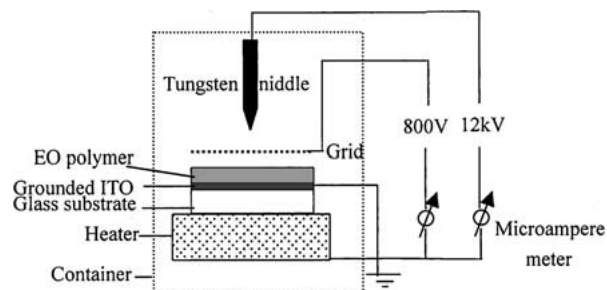


Figure 3 Schematic drawing of experimental setup for corona poling.

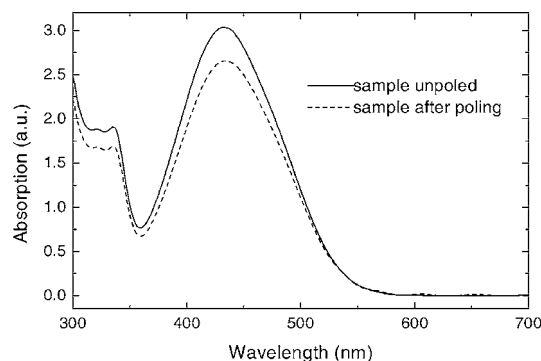


Figure 4 Optical absorption spectra of NAEC-PMMA film before and after poling.

2.3. Absorption spectra

The UV/Visible absorption spectra for the unpoled and poled polymer NAEC-PMMA were determined by HITACHI U-3500 spectrometer. Fig. 4 shows the measured absorbance with the wavelength from 300 nm to 700 nm.

2.4. Linear optical properties

The refractive index of NAEC-PMMA was determined from measurements of the coupling angles with the reflective intensity for the transverse electric (TE) and transverse magnetic (TM) modes in a slab waveguide at 632.8 nm wavelength by Model 2010 Prism Coupler System (Metricon®). The measured refractive indices are 1.5468 and 1.5462 respectively for TE and TM modes. Fig. 5 shows the observed reflective intensity as a function of incident angle due to the excitation of TE modes in the polymer film. Using the simple reflection technique [12], the EO coefficient γ_{33} was measured as 60 pm/V at 632.8 nm wavelength.

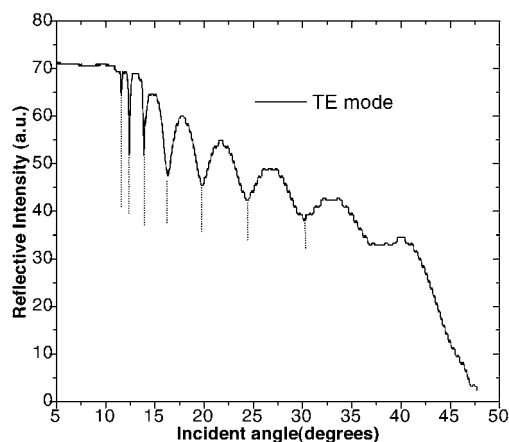


Figure 5 Reflective intensity pattern as a function of incident angle.

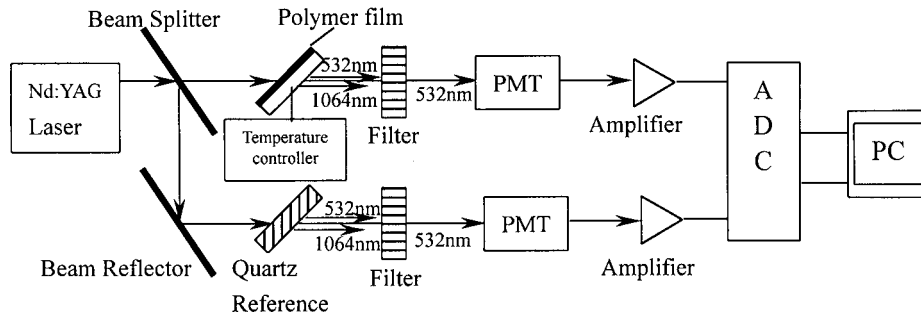


Figure 6 Experimental setup used for the measurement of NLO coefficient.

2.5. Second-harmonic-generation (SHG)

Macroscopic optical nonlinearity is characterized by second harmonic generation (SHG) coefficients d_{ij} . The second-order nonlinear coefficients, d_{33} and d_{13} were measured by the SHG experimental setup shown in Fig. 6.

The polymer sample was mounted on a heated stage and its temperature was monitored with a thermocouple placed under the film. A temperature controller controlled the power to the stage. A single-crystal quartz plate was used as a reference ($d_{11} = 0.45$ pm/V). The beam of a Q-switched Nd:YAG laser was simultaneously focused into the polymer sample and quartz reference. The output beams were blocked by two 532 nm filters and the second-harmonic signals were detected by photomultiplier tubes (PMT) and amplified. Then the two output pulse trains were digitized by an analogue to digital converter (ADC).

3. Discussions and results

From the optical absorption spectra of the film (Fig. 4), we can see the absorption peak wavelength is in the vicinity of 430 nm, so absorption at harmonic (532 nm) and fundamental (1064 nm) wavelengths can be neglected. In the SHG measurements, the second harmonic intensity produced by the film $I_s^{2\omega}$ was made relative to the second harmonic intensity produced by the quartz reference $I_q^{2\omega}$. Neglecting multiple boundary reflection, the relation between them is [9]

$$\frac{I_s^{2\omega}}{I_q^{2\omega}} = \frac{\pi^2 \chi_{eff}^2 L_s^2}{4 \chi_q^2 L_{qc}^2} \cdot \frac{\exp(-\alpha_s^{2\omega} L_s) |\sinh c[(\alpha_s^{2\omega} + i \Delta\beta_s) L_s / 2]|^2 T_s \varepsilon_q^\omega \sqrt{\varepsilon_q^{2\omega}}}{\sin^2(\pi L_q / 2 L_{qc}) \cos^2 \theta_s T_q \varepsilon_s^\omega \sqrt{\varepsilon_s^{2\omega}}}$$

Where the subscripts s and q refer to the sample and quartz, respectively. L is the thickness, L_{qc} is the coherence length of quartz, α is the attenuation constant, $\Delta\beta$ is the phase mismatch between the fundamental (ω) and the second-harmonic (2ω) waves. $\text{sinhc}(x) = \sinh(x)/x$ and $\sinh x = (e^x - e^{-x})/2$, T is the product of the electromagnetic power transmission factors of the fundamental and second-harmonic waves. ε is the permittivity, θ_s is the angle between the boundary normal and the direction of phase propagation inside the film. χ_{eff} is the effective second-order susceptibility.

Then we have the relation between the maximum second harmonic coefficient $d_{33,s}$ for the polymer film and the maximum second harmonic coefficient $d_{11,q}$ for the quartz.

$$\frac{d_{33,s}}{d_{11,q}} = \sqrt{\frac{I_s^{2\omega}}{I_q^{2\omega}}} \cdot \frac{L_{qc}}{L_s} F$$

Where $d_{11,q} = 0.45$ pm/V, the coherence length of the quartz reference $L_{qc} = 20.6$ μm . L_s is the film thickness which was measured approximately as 1.0 μm by Model 2010 Prism Coupler System. The value of factor F approximately is 1.2 on the condition of $L_{qc} \gg L_s$. $I_s^{2\omega}/I_q^{2\omega}$ was measured as a function of the angle of incidence. The measured value for the poled NAEC-PMMA is 2.73378. Multiplying all the numbers together gives $d_{33,s} = 18.4$ pm/V.

Neglecting the chromophore-chromophore as well as chromophore-polymer backbone couplings, the nonlinear coefficients can be calculated from the dominant element β_{zzz} of the first hyperpolarizability tensor [13], which is parallel to the molecular dipole moment [14],

$$d_{33} = \frac{1}{2} N \beta_{zzz} f^0 f^\omega f^{2\omega} \langle \cos^3 \theta \rangle$$

$$d_{31} = \frac{1}{4} N \beta_{zzz} f^0 f^\omega f^{2\omega} (\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle)$$

Here θ represents the angle between the molecular charge transfer axes of the nonlinear optical moieties and the applied external electric field. We can ex-

press the orientational averages $\langle \cos^3 \theta \rangle$ as Langevin function [13] $\langle \cos^3 \theta \rangle = L_3(u) = [f \cos^3 \theta \exp(ucos \theta) d\theta] / [f \exp(ucos \theta) d\theta]$, Where u is the ratio of the electrostatic dipole alignment energy to the thermal energy. N is the number density of chromophore and f^ω , $f^{2\omega}$, f^0 are the local field factors, which can be described with Lorenz-Lorentz-type expressions at optical frequencies

$$f^\omega = \frac{n_\omega^2 + 2}{3} \quad f^{2\omega} = \frac{n_{2\omega}^2 + 2}{3}$$

And f^0 can be defined by the Onsager expression [15]

$$f^0 = \frac{\varepsilon(n_\infty^2 + 2)}{n_\infty^2 + 2\varepsilon} = \frac{\varepsilon(\varepsilon_\infty + 2)}{\varepsilon_\infty + 2\varepsilon}$$

$\varepsilon_\infty = n_\infty^2$ is the optical frequency dielectric constant. ε is the low-frequency dielectric constant, and n_∞ , n_ω , $n_{2\omega}$ are the optical indices of refraction.

Then we have the following relation

$$\begin{aligned} \frac{d_{33}}{d_{31}} &= \frac{2\langle \cos^3 \theta \rangle}{\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle} = \frac{2L_3(u)}{L_1(u) - L_3(u)} \\ &= \frac{u \coth u + \frac{6}{u} \coth u - 3 - \frac{6}{u^2}}{1 - \frac{3}{u} \coth u + \frac{3}{u^2}} \end{aligned}$$

Poled guest-host systems can be described by the rigid oriented gas model (ROGM) [9, 13, 16]. Chromophore order is assessed by measuring the decrease in the absorption associated with poling. Then u has the following dependent relation with the order parameter ϕ [9, 11]

$$\phi = 1 - \frac{A_\perp}{A_0} = 1 + \frac{3}{u^2} - \frac{3}{u} \coth u$$

Where A_0 and A_\perp are respectively the absorption peak value for the polymer film before and after poling. From the absorption spectra (Fig. 4), we have the values $A_0 = 3.03744$ and $A_\perp = 2.65527$, which imply $u = 1.5152$, $\coth u = 1.1015$, then we have the ratio $d_{33}/d_{31} = 3.3$ and the value of d_{31} can be obtained as 5.6 pm/V.

4. Conclusion

The new guest NLO chromophore molecules NAEC were doped in PMMA host with a concentration of approximately 15% by weight. For the poled NAEC-PMMA thin film, the EO coefficient γ_{33} was measured as 60 pm/V at 632.8 nm wavelength by simple reflection

technique and the second-order nonlinear coefficient d_{33} reached 18.4 pm/V at 1064 nm wavelength, which was characterized by the SHG experimental setup.

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