



Ultrafast third-order nonlinear optical properties of an azobenzene-containing ionic liquid crystalline polymer

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ABSTRACT

The ultrafast third-order nonlinear optical properties of an azobenzene-containing ionic liquid crystalline polymer were investigated by optical Kerr effect (OKE) and pump–probe techniques with femtosecond pulses. The third-order nonlinear optical susceptibility of the sample solution was obtained to be 2.1×10^{-14} esu at a concentration of 2×10^{-3} M. The temporal response of the sample solution was decomposed into two components, which could be explained by the relaxation of different singlet excited states. The polymer thin film exhibited strong ultrafast nonlinear optical response of 8.26×10^{-10} esu and show its potential applications for further nonlinear optical devices.

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1. Introduction

Nonlinear optical materials with large third-order optical nonlinearity and fast response time are essential requirement for optical communication, optical limiter and all-optical switching applications [1–4]. Azobenzene-functionalized polymer is one of the most attractive nonlinear optical materials owing to its unusual chemical and optical properties [5,6]. There have been many reports about the nonlinear optical characteristic and optical storage based on their photoisomerization and photoinduced anisotropy [7–9]. Most of these works were done with CW or long pulse lasers as excitation source due to the slow process of *trans*–*cis*–*trans* isomerization cycles of azobenzene molecules. However, these results were not applicable for fast optical response and high-bandwidth optical signal processing because of their long excitation and relaxation times. Employing a ultrashort pulse laser, high power light can be output to create strong nonlinear light–matter interactions, making it possible to explore physical phenomena with unprecedented time resolution [10]. To further exploit the potential applications of azobenzene materials in ultrafast field, it is imperative to accurately determine the nonlinear parameters under the excitation of ultrashort pulse lasers and then to understand the photodynamic behaviors which are very important for designing all optical switching devices. In this Letter, we employed an azobenzene-containing ionic liquid crystalline polymer which can be easily formulated from readily available components based on ionic self-assembly, and reported its ultrafast third-order nonlinear optical properties by using optical Kerr effect (OKE) technique with femtosecond pulses.

2. Experiment

The sample is a supramolecular prepared through self-assembly. 5 mg/mL sodium polyacrylate (PANa) aqueous solution, obtained from the neutralization of polyacrylate with sodium hydroxide, was added dropwise to NDAZO (3-(6-(4-((4-(dimethylamino)phenyl)diazenyl)phenoxy)hexyl)-1-methyl-1H-imidazol-3-ium bromide) aqueous solution with the concentration of 1 mg/mL, in a 1:1 M charge ratio. The resulting precipitated was collected by filtration and washed thoroughly with deionized water to remove residual salts and possible noncomplexed precursors and then dried in vacuum at 60 °C for 24 h. To investigate its stability and phase behaviors, TGA and DSC of the polymer were obtained. TGA curve showed that the polymer was stable under high temperature of 250 °C. DSC thermograms of the polymer displayed phase transition peak at 93 °C, indicating its crystalline nature. The polymer solution with a concentration of 2×10^{-3} M is prepared by dissolving the appropriate amount of the solute into the chloroform solvent. The molecular structure and the UV–vis absorption spectra of the polymer are shown in Figure 1. Thin films of the synthesized polymer were prepared by spin-coating chloroform solution (concentration: 30 mg/mL) onto the quartz slides (speed: 2000 rpm, time: 20 s). The thickness of the resultant films was about 300 nm, measured by a Dektak profilometer.

The third-order nonlinear optical (NLO) properties of the polymer were examined via a time-resolved optical Kerr effect (OKE) and pump–probe experiments. A standard femtosecond OKE experiment was performed. The femtosecond laser pulse was generated from a mode-locked Ti:Sapphire oscillator (Mai Tai HP-1020) generating 100 fs pulses at 800 nm. A regenerative amplifier system (Spectra-Physics, Spitfire Pro) was used to amplify the pulses 10^6 times at a repetition rate of 1 kHz. The laser beam was divided into

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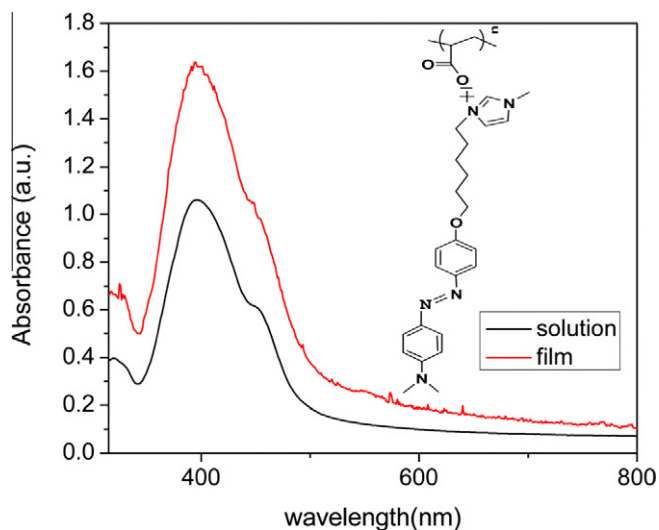


Figure 1. Linear absorption spectrum of the polymer solution and film. Inset: the molecular structure of the polymer.

probe beam and pump beam by a beam splitter. The pump beam traveled through a 1-mm thickness type-I BBO nonlinear crystal to generate pulse at 400 nm. This wavelength falls in the range of relatively strong absorption of the sample allowing us to obtain information on the dynamic behavior of the resonant third-order nonlinearity. A polarizer P1 was put into the probe beam path to set its polarization to be 45° with respect to that of the pump beam. The two beams were focused by a 50 cm focal length lens and overlapped on the same spot of the sample with a spot size of 200 μm . After transmitting the sample cell, the pump beam was blocked, while the transmitted probe beam passed through an analyzer P2 with crossed polarization to P1. The generated OKE signal was detected by a silicon photodiode connected to a lock-in amplifier. In the OKE experiment, CS_2 was used as the reference. The $\chi^{(3)}$ of CS_2 is accredited as 1×10^{-13} esu in fs domain [11]. The value of the third-order NLO susceptibility of the sample can be calculated from the OKE measurement by using the following formula [12,13]:

$$\chi^{(3)} = \chi_r^{(3)} \times \left(\frac{I_s}{I_r}\right)^{1/2} \times \left(\frac{n_s}{n_r}\right)^2 \times \left(\frac{L_r}{L_s}\right) \times \frac{\alpha L_s}{\exp(-\frac{\alpha L_s}{2}) \times [1 - \exp(-\alpha L_s)]} \quad (1)$$

where I is the intensity of the OKE signal at zero delay time, α is the linear absorption coefficient of the sample, n is the refractive index, and L is the interaction length of pump beam and probe beam over the CS_2 and the sample. The subscripts s and r denote the sample and CS_2 , respectively. For pump-probe measurement, a half-wave plate and a polarizer were inserted into the probe beam. The polarization of both pump and probe beams was set to be parallel by rotating the polarizer. There was no second polarizer in the probe beam after the sample, and the other parts in the pump-probe experiment were the same as that of the OKE experiment.

3. Results and discussion

The typical optical Kerr signal of the polymer solution is illustrated in Figure 2, consisting of two different processes: an ultrafast peak near the zero point followed by a slow decay process. Exploiting the method reported in Refs. [11,13], a Gaussian function was used to represent the ultrafast peak and a biexponential decay function $I_t = A \exp(-t/\tau_1) + B \exp(-t/\tau_2)$ was employed

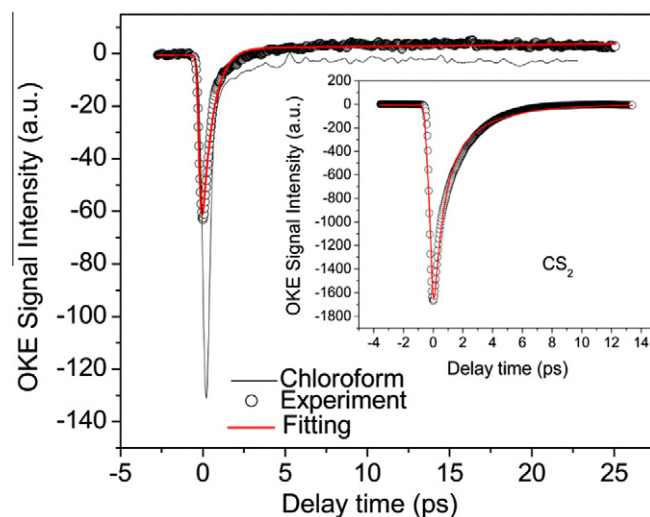


Figure 2. The OKE response of the polymer solution and chloroform solvent under a pump intensity of 10.6 GW/cm^2 . The inset is the OKE signal of CS_2 measured under the same conditions.

to describe the slow decay process. The fit yields a fast component of 900 fs and a slow component of 50 ps. The OKE signal of chloroform is also shown in Figure 2, and the results suggest that the OKE signal of the sample solution does not include the influence of the solvent in the delay time of 0.8–25 ps. Based on the magnitudes of the OKE signal of the sample and the reference under identical experimental condition, the $\chi^{(3)}$ of the sample solution is determined as 2.1×10^{-14} esu. The corresponding second hyperpolarizability was deduced to be 2.3×10^{-32} esu according to the formula [14]:

$$\gamma = \chi^{(3)}/NL, \quad (2)$$

where N is the concentration of the molecule and L is the local field correction factor, which is defined as $L = [(n^2 + 2)/3]^4$. This value is much larger than that of C_{60} (1.5×10^{-36} esu), C_{70} (7.0×10^{-35} esu) as well as carbon nanotube (4.3×10^{-33} esu) reported before [15–17].

A 300-nm thick polymer film was also prepared and tested. The absorption spectrum of this film is similar to the polymer solution as shown in Figure 1. A typical temporal behavior of the optical Kerr signal observed for the polymer thin film was shown in Figure 3. The response time, i.e., the full width at half maximum of the Kerr signal, was as fast as 300 fs. From calculated results, the third-order nonlinear optical susceptibility of the thin film was estimated to be 8.26×10^{-10} esu. Ikeda and Tsutsumi have studied the nonlinear response of azobenzene liquid-crystal film by ns time-resolve technique, and found a nematic-to-isotropic phase transition with a response of 200 μs [18]. Mysliwiec et al. have investigated the nonlinear response in a biopolymer matrix containing azo-dye molecules by using of ns and CW OKE techniques, and got the response time in the range of microseconds [19]. Dong et al. have reported pure electronic origin nonlinear response in azobenzene-doped polymer films using sub-picosecond time-resolved degenerate four-wave mixing and Z-scan techniques, and observed a fast dephasing time of 1 ps [20]. In our experiments, the sub-picosecond ultrafast response was mainly attributed to the resonant electronic nonlinearities. It is estimated that the characteristic response time of the electronic nonlinearity could be as short as 10^{-15} s, which is much shorter than that of other physical processes, such as molecular orientation (10^{-12} s), electrostriction (10^{-9} s), and thermal effects (10^{-3} s) [21].

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