Nonlinear Optical Response of Liquid Crystalline Azo-Dendrimer in Picosecond and CW Regimes

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ABSTRACT: The nonlinear optical response of the liquid crystalline multiarm star-shaped azodendrimer was investigated in picosecond pulse and CW regimes at 532 nm. The polymer exhibited large nonlinear refractive coefficient in two regimes ($n_2 = -2.88 \times 10^{-13}$ cm^2/W and -1.1×10^{-10} cm^2/W under picoseconds pulse excitation, whereas $n_2 = -1.4 \times 10^{-6}$ cm^2/W and $n_2 = -8.8 \times 10^{-5}$ cm^2/W under CW laser excitation in solution and film, respectively). The mechanism accounting for the process of nonlinear refraction was discussed. The value of photoinduced birefringence in the polymer film was also measured ($\Delta n \sim 10^{-3}$) under CW laser excitation at 532 nm. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3065–3070, 2011

Key words: liquid crystalline azodendrimer; nonlinear refractive index; photoinduced birefringence

INTRODUCTION

Dendrimers, which are new classes of synthetic polymers, have been the subject of intense academic and industrial research for their interesting optical, electronic properties[1–5] and their potential applications in optical devices, such as OLEDs.[6,7] The material is highly branched and has standardized structure with characteristic of single dispersion. They can be produced via a modular synthesis giving a greater flexibility over controlling the properties. The processing, optical and electronic properties can be optimized independently. On the other hand, great interests have been plunged into the nonlinear optical properties of azo-containing polymers for their large third-order nonlinear optical susceptibility, fast response, and ease of processing.[8–11] Some azobenzene LC polymers have been used in applications of optical storage, optical limiting, and optical switching.[12,13] Thus, dendrimers with LC phase and azobenzene group should be studied because of their standardized structure, controllable properties, and good optical response. There have been many reports on the optical properties of the liquid crystalline photosensitive dendrimers.[14–16] In most of these

papers, Z-scan technique,[17] which can give both the nonlinear refraction index and the nonlinear absorption index, are used to investigate the NLO properties of materials. In this work, we investigated the nonlinear optical properties of a liquid crystalline multiarm star-shaped azodendrimer under picosecond and CW regimes laser excitations by employing Z-scan technique. The nonlinear optical processes in different laser regimes in the material were discussed. Moreover, azo groups can exhibit the anisotropic orientation under laser irradiation. Photoinduced birefringence of the polymer was measured to investigate the LC alignment behavior on the film.

EXPERIMENT

The molecular structure of multiarm star-shaped azodendrimer was shown in Figure 1. It was synthesized via radical polymerization as described elsewhere.[18] The liquid-crystalline polymers (LCP) film was prepared by spin coating a THF solution onto quartz plate. The thickness of the resultant film was about 180 nm measured by atomic force microscopy (AFM). We also used the LCP in THF solution (0.07 mg/mL) in our measurements. The LCP solution was enclosed in a 1-mm fused quartz cell. The THF was purchased from Shanghai SSS Reagent (Shanghai, China, technical grade) and the quartz plate was bought from Shanghai Haiguang optical instruments factory (Shanghai, China). The LCP film was kept at 90°C for 30 min and then cooled immediately to room temperature to measure the UV–Vis spectra. The absorption spectra of the LCP film and
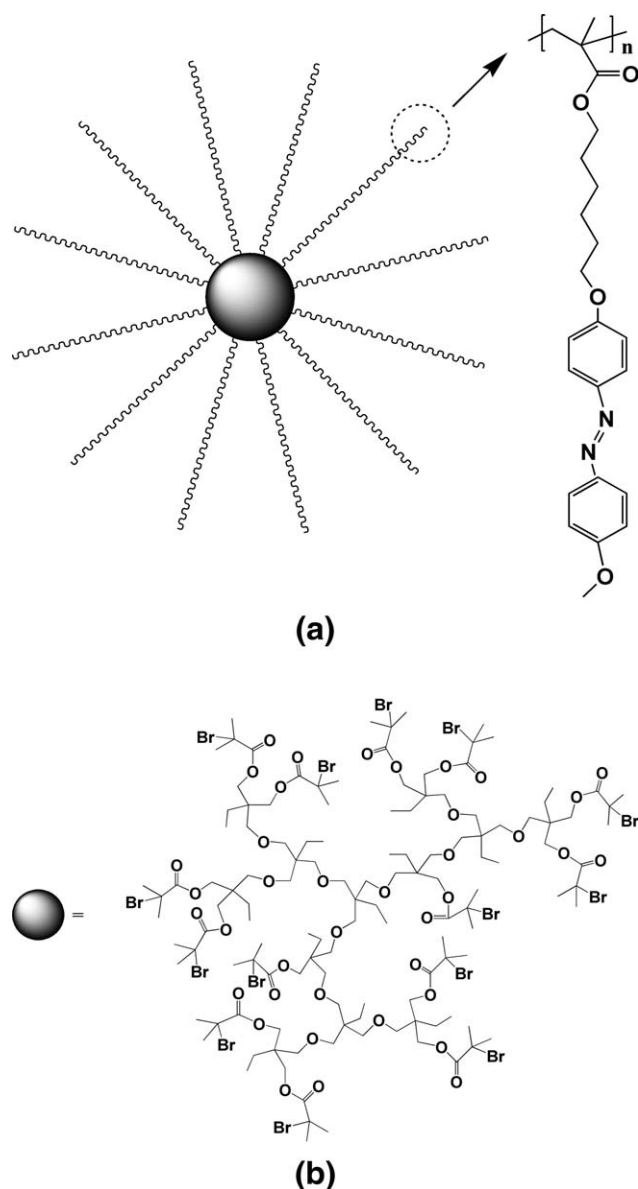
Figure 1 Schematic chemical structure of the multiarm star-shaped azodendrimer.

solution were shown in Figure 2. Φ–Φ* electronic transition of aromatic rings caused the absorption peak at $\sim$ 240 nm, n–π* transition gave rise to the small shoulder at $\sim$ 460 nm, and a strong π–π* electronic transition can be used to explain the maxima of the absorbance in the range of 340–360 nm. On the other hand, the thin film shows a wider absorbance band and smaller absorbance in comparison with that of the solution. The obvious blue shift of the λ_{max} from $\sim$ 358 to $\sim$ 343 nm and a red shift which are shown by the thin film are attributed to the "card pack" (H aggregate → blue shift) and "head-to-tail" (J aggregate → red shift) arrangement of the chromophores.[19]

Z-scan method is a simple and effective tool to measure the nonlinear refractive index and has been

used widely in material characterization. The Z-scan experimental setup in our experiment was shown in Figure 3 and it was similar to Ref. 17. First, we used a picosecond pulse Nd: YAG laser (Continuum Co.) at 532 nm as the excitation source. The laser's repetition frequency was 10 Hz and the pulse duration was 38 picoseconds, respectively. The spot size at the focal point was 26.7 μm in radius and the Rayleigh length was 4.2 mm. The focal length of the lens was 30 cm. The detector was a dual-channel joulemeter EPM2000 (Molectron Co.). In the CW Z-scan measurement, the excitation source was Nd: YAG CW laser at 532 nm. The radius of the beam waist and the corresponding Rayleigh length were 32.3 μm and 6.1 mm, respectively. The experimental setup for the measurement of photoinduced birefringence in LCP film was shown in Figure 4 and it is similar to Ref. 20. The photoinduced birefringence was investigated with a diode laser at 650 nm as probe light, which was far from the absorption band of azobenzene ionic liquid-crystalline polymer, and a CW 532 nm laser as pump light.

RESULTS AND DISCUSSION

Using Z-scan technique, on-axis phase shift at the focus can be calculated by the following[17]:

$$\Delta T_{P-V} = 0.406(1-s)^{0.25}|\Delta\Phi_0|. \tag{1}$$

Here, $\Delta T_{P-V} = T_P - T_V$ which denotes the difference between normalized peak and valley transmittance can be obtained through the best theoretical fit from the results of the Z-scan curve. $s = 1 - \exp(-2r_0^2/\omega_0^2)$ is the aperture linear transmittance, r_0 is the aperture radius, and ω_0 is beam radius at the aperture in the linear region. The nonlinear
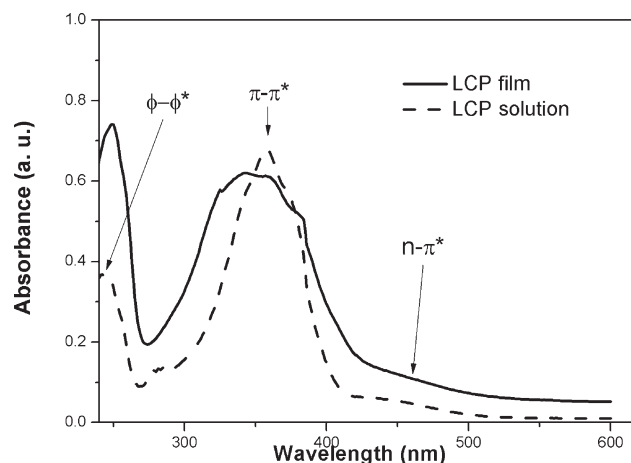

Figure 2 Absorption spectra of LCP film (annealed at 90°C) and LCP in THF solution.
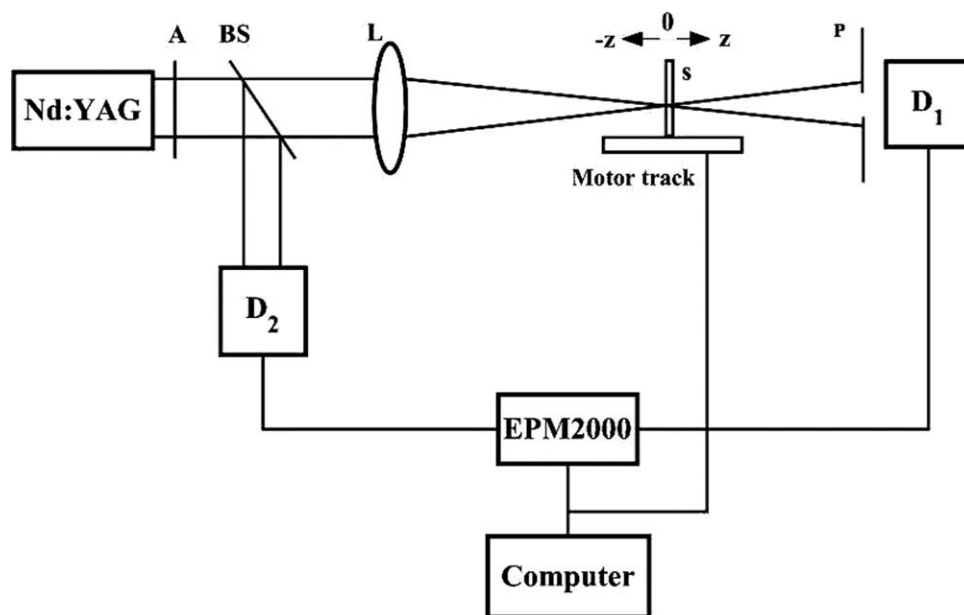
Figure 3 Schematic diagram of Z-scan experimental setup. A, attenuator; BS, beam splitter; L, lens; P, aperture; S, sample.

refractive index n_2 (m^2/W) can be obtained by the following[17]:

$$\Delta\Phi_0 = kL_{eff}n_2I_0 = (2\pi/\lambda)L_{eff}n_2I_0. \quad (2)$$

Here, I_0 is the intensity of the laser beam at focus $z = 0$, $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, α is the linear absorption coefficient, and L is the thickness of the sample. Z-scan measurement is employed to obtain the normalized transmittance not only for the closed aperture but also for the open one, since the nonlinear absorption β cannot be neglected for many materials. After the division of closed aperture experimental data and open experimental data, we will get the Z-scan curve without the effect of nonlinear absorption. The nonlinear absorption indexes can be calculated according to Ref. 17.

Figure 5(a,b) are the Z-scan closed aperture curves of LCP solution and film under ps pulse laser at 532 nm. The closed curves were symmetric with respect to the focus ($z = 0$) in the figure and the normalized transmittances remained basically unchanged using
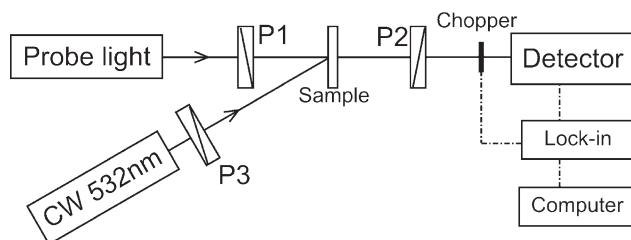

Figure 4 Schematic diagram of photoinduced birefringence experimental setup. P1–P3, polarizers.

open aperture Z-scan measurement. The solid lines in the Figure 5 are the theoretical fits. The result shows the nonlinear absorption in LCP under picosecond pulse laser is negligible. The peak followed by a valley-normalized transmittance obtained from the closed aperture curve indicates that the sign of the nonlinear refraction is negative, which results from self defocusing. In Z-scan experiments, the input energy was 0.25 µJ and peak intensity of the incident laser was calculated to be 0.59 GW/cm^2 at the focal point, the aperture linear transmittance $s = 0.25$. The nonlinear refractive indexes of LCP solution and film can be calculated as $n_2 = -2.88 \times 10^{-13}$ cm^2/W and -1.1×10^{-10} cm^2/W, respectively. The results showed that the nonlinear refractive index in the film was 300 times larger than that in solution. Compared with many other organic materials, such as DDLC,[21] Sudan I,[22] and some organic D-π-A compounds,[13] the nonlinear refractive index in LCP was larger. The good nonlinear response of this material indicates it has potential applications in optical devices such as all-optical switches and modulators. The large optical nonlinearities of this liquid crystalline azodendrimer mainly arise from its special morphology. For nonlinear response under pulse laser which is caused by electronic effect, high density of conjugation bond and large conjugation length can both lead to large nonlinear refraction indexes.[2] From the molecular structure of LCP, the large length of the chain, where π-conjugation system in the azobenzene molecule is contained, which means high degree of electron delocalization, is favorable to increase the NLO susceptibility value. Furthermore, dendritic architecture of LCP has
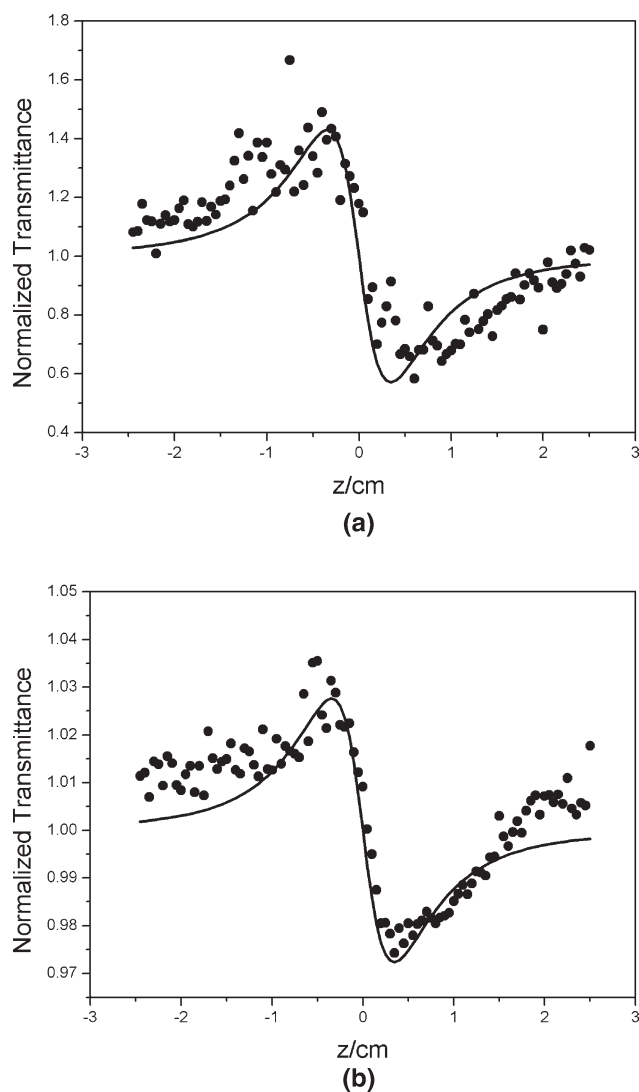
(a)

(b)

Figure 5 a: The closed aperture Z-scan curve of LCP solution under ps pulse laser; b: The closed aperture Z-scan curve of LCP film under ps pulse laser.

brought a broad and uniform distribution of chromospheres. The increase of chromospheres density would lead to an enhancement in the optical nonlinearity. However, it was also noticed that azo groups in polymers with LC nature show a strong tendency to aggregate, and the aggregation is even more pronounced in the thin-film state.[23] This aggregation will decrease the NLO response. Therefore, the larger molecular weight, which means higher polydispersity index, can reduce the aggregation of chromospheres and eventually improve the NLO response.[24] The thermal treatment temperature can also influence the film's aggregation behavior. For instance, when the film is treated at 90°C, azo groups in the dendrimer film are mainly assembled in the smectic LC order. The dipoles tended to redistribute in a form of parallel arrangement (H-aggregates). However, when the film is treated at

140°C, the azo groups will not be organized as H-aggregation due to high motional ability of molecules at this temperature and the azodendrimer will be in the isotropic state. The higher motional ability can lead to larger NLO susceptibility value.

Z-scan measurements were also employed using a CW laser excitation at 532 nm for both LCP solution and film. Peak intensity of the laser was set to be 1.2×10^2 W/cm^2 and 2.4×10^3 W/cm^2 at the focal point for LCP solution and film, respectively. The z-scan curves are shown in Figure 6(a,b). The nonlinear refraction indexes can be calculated as $n_2 = -1.4 \times 10^{-6}$ cm^2/W and $n_2 = -8.8 \times 10^{-5}$ cm^2/W for LCP solution and film, respectively. Both the LCP solution and film show good nonlinear response. Under CW laser excitation, the nonlinear optical process of LCP could be caused by laser heating-induced nonlinearity. This kind of nonlinearity arises from temporal variation of optical
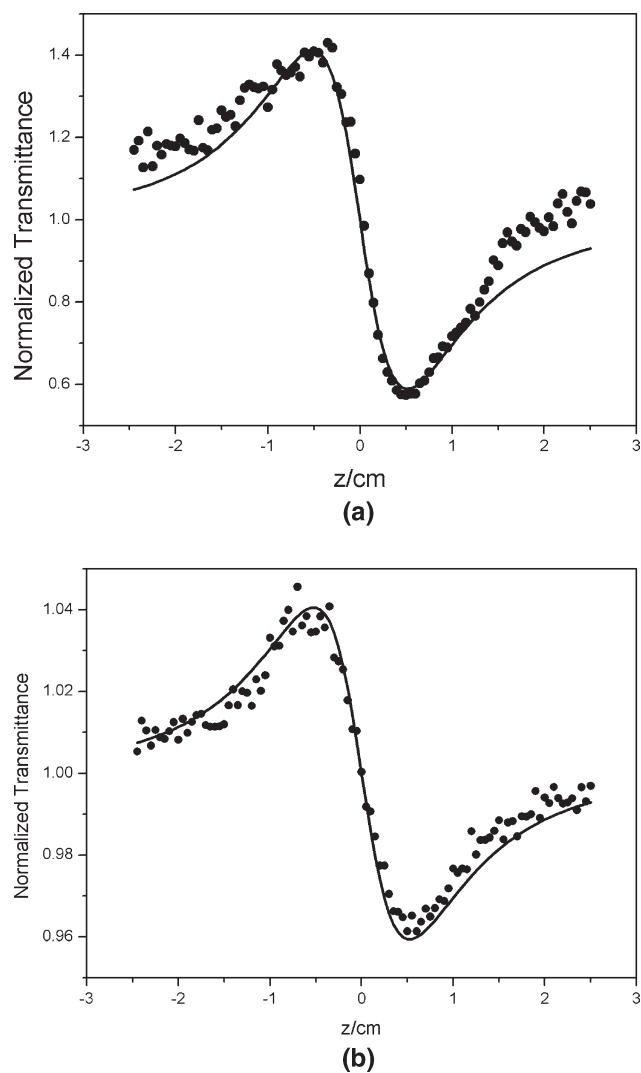

(a)

(b)

Figure 6 a: The closed aperture Z-scan curve of LCP solution under CW laser; b: The closed aperture Z-scan curve of LCP film under CW laser.
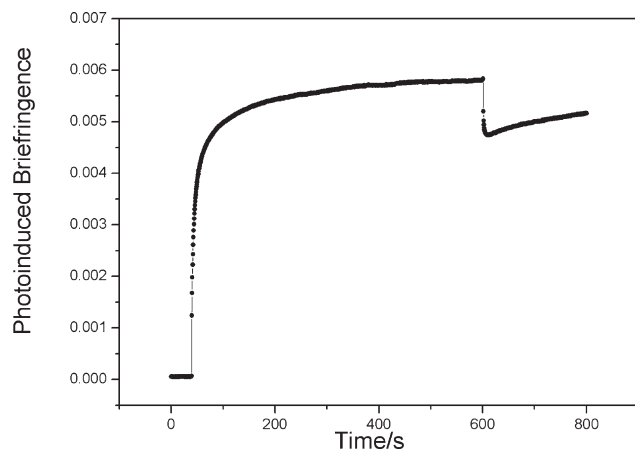
Figure 7 Photoinduced birefringence of LCP film.

parameters (in particularly, refractive index) due to linear and/or nonlinear absorption followed by a nonradiative relaxation down to the ground state. The generation of acoustic wave was caused by the laser heating and then the density in the materials changed, where a variation of refractive index was followed. The laser heating process was very slow (in the order of a few nanoseconds) and could be observed in the case of CW laser, long pulse duration laser, or in the case of high pulse repetition rate when the heat accumulation started to play important role. From Ref. 25, the average on-axis nonlinear index change at focus can be determined in terms of the thermo-optic coefficient dn/dT as follows:

$$< \Delta n_0 > \approx \frac{dn}{dT}\frac{I_0\alpha}{2\rho C_V} \qquad (3)$$

where I_0 is the intensity of laser at the focal point, $\alpha = 0.06$ is the linear absorption coefficient at 532 nm as defined before, ρ is the density, C_V is the specific heat, and 1/2 denotes the intensity averaging factor. For LCP solution, since the concentration of the LCP solution is very low, we can deal with it as pure THF solution. According to the known value of $\rho = 0.89$ g/cm^3, $C_V = 1.7$ J/gK and $dn/dt = 4.4 \times 10^{-4}$ K^{-1} for THF, n_{2t}, which is the nonlinear refraction caused by thermal effect, can be calculated as[17] $n_{2t} = \frac{<\Delta n_0>}{\sqrt{2}\cdot I_0} = 1.25 \times 10^{-6}$W/cm^2. The value is in the same order of magnitude as the nonlinear refraction index of LCP 1.4×10^{-6} cm^2/W. The result indicates that the laser heating effect plays a main role in the origin of nonlinearity.

It is well known that the azobenzene molecules can undergo *trans-cis-trans* isomerization under laser irradiation.[26] Especially, for an azobenzene liquid-crystalline polymer, under actinic irradiation, azobenzene groups display trans to cis transformation and induce LC alignment in the direction perpendicular to the polarization of pump light. To investigate this

physical process more deeply, the real-time behavior of photoinduced birefringence was investigated employing the LCP film. The birefringence value can be obtained by the following[27]:

$$I_\perp = I_0 \sin^2(\pi\Delta nd/\lambda). \qquad (4)$$

Here, Δn is the photoinduced birefringence, $I_\perp$ is the probe intensity passing through the crossed polarizers, and $I_0 = 100$ mW/cm^2 is the probe intensity passing through the parallel polarizers before pump irradiation. Figure 7 shows the experimental result of photoinduced birefringence in LCP film. With continuous-wave irradiation to the film, the curves for the buildup of birefringence can be fitted with the biexponential functions in the form as follows:

$$y = A(1 - e^{-t/t_f}) + B(1 - e^{-t/t_s}). \qquad (5)$$

where A and B are the pre-exponential factors, t is the times, t_s and t_f are the time constants for writing of the slow and the fast processes, respectively.[28] Biexponential functions are normally employed for representing the photoisomerization buildup process. When the pump is on, a fast process and a slow process in the buildup of birefringence can be seen under irradiation. For LCP, the fast process is related to the local movement of azobenzene groups in the *trans-cis-trans* photoisomerization, and the slow process is attributed to the movement of azobenzene groups linked to the LC polymeric chain.[29,30] From the figure, when the pump intensity was 100 mW/cm^2, the saturation value was $\Delta n = 5.8 \times 10^{-3}$. It indicates that the material has potential value in the application of nonlinear photonic devices and optical storage. The sign of photoinduced birefringence, which is helpful to provide the directional information of azobenzene molecules and investigate the mechanism of photoinduced birefringence in the azo polymer film further, can be determined by adding a quarter waveplate between the polymer film and the analyzer of the conventional two-crossed polarizers setup as in Refs. 31 and 32. The related work is in progress in our lab. When the pump is off, there is usually some loss for photoinduced birefringence due to the thermal relaxation of the induced orientation. However, in our experiments, the birefringence does not show significant decay. We have found that the characteristic of long term and reversible optical storage of the polymer can last for months. The phenomenon can be explained with the self organization effect of the molecules.[33] The molecules keep well ordered (or continue the reorientation) spontaneously after removing the pump irradiation, instead of relaxing back to the isotropic state. For ps pulse laser as the pump light, in which case the laser energy density is set to 0.25 mJ/cm^2 in our experiment (high

excitation density for ps width pulse), the value of photoinduced birefringence in LCP film is in the order of 10^{-4}, which is much smaller than that in CW cases. One reason to the much smaller value of Δn is that the pump laser power density of ps pulse laser is lower than CW laser. The other reason can be seen in Ref. 34. Some longer pulse laser excitations (i.e., ns pulse laser) can introduce the local thermal heating which supports the mobility of molecules and enhance the value of photoinduced birefringence. However, for unltrashort pulse width laser (i.e., ps and fs), there is a time limitation to the enhancement of photoinduced birefringence.

CONCLUSIONS

Using Z-scan method, the nonlinear optical properties of the liquid crystalline multiarm star-shaped azodendrimer were investigated under picosecond pulse and CW laser excitation at 532 nm. The polymer exhibited large nonlinear refractive coefficient under two regimes both in solution and film. The results showed the polymer was valid candidate for all-optical switching devices. The mechanism accounting for the process of nonlinear refraction was discussed. Moreover, photoinduced birefringence in the polymer film was studied under CW laser excitation at 532 nm.

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