Preparation, Thermo-Optic Property and Transmission Loss of Chiral Azobenzene Polyurethane

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ABSTRACT: A novel chiral azobenzene polyurethane (CAPU) was prepared from chromophore, chiral reagent L(−)-tartaric acid and toluene diisocyanate (TDI). The chemical structure and the thermal property were characterized by UV-Vis spectrum, FT-IR, ^{1}H NMR, circular dichroism (CD) spectrum, differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). DSC and TGA experiments showed that the glass transition temperature (T_g) and the decomposition temperature (T_d) at 5% mass loss were 110°C and 199°C, respectively. The refractive index (n) and thermo-optic coefficient (dn/dT) of the CAPU were measured at 650 nm wavelength and different temperature by attenuated total reflection (ATR) technique. By using CCD digital imaging devices, transmission loss of CAPU was measured and the value is 0.565dB/cm. The results will provide the foundation for many potential applications such as digital thermo-optic switch materials and other fields in the future. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2567–2572, 2011

Key words: azo polymer; optics; thermo-optic coefficient; transmission loss

INTRODUCTION

Organic materials containing azobenzene groups have been widely investigated due to their unique properties, which promote them to be used in optical data storage or optical switching. Furthermore, their structure must be noncentrosymmetric on the molecular and macroscopic scales. Noncentrosymmetry on the molecular scale is easy to achieve, for example by connecting an electron donor and acceptor by a one-dimensional π-conjugated bridge. On the other hand, macroscopic noncentrosymmetry has proven more difficult. Methods to achieve macroscopic noncentrosymmetry are electric-field poling, crystal growth, self-assembly, and deposition of Langmuir-Blodgett (LB) films. An alternative approach is the use of chiral materials.

Recently, much attention has been paid to chiral polymers, and these materials have exhibited a number of interesting properties. Much of the attention in chiral polymers results from the potential of these materials for several specialized utilizations that are chiral matrices for asymmetric synthesis,[1–3] chiral stationary phases[4–6] for the separation of racemic mixtures, synthetic molecular receptors and chiral liquid crystals[7–9] for ferroelectric and nonlinear optical applications.[10,11] Zhang et al.[12] synthesized a kind of chiral azo molecule (C$_8$-Azo-L-Glu) was from L-glutamic acid and studied the photochromism, photoinduced birefringence, and holographic recording of C$_8$-Azo-L-Glu doped PMMA films. Kozlovsky et al.[13] reported 5-Chiral Polymers with photoaffected phase behavior for optical data storage. Philip et al.[14] synthesized chiral azo polyester and studied the second-harmonic generation (SHG) efficiency. Rahman et al.[15] prepared azo liquid crystal and investigated the dielectric relaxation dynamics in liquid crystal dye composites. This article is not included in your organization's subscription. However, you may be able to access this article under your organization's agreement with Elsevier.

In this article, we synthesized azobenzene polyurethane (CAPU) containing chromophore and the chirality skeleton. The chemical structure, thermo-optic property and transmission loss of CAPU were characterized and determined.

THEORY

Measurement of refractive index

It is well known that the n dependence of temperature gives a thermo-optic coefficient (dn/dT or TOC) for
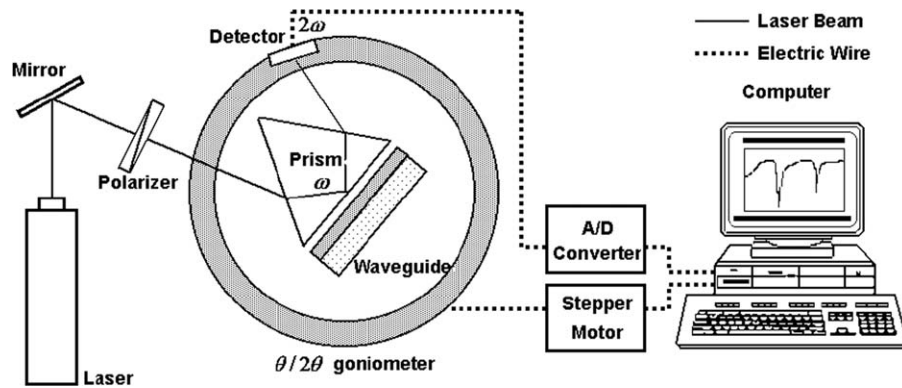
Figure 1 ATR experimental set for the refractive index of CAPU waveguide.

any material.[16,17] The refractive index at a given temperature is an important parameter to characterize any material. The dn/dT is the main factors to affect the driver power and response speed of the optical switch.

Measurement of n is preformed in an attenuated total reflection (ATR) setup with its temperature precisely controlled as shown in Figure 1. On the basis of the principle of ATR, we designed the most common form of guided-wave resonance of the experimental apparatus to measure the thermooptic polymer film coefficient. The dielectric planar waveguide is a three-tier, and there is the waveguide layer between the substrate and cover layer. The refractive indices of substrate-based, waveguide layer and cover layer are assumed to be n_2, n_1, and n_0, respectively. The waveguide thickness is assumed to be h. For the TM polarization mode, dispersion equation can be expressed as follows:

$$\kappa h = m\pi + \tan^{-1}\left(\frac{n_1^2}{n_2^2}\frac{p}{\kappa}\right) + \tan^{-1}\left(\frac{n_1^2}{n_0^2}\frac{q}{\kappa}\right) \qquad (1)$$

There is, $\kappa = (k_0^2 n_1^2 - \beta^2)^{1/2}$, $p = (\beta^2 - k_0^2 n_2^2)^{1/2}$, $q = (\beta^2 - k_0^2 n_0^2)^{1/2}$

k_0 is wavenumber of vacuum. $k_0 = 2\pi/\lambda$, λ is wavelength of used laser (vacuum) and m is the ordinal number of the module. β is guided-mode for the propagation constant, K is the wave vector of the z-component, κ is the wave vector K of the x-component, $\mathbf{K} = k_0 n_1$

The effective refractive index of guided-mode is defined $N = \beta/k_0$. The effective refractive index can be calculated by measuring the angle of sample and the guided-mode propagation constant β was also obtained.

For multimode waveguide, if propagation constants (β_{m-1}, β_m, and β_{m+1}) of the three-modes are obtained, the transcendental equations can be expressed:

$$\kappa_{m-1}h = (m-1)\pi + \tan^{-1}\left(\frac{n_1^2}{n_2^2}\frac{p_{m-1}}{\kappa_{m-1}}\right) + \tan^{-1}\left(\frac{n_1^2}{n_0^2}\frac{q_{m-1}}{\kappa_{m-1}}\right)$$

$$\kappa_m h = m\pi + \tan^{-1}\left(\frac{n_1^2}{n_2^2}\frac{p_m}{\kappa_m}\right) + \tan^{-1}\left(\frac{n_1^2}{n_0^2}\frac{q_m}{\kappa_m}\right)$$

$$\kappa_{m+1}h = (m+1)\pi + \tan^{-1}\left(\frac{n_1^2}{n_2^2}\frac{p_{m+1}}{\kappa_{m+1}}\right) + \tan^{-1}\left(\frac{n_1^2}{n_0^2}\frac{q_{m+1}}{\kappa_{m+1}}\right)$$

$$(2)$$

From these equations, refractive index n_1 of Capu at different temperature can be obtained.

Measurement of transmission loss

Transmission loss of optical waveguide in thin film is an important parameter which evaluates the dielectric slab waveguide. Transmission loss of optical waveguide devices is produced mainly by the following factors: waveguide material loss caused by scattering and absorption; substrate surface finish by polishing process constraints, irregular interface leading coupling loss between guided mode and radiation mode; curved waveguide surface, causing the loss caused by energy radiation. The digital imaging device Charge Coupled Device (CCD) was used to record the scattered light intensity of points on the transmission line, and transfer into an internal light intensity.

After spatial average filter, a transmission attenuation curve can be obtained. The attenuation loss of the guided mode power with propagation distance can be expressed:

$$P_Z = P_0 e^{(-\alpha \cdot Z)} \qquad (3)$$

where P_0 is initial incident light intensity of $Z = 0$, P_Z is transmission light intensity of $Z = z$, the attenuation coefficient is defined as:

$$\alpha = \frac{1}{z_2 - z_1}\ln\left(\frac{P_{z_1}}{P_{z_2}}\right) \qquad (4)$$

$$L = -10\alpha(\lg\ e) \qquad (5)$$

L is the transmission loss of optical waveguide.

EXPERIMENTAL

Materials and characterization

3,3′-dichloro-4,4′-diamino-diphenylmethane (MOCA) was supplied from Jiangsu Changyu Chemical Co., Ltd., Zhangjia Gang, China. L(−)-tartaric acid and Dibutylbis (lauroyloxy) tin(T-12)were obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Toluene diisocyanate (TDI) was supplied by Rongrong Chemical Co., Ltd., Shanghai, China. Other reagents and solvents were obtained commercially and were used as received.

Fourier transform infrared (FTIR) spectra of samples were obtained on a KBr pellet with a Nicolet (USA) AVATAR 360 FT-IR spectrometer. A minimum of 32 scans was signal-averaged with a resolution of 2 cm^{-1} in the 4000–450 cm^{-1} range. Ultraviolet-visible (UV-vis) spectra of samples were recorded with a Shimadzu (Japan) UV-2450 spectrometer at 25°C. Circular dichroism (CD) spectrum was carried out at 25°C on DMF solution on a Jasco-815 (Japan) dichrograph. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Netzsch (Germany) STA 449C instrument. The programmed heating range was from room temperature to 500°C at a heating rate of 10°C/min under a nitrogen atmosphere. The measurement was taken with 6–10 mg samples. The optical rotation was performed with a WXG-4 visual spin spectrometer (Shanghai Optical Instruments Factory, China), and the melting point was measured by an X-5 microsurgery melting point detector (temperature control type) (Beijing Tech Instrument Co., Ltd., China). The ^{1}H NMR spectrum was collected on a DXT-300 MHz Bruker (Germany) NMR spectrometer. The contents of C, H, H, and N were obtained by FLASH EA-1112A element analyzer (Italy).

Preparation of chiral azobenzene polyurethane (CAPU)

A solution of sodium nitrite in distilled water was slowly added to a solution of MOCA in hydrochloric acid through a dropping funnel over a 40-min period. The solution was kept at 0°C for 2 h with vigorous mechanical agitation. The resultant diazonium salt solution with reddish brown color was then slowly added to a solution of aniline at 0°C and kept there for 2 h under stirring. The resulting orange suspension was acidified and filtered. The solid precipitate was washed with ammonia water and deionized water until the pH of the filtrate reached 7. The orange compound CAAPM was purified on a silica gel column with the eluate acetone, and yield was 78.8%. Anal. Calcd for $C_{25}H_{20}N_6Cl_2$: C, 63.16%; H, 4.21%; N, 17.68%. Found: C, 63.96%; H, 4.44%; N, 16.98%. ^{1}H-NMR (300MHz, acetone-d$_6$, ppm): 3.40 (—NH$_2$, 4H), 6.90 (ArH, 4H), 7.73 (ArH, 4H), 7.67 (ArH, 2H), 7.38 (ArH, 2H), 6.78 (ArH, 2H), 3.12 (—CH$_2$—, 2H).

CAAPM and chiral reagent L(−)-tartaric acid were added to DMF under magnetic stirring, and the reaction mixture was heated to 55°C and refluxed for 1 h. After the reaction was completed, the solution containing hydroxyl groups and the azobenzene chromophore groups was obtained and reacted with Toluene diisocyanate (TDI) in the presence of catalyst T-12. Then, the mixture was stirred at 80°C for 1 h. The obtained solution was dried at 80°C and the red, optically chiral azobenzene polyurethane (CAPU) was prepared. Anal. Calcd for $C_{51}H_{36}N_{10}O_{12}Cl_2$: C, 58.23%; H, 3.43%; N, 13.32%. Found: C, 58.82%; H, 3.68%; N, 14.01%. ^{1}H-NMR (300MHz, acetone-d$_6$, ppm): 9.11 (—NHCOO—, 4H), 7.52 (ArH, 2H), 7.02 (ArH, 2H), 6.85 (ArH, 2H), 2.02 (—CH$_3$, 6H), 4.18 (—CH—OCO—, 4H), 6.88(ArH, 4H), 7.75(ArH, 4H), 7.69(ArH, 2H), 7.40(ArH, 2H), 6.80(ArH, 2H), 3.15(—CH$_2$—, 2H). The synthetic route is shown in Figure 2.

RESULTS AND DISCUSSION

UV-Vis and FT-IR spectra of CAAPM and CAPU

The UV-Vis spectra of the prepared CAAPM and CAPU were shown in Figure 3. The content of CAAPM or CAPU was 2.6×10^{-5} mol L^{-1}. From the Figure 3, the strong absorption peak of CAAPM in DMF appeared at 375nm which was attributed to the π-π* transition of the group —N=N— and, while the absorption peak of CAPU in DMF was 268 nm. The result indicated that the diazo coupling reaction was successful, and the structure of the azobenzene was constructed and the absorption peak had blue shift after polymerization.[18] This is mainly because the azo chromophore in the polymer chain interacted with the aromatic group in the same or adjacent elements. The interaction also reduced electron energy of the ground state level and increased the excited state level of the azogroup; therefore, the characteristic absorption peak of the azogroup occurred blueshift. FT-IR spectra of CAAPM and CAPU were shown in Figure 4. From the FT-IR spectrum of CAAPM, it showed that the band at 3300 cm^{-1} was fairly broad and corresponded to the stretching vibration of free and hydrogen-bonded NH groups. The symmetrical vibration of —N=N— group was observed at 1512 cm^{-1}.[19,20] According to
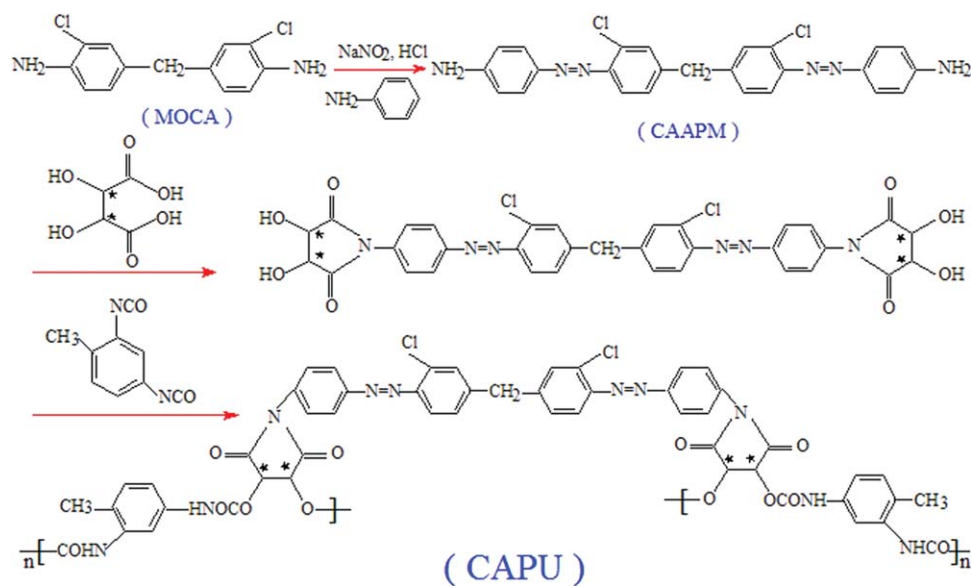
Figure 2 The synthetic route of chiral azobenzene polyurethane CAPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the FT-IR spectrum of CAPU, the peak 1749cm^{-1} was the ester stretching vibration peaks, indicating that the —OCON— group existed. The bands at 2960, 1518, and 1412cm^{-1} can be attributed to —CH$_3$ groups, —N=N— group vibrations, and asymmetric vibration of nitro groups, respectively.

The physical properties of the CAPU

The solubility of CAPU was measured in different solvents. The CAPU has excellent solubility at strong polar solvent such as N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAc), and 1-methyl-2-pyrrolidone (NMP). In addition, CAPU could also dissolve in the low boiling point solvent such as tetrahydrofuran (THF). The melting point of CAPU was found to be 170.5°C. The specific rota-

tions of CAPU in the different solvents were $[\alpha]_D^{25} = +102^0$ (DMF, $c = 0.05$ g/mL), $[\alpha]_D^{25} = +118^0$ (DMAc, $c = 0.05$ g/mL), $[\alpha]_D^{25} = +152^0$ (THF, $c = 0.05$ g/mL), respectively. To investigate in detail the chiroptical property, the CAPU (10^{-5} mol L^{-1}) has been submitted to CD spectroscopy in DMF solution in the spectral region between 200 and 700 nm (Fig. 5). From the Figure 5, the CD spectrum showed two strong dichroic bands of opposite sign, with the crossover point close to the position of the maximum of the UV-visible absorption band. Such a behavior, quite similar to that observed in dilute solution of the polymer, is typical of exciton splitting originated by cooperative interactions between chromophores disposed in a mutual chiral geometry of one prevailing handedness.[21] This implies that the polymer chains
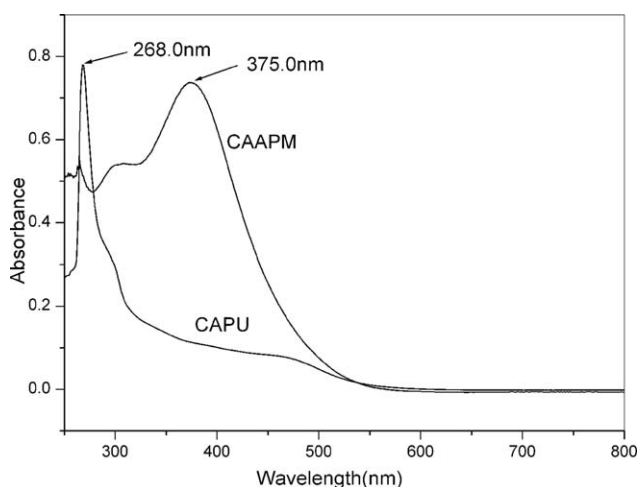

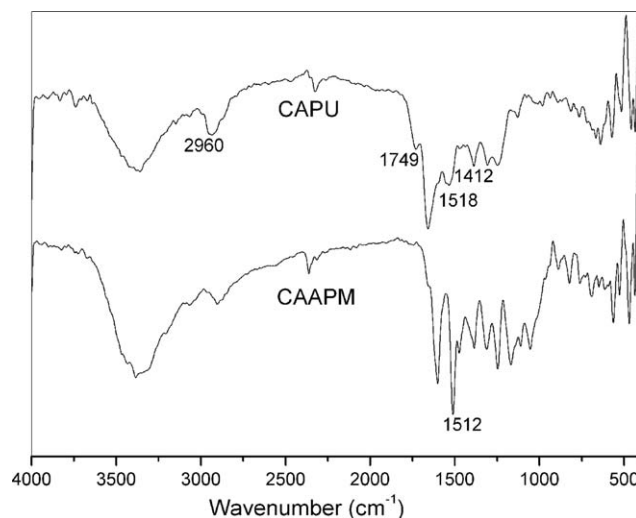**Figure 3** UV-Vis spectra of CAAPM and CAPU.
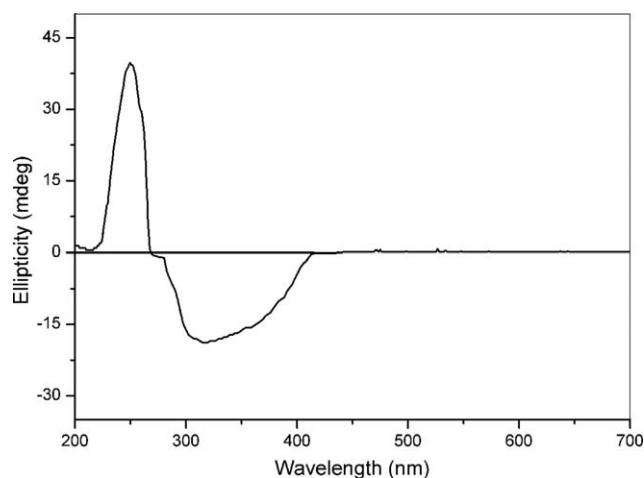

Figure 4 FT-TR spectra of CAAPM and CAPU.

Figure 5 The CD spectrum of CAPU in DMF solution.

have a predominant helical structure with a well-defined sense.

To examine thermal activities of CAPU in higher temperature range and its thermal decomposition characteristic, DSC and TGA experiments were carried out on Netzsch STA449C with the heating rate 10°C/min under nitrogen. The DSC and TG curves were shown in Figure 6 and the results indicated that the glass transition temperature (T_g) and the decomposition temperature (T_d) at 5% mass loss were 110°C and 199°C, respectively.

Thermo-optic properties of the CAPU

Thermo-optic coefficient (dn/dT) is the variation of refractive index depended on the temperature and is the main factors to affect the driver power and response speed of the optical switch. According to the Figure 1, a collimated light beam ($\lambda = 650$ nm) from a diode laser passes through a polarizer and is then incident upon the interface between the prism
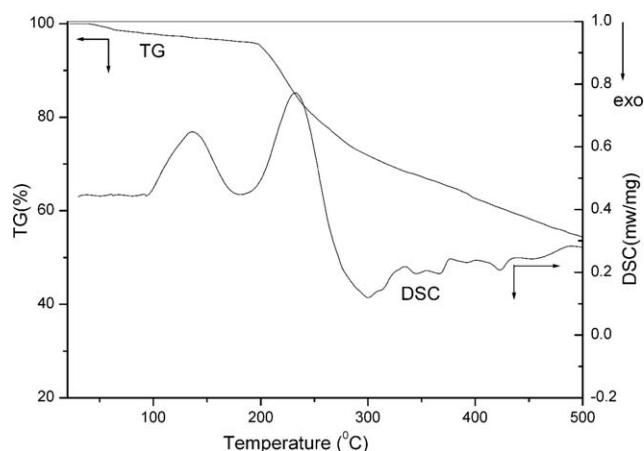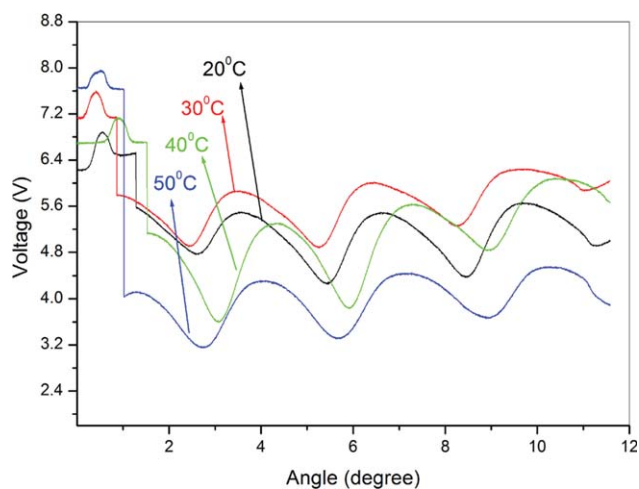

Figure 6 The DSC and TG curves of CAPU.

Figure 7 The ATR spectra of CAPU at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and the gold film with an appropriate angle. The reflected light is detected by a photodiode and averaged to reduce the noise. The prism-waveguide coupling system and detector are mounted on a high precision θ/2θ computer-controlled goniometer and a series of dips in reflectivity due to resonant transfer of energy into guide modes are generated on a computer screen and saved in a data file. At the synchronous angles, energy of incident light is transferred into the guided modes of the polymer waveguide due to resonance coupling and the reflected intensity is drastically reduced. From the room temperature, ATR spectra of different temperature were obtained and shown in Figure 7. The various synchronization angles of the ATR spectra at different temperature were measured. The refractive index of polymer film was calculated at different temperatures from the transcendental equations.
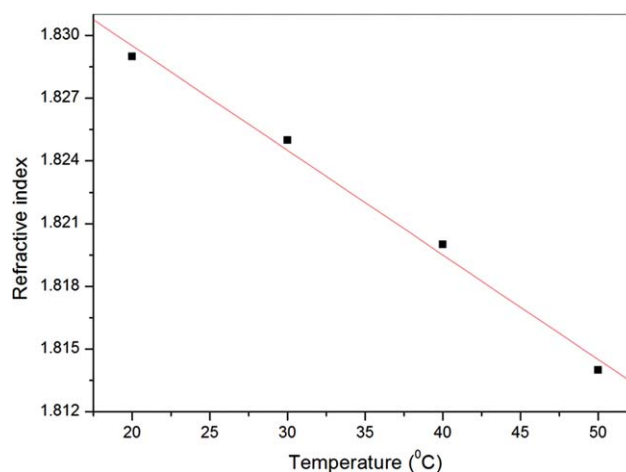

Figure 8 The refractive indices of CAPU at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
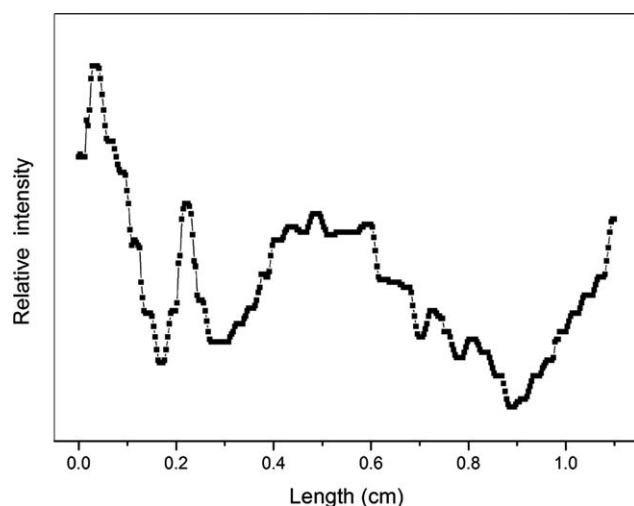
Figure 9 The scattered relative light intensity distribution of optical waveguide CAPU.

In the experiment, the prepared CAPU solution, which is filtered through a syringe with a 0.45-μm Teflon filter and spin-coated onto the hypotenuse face of a prism. The CAPU film is dried in vacuum overnight at room-temperature to evaporate traces of the solvents. The refractive index of TM polarization with temperature at 650 nm was shown in Figure 8. From Figure 8, the thermo-optic coefficient (dn/dT) was $-5.0 \times 10^{-4} {}^{\circ}C^{-1}$. The correlation coefficient was 0.9960 and standard deviation (SD) was 0.0707%. The dn/dT was bigger than inorganic materials such as silica glass ($10.8 \times 10^{-6} {}^{\circ}C^{-1}$), zinc silicate glass ($5.5 \times 10^{-6} {}^{\circ}C^{-1}$), borosilicate glass ($4.1 \times 10^{-6} {}^{\circ}C^{-1}$) and the organic materials of polystyrene ($1.23 \times 10^{-4} {}^{\circ}C^{-1}$), poly(methyl methacrylate) ($1.20 \times 10^{-4} {}^{\circ}C^{-1}$), and azopolymers of DR1/PMMA ($1.215 \times 10^{-4} {}^{\circ}C^{-1}$),[22] azonitrothiazole polyimide ($1.698 \times 10^{-4} {}^{\circ}C^{-1}$),[23] azonitrobenzothiazole polyimide ($1.460 \times 10^{-4} {}^{\circ}C^{-1}$),[23] DR1 polyimide ($1.331 \times 10^{-4} {}^{\circ}C^{-1}$),[23] azo PUI ($-4.0296 \sim -4.9032 \times 10^{-4} {}^{\circ}C^{-1}$).[17]

Transmission loss of the CAPU

In optical communication systems, light is used to transport information between different users. The scattered relative light intensity distribution of optical waveguide CAPU along the propagation path was measured by CCD device and the result was shown in Figure 9. The transmission loss was obtained and the value was 0.565 dB/cm. It is clearly seen that the optical transmission loss of CAPU thin film waveguide are comparatively smaller. Digital optical switch (DOS) has become, since its invention, a very attractive component for space switching in multiwavelength optical communication system applications. Therefore, the conclusion of the experiment has a little significance to develop new DOS.

CONCLUSIONS

In summary, chiral azobenzene polyurethane was successfully synthesized and characterized. The dn/dT was bigger than inorganic materials (e.g., silica glass, zinc silicate glass, borosilicate glass), the organic materials (e.g., polystyrene and PMMA), and some azopolymers. By using CCD digital imaging devices, transmission loss of the internal waveguide was measured and the value is 0.565 dB/cm. This work opens up a possibility for the preparation of high thermo-optic materials.

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