Synthesis, Characterization, and Thermo-Optical Properties of Azobenzene Polyurethane Containing Chiral Units

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ABSTRACT: An optically active levoazobenzene polyurethane (PU) was synthesized and was based on the chromophore 4-(4′-nitrophenylazo) phenylamine, the chiral reagent L(−)-tartaric acid, and toluene diisocyanate. The chemical structure and thermal properties were characterized by ultraviolet–visible spectroscopy, Fourier transform infrared spectroscopy, ^{1}H-NMR spectroscopy, and differential scanning calorimetry. The PU had high number- and weight-average molecular weights up to 52 300, a large glass-transition temperature of 235.7°C, and an optical rotation of −18.06°, The optical parameters, including the refractive index (n) and thermo-optic coefficient (dn/dT); the dielectric constant (ε) and its variation with temperature; and the thermal volume expansion coefficient and its variation with temperature of PU were obtained. The dn/dT and ε values for the polymer were in the range −4.1200 to 3.6257 × 10^{-4} °C^{-1} and 2.00 ± 0.11, respectively. The dn/dT values were one order of magnitude larger than those of inorganic glasses, such as zinc silicate glass (5.5 × 10^{-6} °C^{-1}) and borosilicate glass (4.1 × 10^{-6} °C^{-1}), and were larger than organic materials, such as polystyrene (−1.23 × 10^{-4} °C^{-1}) and poly(methyl methacrylate) (−1.20 × 10^{-4} °C^{-1}). The ε values were lower than that of alicyclic polyimide and semiaromatic polyimide. The obtained PU is expected to be useful for optical switching and optical waveguide areas. The conclusion has a little significance for the development of a new digital optical switch. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 146–151, 2010

Key words: azo polymers; optics; polyurethanes

INTRODUCTION

Polymeric-based azo materials have been paid great attention in past decades because of their huge potential applications in high-technology fields, such as waveguide switches, photomechanical systems, data manipulation, nonlinear optical materials, holographic memories, and information processing.[1–4] The polymer-containing azobenzene chromophore's extended aromatic structure gives rise to the azobenzene's intense optical absorption and related optical properties. Many optical polymer materials require either noncentrosymmetric or polar packing (space group) of the active material. However, controlling the organization/packing of the polymer molecule is a very difficult task to accomplish; an easier method is making a polymer candidate containing chiral units and use its inherent chirality to prevent centrosymmetric packing. Recently, several materials with chiral functionality have been studied because these materials provide properties useful in various research areas, including molecular switches,[5,6] optically active polymers,[7–10] liquid crystals,[11] nonlinear optics,[12,13] imprinted polymers,[14] and heterogeneous asymmetric catalysis.[15,16]

In this study, we synthesized an optically active levoazobenzene polyurethane (PU) containing a chromophore and a chiral skeleton. The chemical structure, thermal properties, and thermo-optical properties of the PU were determined.

THEORY

It is well known that the n dependence of temperature gives a thermo-optic coefficient (dn/dT or TOC) for any material. The n value at a given temperature is an important parameter for characterizing any material. Theoretically, n is a function of the density (ρ) and mean polarizability (α) of a medium, which varies with temperature and pressure. For the optical switch, the TOC of a polymer is one of the main factors affecting the driving power and response speed.

For an organic polymer, n decreases with increasing temperature. In this study, n of the PU polymer was determined at different temperatures, different contents, and with complex light. Then, the dielectric constant (ε) was calculated according to the following relationship between n and ε: $\varepsilon = n^2$.

According to the Lorentz-Lorenz[17] relation for optical polymers, the relationship among n, α, and ρ can be expressed by eq. (1):

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3M} \pi N_A \alpha \rho \qquad (1)$$

where M is the molar mass of PU and N_A is Avogadro's constant. The polarizability temperature coefficient ($d\alpha/dT$) of the polymer molecular is very small and can be ignored ($d\alpha/dT \approx 0$), so from eq. (1), n change with temperature (dn/dT) is the density change with temperature change ($d\rho/dT$). Equation (1) could be changed as follows:

$$\frac{2n(n^2 + 2) - 2n(n^2 - 1)}{(n^2 + 2)^2} \frac{dn}{dT} = \frac{4}{3M} \pi N_A \alpha \frac{d\rho}{dT} \qquad (2)$$

If one connects eqs. (1) and (2), they can be expressed by eq. (3):

$$\frac{dn}{dT} = \frac{(n^2 + 2)(n^2 - 1)}{6n} \frac{1}{\rho} \frac{d\rho}{dT} \qquad (3)$$

In fact, $d\rho/dT$ is the coefficient of thermal expansion:

$$\beta = \frac{1}{V} \frac{dV}{dT} = -\frac{1}{\rho} \frac{d\rho}{dT} \qquad (4)$$

where V is the volume, dV/dT is volume temperature coefficient.

eq. (3) can be simplified as

$$\frac{dn}{dT} = -f(n)\beta \qquad (5)$$

with

$$f(n) = \frac{(n^2 - 1)(n^2 + 2)}{6n} \qquad (6)$$

where β is the thermal volume expansion coefficient, which can be calculated according to $f(n)$ and dn/dT.

EXPERIMENTAL

Materials and characterization

p-Nitroaniline, phenylamine, L($-$)-tartaric acid, and tetrahydrofuran (THF) were obtained from Guoyao Chemical Plant (Shanghai, China). Toluene diisocyanate (TDI) was supplied by Huls Co. N,N-Dimethylformamide (DMF) was provided by Shanghai Gaoqiao Petrochemical Co. (Shanghai, China).
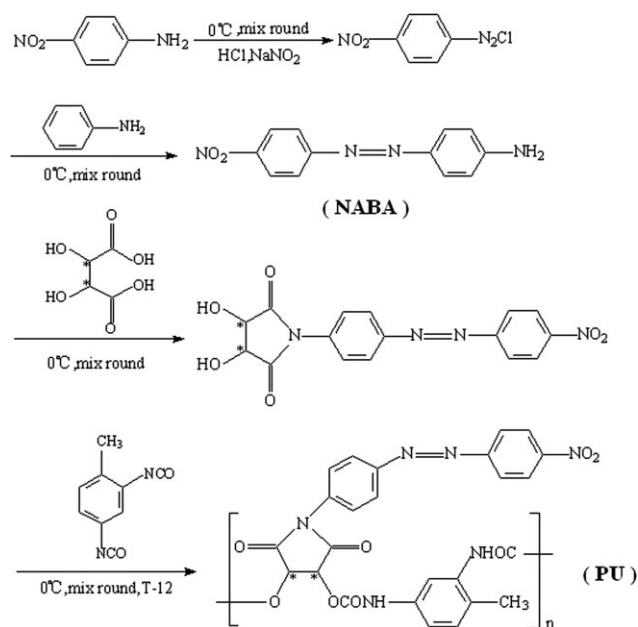
Fourier transform infrared (FTIR) spectra of the samples were obtained on a KBr pellet with a Nicolet (USA) AVATAR 360 FTIR spectrometer. A minimum of 32 scans was signal-averaged with a resolution of 2 cm^{-1} in the 4000–400-cm^{-1} range. Ultraviolet–visible (UV–vis) spectra of samples were recorded with a Shimadzu (Japan) UV-2450 spectrometer at 25°C. Differential scanning calorimetry (DSC) was performed on a Netzsch (Germany) 204 F1 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, and N in the polymer were obtained with a Foss Heraeus (Germany) CHN—O rapid element analysis spectrometer. The molecular weights were determined by gel permeation chromatography with a polystyrene standard with a Waters (USA) SEC-244 system at 25°C in THF.

Synthesis of the optically active azobenzene PU containing chiral units

A solution of sodium nitrite in deionized water was slowly added to a solution of p-nitroaniline 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 a reddish brown color was then slowly added to a solution of phenylamine 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, 4-(4′-nitrophenylazo) phenylamine (NABA), was purified on a silica gel column with the eluate acetone, and the yield was 77.6%.

NABA and the chiral reagent L($-$)-tartaric acid were added to DMF under magnetic stirring, and the reaction mixture was heated to 55°C and refluxed for 24 h. After the reaction was completed, the solution containing hydroxyl groups and the azobenzene chromophore group was obtained and reacted with an aromatic diisocyanate (TDI) in the presence of the 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 active azobenzene PU was prepared.

Scheme 1 Synthesis of the azobenzene PU containing chiral units.

Figure 2 FTIR spectra of NABA and PU. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

UV–vis spectra of NABA and PU

ANAL. Calcd for $C_{25}H_{18}N_6O_8$: C, 56.60%; H, 3.40%; N, 15.85%. Found: C, 56.98%; H, 3.69%; N, 16.09%. ^{1}H-NMR (300 MHz, acetone–d_6, ppm): 9.08 (—NHCOO—, 2H), 7.50 (ArH, 1H), 7.01 (ArH, 1H), 6.83 (ArH, 1H), 2.05 (—CH$_3$, 3H), 4.11 (—CH—OCO—, 2H), 7.01 (ArH, 2H), 7.41 (ArH, 2H), 7.60 (ArH, 2H), 8.01 (ArH, 2H).

Because of the good solubility of the PU in THF, the molecular weight was measured by gel permeation chromatography. The weight-average molecular weight was 52,300 with a polydispersity of 2.09 (with polystyrenes standards).The synthetic route is shown in Scheme 1.
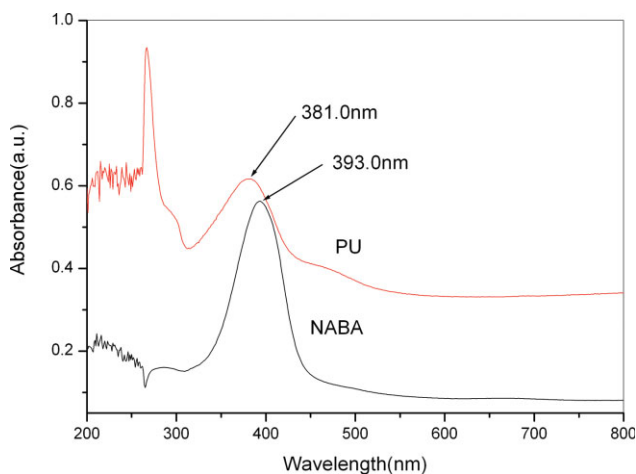
The UV–vis spectra of the prepared NABA and PU are shown in Figure 1. The content of NABA or PU was 3.0×10^{-5} mol/L. As shown in Figure 1, the absorption peaks of NABA and PU were 393.0 and 381.0 nm, respectively. These peaks resulted from the π–π transition of the group —N=N—. The absorption peak of PU had a blueshift compared with NABA; this was mainly because the azo chromophore in the polymer chain interacted with the aromatic group in the same or adjacent elements. The interaction also reduced the electron energy of the ground state level and increased the excited state level of the azo group; therefore, the characteristic absorption peak of the azo group occurred blueshift.

The azobenzene monomer (NABA) containing an amino group was synthesized by a diazo coupling reaction between *p*-nitroaniline and phenylamine in the presence of sodium nitrite and hydrochloric acid followed by an aroylamino reaction with L(−)-tartaric acid containing two carboxyl groups (Scheme 1). The bishydroxyl groups were induced and reacted with TDI by the *in situ* polycondensation of diisocyanate. FTIR spectra of NABA and PU were obtained between 4000 and 400 cm^{-1} on a KBr pellet, and the results are shown in Figure 2. According to the FTIR spectrum of NABA, the characteristic absorption peaks of N—H, Ar—H, and N=N were observed at 3293, 3028, and 1645 cm^{-1}, respectively; this indicated that the —N=N— group existed. The skeleton vibration absorption peaks of the benzene ring were located at 1597, 1520, 1504, and 1463 cm^{-1}, and the stretching vibration absorption peak of —NO$_2$ was found at 1425 cm^{-1}. The FTIR spectrum of PU consisted of some peaks located at

Figure 1 UV–vis spectra of NABA and PU in DMF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
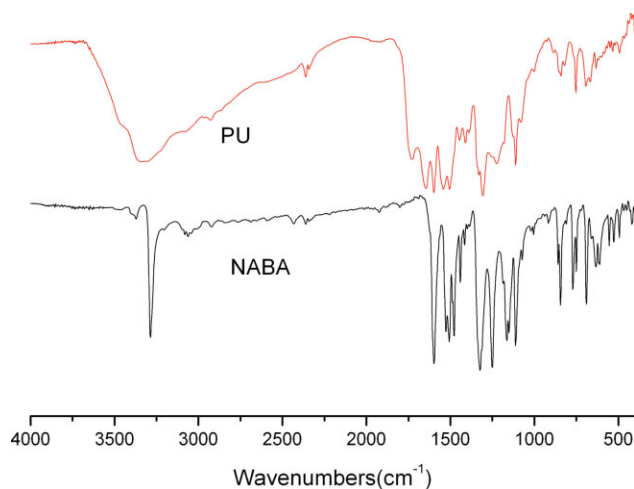
3362 cm^{-1} (—N—H), 1221 cm^{-1} (—C—N—C—), and 1740 cm^{-1} (—C=O); this indicated that the —OCON— group in the structure of PU existed. The ^{1}H-NMR and FTIR spectra were consistent with the proposed chemical structures.

Physical properties of PU

The solubility of PU was measured in different solvents. PU had excellent solubility in strong polar solvents, such as DMF, N,N-dimethylacetamide, and 1-methyl-2-ketopyrrolidine. In addition, PU also dissolved in low-boiling-point solvents, such as THF, although in other organic solvents, PU was insoluble or had relatively poor solubility. The melting point of PU was found to be 302°C, and the optical rotation value was −18.06°; this indicated that PU was a levopolymer.

DSC analysis of PU

The DSC thermogram is shown in Figure 3. The programmed heating range was from room temperature to 500°C with a heating rate of 10°C/min under a nitrogen atmosphere. The DSC curve showed that the glass-transition temperature (T_g) of PU was 235.7°C, which indicated that the obtained PU possessed excellent thermal stability. The specific heat changed in the process of glass state to high-elastic state, and the heat capacity change was 3.195 J·g^{-1}·K^{-1}, the crystallizing point was 265.2°C, and the melting point was 300.1°C, which was similar to the 302°C of the measured experimental value (see 4.3). These results show that the obtained PU had a high purity.
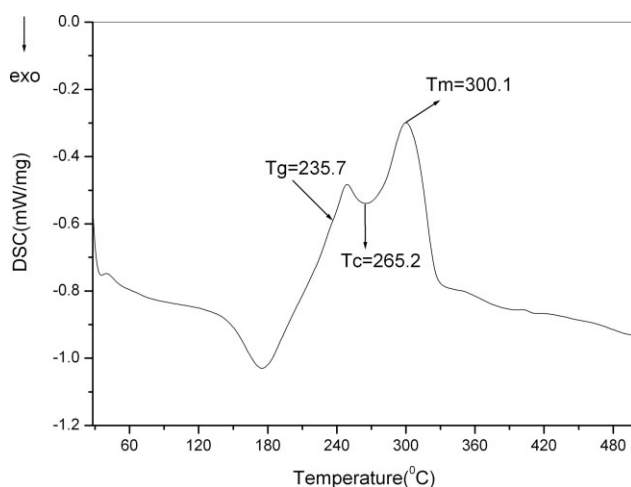

Figure 3 DSC curve of PU (T_c = crystallization temperature; T_m = melting temperature).
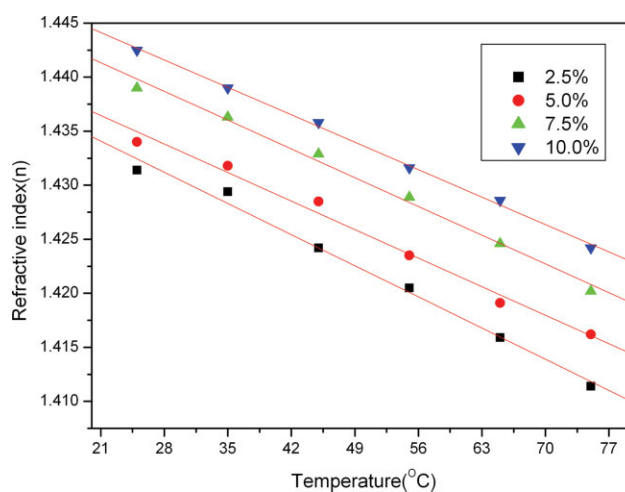

Figure 4 N of the azobenzene PU. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thermo-optical properties of PU

Different contents of PU solution in DMF were prepared: 2.5, 5.0, 7.5, and 10.0%. The n values of the different content polymer solutions with an Abbé refractometer (WAY-2S, Nanjing Li'er Lab Instrument Equipment Co., Ltd., China) were measured in the temperature interval 25.0–75.0°C at atmospheric pressure. We controlled the temperature by circulating water into the refractometer through a thermostatically controlled bath with a digital temperature control unit to maintain the desired temperature within ±0.01°C. We calibrated the apparatus by measuring n of Millipore quality water and toluene before measurements. Samples were directly introduced in the cell with a syringe. At least seven independent measurements were taken for each sample at each temperature to assure the effectiveness of the measurement. N values were measured to an accuracy of ±0.0001 after the sample mixture was thermostatically at equilibrium. To obtain consistent values, we held the temperature constant throughout each set of measurements and repeated every experiment three times under the same conditions. The n values of different contents of PU at different temperatures were measured and are listed in Figure 4. Then, ε and the volume expansion coefficient were calculated and are listed in Figures 5 and 6. The n, ε, and thermal expansion coefficient changes with temperature are listed in Table I.

It is known that a large TOC corresponds to a small temperature change, and thus, small power input is needed to cause the necessary change in n of polymer waveguides. As shown in Figure 4 and Table I, the slope of the n curve (dn/dT) was −4.1200 to 3.6257 × 10^{-4} °C^{-1}. The correlative coefficient was 0.9938–0.9989, which indicated that n and

Figure 5 ε of the azobenzene PU. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
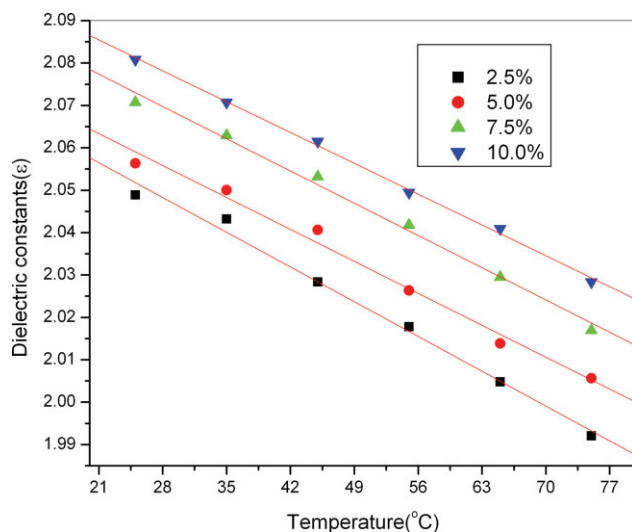

Figure 6 Volume expansion coefficient of the azobenzene PU. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature had a good linear correlation in the selected temperature range. The standard deviation was very low. The TOCs of the obtained PU were one order of magnitude larger than those of inorganic glasses, such as zinc silicate glass (5.5×10^{-6} °C^{-1}), borosilicate glass (4.1×10^{-6} °C^{-1}), SiO$_2$ (1.1×10^{-5} °C^{-1}), and LiNbO$_3$ (4×10^{-5} °C^{-1}), and was larger than organic materials, such as polystyrene (-1.23×10^{-4} °C^{-1}) and poly(methyl methacrylate) (-1.20×10^{-4} °C^{-1}).

As shown in Figure 5 and Table I, the variation of the dielectric constant with temperature ($d\varepsilon/dT$) of PU was -1.04 to 1.17×10^{-3} °C^{-1}. The correlative coefficient was 0.9939–0.9989, which indicated that ε and temperature had a good linear correlation in the selected temperature range. The standard deviation was very low. In microelectronic device circuits, the propagation velocity of the signal is inversely proportional to the square of ε of the propagation medium. Therefore, materials with the low ε are required for faster signal propagation in microelectronic devices without cross-talk in new multilevel
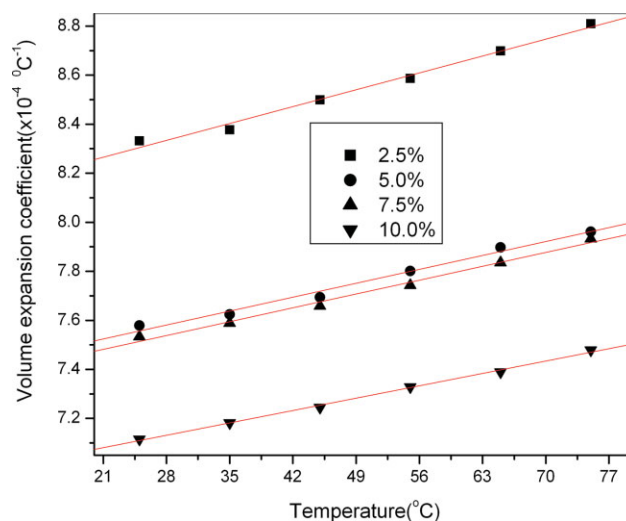
high-ρ and high-speed electronic circuits.[18] In this experiment, the obtained PU containing chiral units was 2.00 ± 0.11 (1.99–2.10). The values were lower than the optically estimated ε of a conventional polymer (3.00)[19] and alicyclic polyimide (2.55) and significantly lower than that of a semiaromatic polyimide (2.83).[20] The results indicate that the obtained PU could be expected to be applied in optical switches, waveguide fields, and the microelectronics industry as a dielectric layer.

The possibility of controlling the coefficient of thermal expansion in pure and composite materials has been a principal driving force. As shown in Figure 6 and Table I, the variation of the thermal volume expansion coefficient with temperature ($d\beta/dT$) of PU was 7.21 to 9.83×10^{-7} °C^{-1}. The correlative coefficient was 0.9933–0.9984, which indicated that β and temperature had a good linear correlation in the selected temperature range. The standard deviation was very low. Figure 4–6 also show that the reflective indices and ε values of this system decreased linearly with increasing temperature at the same PU

TABLE I
Optical Properties of the Azobenzene PU

		PU content (wt %)			
	Property	2.5	5.0	7.5	10.0
Thermo-optic	dn/dT ($\times 10^{-4}$ °C^{-1})	−4.1200	−3.7743	−3.8029	−3.6257
	Correlation coefficient	0.9956	0.9938	0.9964	0.9989
	Standard deviation ($\times 10^{-4}$)	8.0953	8.7988	6.7605	3.5943
Dielectric	$d\varepsilon/dT$ ($\times 10^{-3}$ °C^{-1})	−1.1700	−1.0800	−1.0900	−1.0400
	Correlation coefficient	0.9957	0.9939	0.9966	0.9989
	Standard deviation ($\times 10^{-3}$)	2.2800	2.4900	1.8900	1.0100
Thermal expansion	$d\beta/dT$ ($\times 10^{-7}$ °C^{-1})	9.8300	8.1200	8.0700	7.2100
	Correlation coefficient	0.9949	0.9933	0.9954	0.9984
	Standard deviation ($\times 10^{-2}$)	2.0840	1.9740	1.6300	0.8400

mass content, whereas β increased linearly. If one considers the control of n, an appropriate temperature, and the proper orientation of the constant, the material could be used to design high-performance thermo-optic polymer devices.

The digital optical switch (DOS) has become, since its invention, a very attractive component for space switching in multiwavelength optical communication system applications. Yeo and Shin[21] reported a polymer–silica hybrid 1×2 DOS. The polymer that was used had a TOC of -1.8×10^{-4} $^\circ C^{-1}$, whereas the TOC of silica is about $+1.1 \times 10^{-5}$ $^\circ C^{-1}$. Noh et al.[22] reported a Y-branch DOS. The used polymer had a TOC of 1.4×10^{-4} $^\circ C^{-1}$. Therefore, the conclusion of the experiment had a little significance for the development of new DOSs.

CONCLUSIONS

We synthesized an azobenzene PU containing chiral units and with high thermal stability. It was a levo-polymer whose optical rotation and melting point were -18.06° and $302^\circ C$, respectively. The following parameters were investigated: n, dn/dT, ε, $d\varepsilon/dT$, β, and $d\beta/dT$. The n of the azobenzene PU containing chiral units changed with temperature. The organic polymer exhibited a negative dn/dT. ε met the requirements of the microelectronics industry. These parameters are of great significance for the optical application of the material, particularly for the development of optical materials because of the control of their n values. The results indicate that the PU polymer could be used in the design of high-performance thermo-optic polymer devices.

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