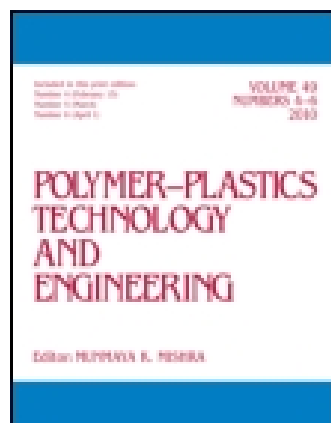


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Optically Active Polyurethane Containing Asymmetric Center: Preparation, Characterization and Thermo-Optic Properties

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Optically active azobenzene polyurethane (OAAPU) containing donor- π -acceptor azo group and asymmetric center was obtained from chromophore NABZ, chiral reagent L(-)-tartaric acid and toluene diisocyanate (TDI). The chemical structure and the thermal property were characterized by UV-Vis spectroscopy, FT-IR, ^1H NMR and differential scanning calorimeter. The optical switching parameters: refractive indices, thermo-optic coefficients, the dielectric constants and volume expansion coefficients of OAAPU were obtained. The refractive index of OAAPU polymer decreased linearity with the increasing of temperature at the same OAAPU content and had a high thermo-optic coefficient $-4.0714 - 3.8686 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$. The conclusion has a little significance to develop new digital optical switch material.

Keywords Optically active polymer; Polyurethane; Thermo-optic property

INTRODUCTION

The polymer containing azobenzene chromophore has been studied for over 70 years, yet it continues to present new and unique optical effects^[1–4]. They have been incorporated into a wide variety of materials and molecular architectures, including polymers and molecular glasses. Compared with inorganic materials, conjugated organic materials are more predominant in properties such as large nonlinear optical susceptibility, fast response, high resistance to laser radiations, low dielectric constant, and ease of processing. These nonlinear optical materials can be used with low intensity lasers for applications, such as phase conjugation, image processing, and optical switching. So far, many organic donor- π -acceptor (D- π -A) compounds have been studied experimentally and theoretically, including derivatives of benzene, azobenzene, styrene and stilbene. The studies indicate organic D- π -A compounds are highly promising candidates for NLO applications^[5,6].

All-optical switches aroused a lot of interests due to their attractive features, such as high speed and huge bandwidth.

However, a major obstacle to the practical realization of a variety of nonlinear waveguide devices is the relatively high switching power required. The organic conjugated polymers are attractive candidates for fabrication of all-optical switches due to their large nonlinearities with subpicosecond responses^[7–9]. But in these polymers, the adiabatic approach utilizing the isotropic thermal optical effect is most promising due to a comparably high $\partial n / \partial T$, polarization and wavelength independence. With given polarization and wavelength independence, the performance of a switch can solely be judged by its insertion loss, cross talk (CT), space requirements on the substrate and power consumption. The polymers should, however, be commercially available which somewhat restricts the possibilities for different switch designs.

In this paper, we designed and synthesized conjugated organic D- π -A compound by introducing the electron donor-acceptor pair at the ends and optically active azobenzene polyurethane (OAAPU) containing the donor-acceptor azobenzene group chromophore and asymmetric center. Their structures were characterized by UV, FT-IR, ^1H NMR and elemental analysis. The thermal property and thermo-optic properties of OAAPU were measured. The absolute values of TO coefficients are much larger than that the inorganic materials such as SiO_2 and LiNbO_3 . These showed that the OAAPU could be made low loss optical communication device and optical switch with low driving power.

EXPERIMENTAL

Materials and Characterization

The chemicals p-nitroaniline, benzylamine, L(-)-tartaric acid and THF were obtained from Guoyao Chemical plant. Toluene diisocyanate (TDI) was supplied by Huls Co. The N,N-dimethylformamide (DMF) was provided by Shanghai Gaoqiao petrochemical company.

The UV-Vis spectroscopy of the sample solution was determined by Shimadzu UV-2450 spectrophotometer. FT-IR spectra of samples were obtained on a KBr pellet using Nicolet AVATAR 360 spectrometer. A minimum

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of 32 scans was signal-averaged with a resolution of 2 cm^{-1} in the $4000\text{--}400\text{ cm}^{-1}$ ranges. The ^1H NMR spectrum was collected on a DXT-300 MHz Bruker NMR spectrometer. The contents of C, H, and N in the polymer were obtained by Foss Heraeus CHN-O-Rapid element analysis spectrometer.

Differential Scanning Calorimetry (DSC) was performed on NETZSCH 204 F1. The programmed heating range was from room temperature to 500°C , at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The measurement was taken using 6–10 mg samples. The optical rotation was performed using a WXG-4 Polarimeter and the melting point was estimated by X-5 micro-surgery melting point detector (temperature control type). Molecular weights were determined by gel permeation chromatography (GPC) with a polystyrene standard using a WATERS SEC-244 system at 25°C in THF.

Synthesis of Optically Active Azobenzene Polyurethane (OAAPU)

A solution of sodium nitrite in deionized water was slowly added to the 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 reddish-brown color was then slowly added to the solution of benzylamine 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) benzylamine (NABZ) was purified on a silica gel column with the eluate acetone and yield was 77.6%.

NABZ 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 24 h. After the reaction was completed, the solution containing hydroxyl groups and azobenzene chromophore group was obtained and reacted with an aromatic 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 active azobenzene polyurethane (OAAPU) solid containing donor- π -acceptor chromophore and asymmetric center was prepared. Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{N}_6\text{O}_8$: C, 57.35%; H, 3.68%; N, 15.44%. Found: C, 57.20%; H, 3.71%; N, 16.00%. ^1H NMR (300 MHz, acetone- d_6 , ppm): 9.06 (-NHCOO-, 2H), 7.51 (ArH, 1H), 7.03 (ArH, 1H), 6.85 (ArH, 1H), 2.06 (-CH₃, 3H), 4.12 (-CH-OCO-, 2H), 3.40 (-CH₂, 2H), 7.09 (ArH, 2H), 7.45 (ArH, 2H), 7.63 (ArH, 2H), 8.06 (ArH, 2H). Due to the good solubility of the OAAPU in THF, the molecular weight can be measured by GPC. The weight-averaged molecular weight (M_w) is 53500 with a polydispersity of

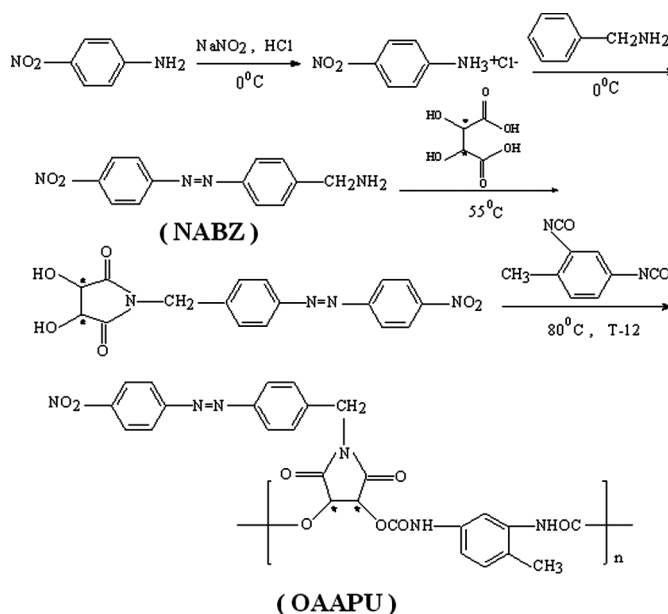


FIG. 1. The synthesis of optically active azobenzene polyurethane (OAAPU).

2.12 (polystyrenes as standards). The synthetic route is shown in Figure 1.

RESULTS AND DISCUSSION

UV-Vis Spectra of NABZ and OAAPU

The UV-Vis spectra of the NABZ and OAAPU were shown in Figure 2. The content of NABZ or OAAPU was $3.0 \times 10^{-5}\text{ mol}\cdot\text{L}^{-1}$. From Figure 1, the maximum absorption wavelength of NABZ and OAAPU were observed at 365.0 and 583.0 nm, 381.0 and 508.0 nm, respectively, which was indicated by the $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transition of the absorption peak (-N=N-). The maximum

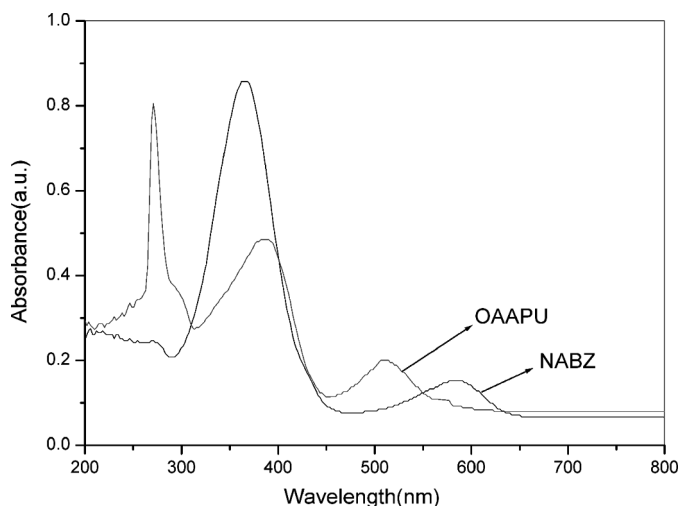


FIG. 2. UV-Vis spectra of NABZ and OAAPU in DMF.

absorption wavelength of OAAPU occurred blue shift in the visible light region compared with the NABZ, which was largely because of that the azo chromophore in the polymer chain interacted with the aromatic group in the same or adjacent elements, so the E-ground state-level of azo-group debased or the excited level of azo-group increased, therefor the characteristic absorption of azo-group occurred blue shift.

FT-IR Spectra of NABZ and OAAPU

FT-IR spectra of NABZ and OAAPU were shown in Figure 3. According to FT-IR spectrum of NABZ, the characteristic absorption peaks of N-H, Ar-H and N=N were observed at 3293, 3028, 1645 cm^{-1} , respectively, indicating that the N=N group existed. The skeleton vibration absorption peak of benzene ring were located at 1597 cm^{-1} , 1520 cm^{-1} , 1504 cm^{-1} , 1463 cm^{-1} , and the stretching vibration absorption peak of $-\text{NO}_2$ was found at 1425 cm^{-1} . The FT-IR spectrum of OAAPU consisted of some peaks located at 3362 cm^{-1} (ν_{as} , -N-H), 1221 cm^{-1} (ν_{str} , -C-N-C-), 1740 cm^{-1} (ν_{as} , -C=O), indicating that the -OCON- group in the structure of OAAPU existed.

The Physical Properties of OAAPU

The solubilities of OAAPU were measured in some organic solvents. The OAAPU had excellent solubility in strong polar solvent such as N, N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) and 1-methyl-2-pyrrolidone (NMP). In addition, OAAPU can also dissolve in the low boiling point solvent such as tetrahydrofuran (THF). However, in other organic solvents, OAAPU was insoluble or had relatively poor solubility.

The melting point of OAAPU was measured and the value was 301°C. The optical rotation was +6.02°, indicating that OAAPU was dextrogyric polymer.

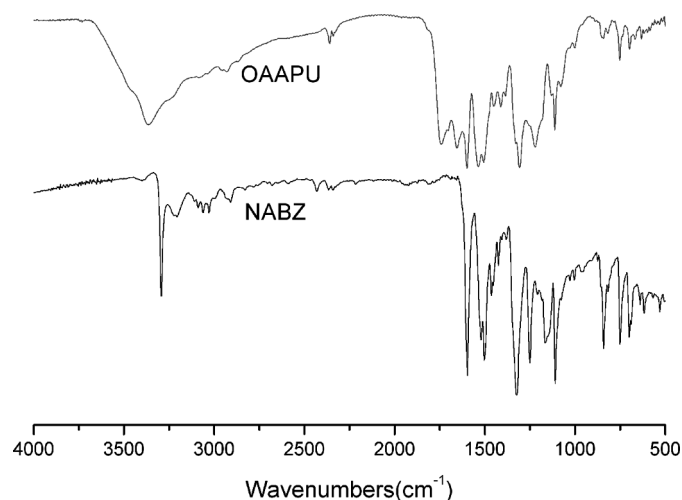


FIG. 3. FT-TR spectra of NABZ and OAAPU.

Differential Scanning Calorimeter Analyze of OAAPU

Differential Scanning Calorimetry (DSC) was performed and the curve was shown in Figure 4. The DSC curve showed that the glass transition temperature of OAAPU was 227.6°C, which indicated that the thermal stability of the OAAPU containing the donor-acceptor azobenzene group chromophore and asymmetric center was high. The specific heat changed in the process of glass state to high-elastic state, and the ΔC_p was 2.686 $\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$, the crystallizing point was 247.5°C, the melting point was 300.5°C, similarity to the 301°C of measured experiment value (see 3.3). These results showed that the obtained OAAPU had high purity.

Thermo-Optic Properties of OAAPU

Different content of OAAPU solution in DMF was prepared and the content was 2.5, 5.0, 7.5 and 10.0%, respectively. Refractive indices of the different content polymer solutions using an Abbé refractometer were measured in the temperature interval of 25.0–75.0°C at atmospheric pressure. Temperature was controlled by circulating water into the refractometer through a thermostatically controlled bath with the digital temperature control unit in order to maintain the desired temperature within $\pm 0.01^\circ\text{C}$. The apparatus was calibrated by measuring the refractive index of Millipore quality water and toluene before measurements. Samples were directly introduced in the cell using a syringe. At least 7 independent measurements were taken for each sample at each temperature to assure the effectiveness of the measurement. Refractive index 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

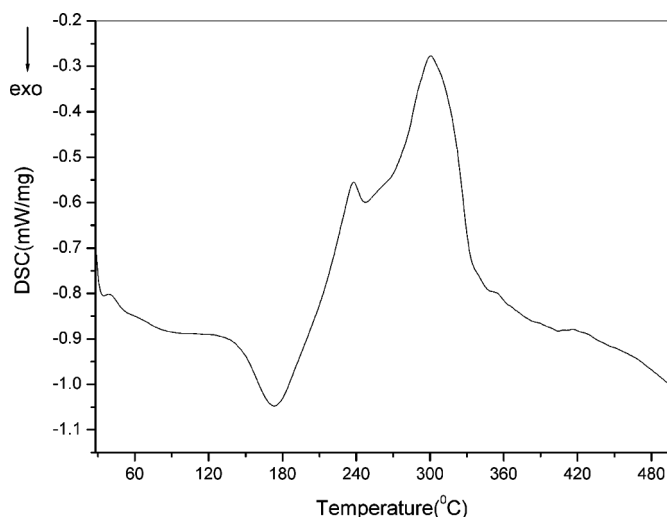


FIG. 4. DSC curve of OAAPU.

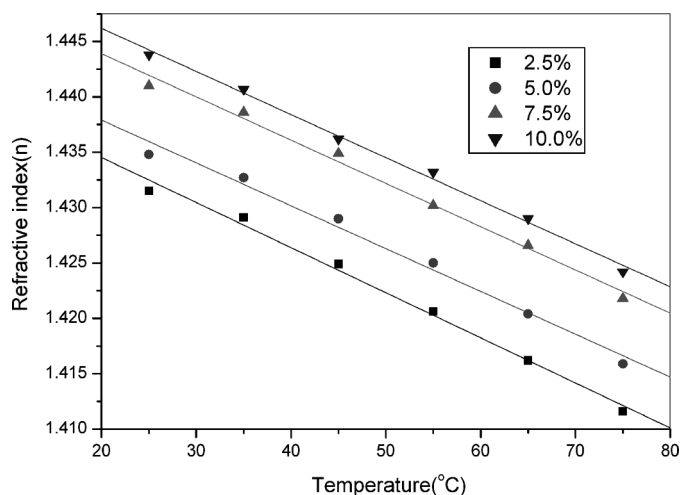


FIG. 5. The refractive index of the different content OAAPU.

times under the same conditions. The refractive index of different content OAAPU at different temperature was measured and listed in Figure 5 and Table 1.

From Figure 5 and Table 1, the dn/dT of OAAPU was $-4.0714 \sim -3.8686 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$. The correlative coefficient was $0.9938 \sim 0.9977$, indicating that refractive index and temperature had a good linear correlation in the selected temperature range. The standard deviations were very low.

The thermo-optic coefficients of the OAAPU containing the donor-acceptor azobenzene group chromophore and asymmetric center are one order of magnitude larger than those of inorganic glasses such as zinc silicate glass ($5.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$), borosilicate glass ($4.1 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$), SiO_2 ($1.1 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$) and LiNbO_3 ($4 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$) and are larger than the organic material such as polystyrene ($-1.23 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$) and PMMA ($-1.20 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$). The result had a little significance to develop new the digital optical switch with low driving power and optical communication.

Then the dielectric constant ϵ was calculated according to the relationship between n and ϵ : $\epsilon = n^2$. The dielectric constant of different content OAAPU at different temperature was listed in Figure 6 and Table 1.

The $d\epsilon/dT$ of OAAPU was $-1.1000 \sim -1.1600 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$. The correlative coefficient was $0.9940 \sim 0.9979$, indicating that dielectric constant and temperature had a good linear correlation in the selected temperature range. The standard deviations were very low.

In microelectronic device circuit, the propagation velocity of the signal is inversely proportional to the square of dielectric constant of the propagation medium. Therefore, materials with the low dielectric constant are required for faster signal propagation in microelectronic devices without cross-talk in new multilevel high-density and high-speed electronic circuits^[10]. In this experiment, the obtained PU containing chiral unit was 2.00 ± 0.11 (1.99–2.10). The values are lower than the optically estimated dielectric constant of conventional polymer (3.00)^[11], alicyclic polyimide (2.55) and significantly lower than that of a semiaromatic polyimide (2.83)^[12]. The obtained OAAPU had a low dielectric constant and was from 1.98 to 2.08. The result indicated that the obtained OAAPU containing the donor-acceptor azobenzene group chromophore and asymmetric center could be expected to apply in the optical switch, waveguide field and the microelectronic industry as a dielectric layer.

According to the Lorentz-Lorenz Equation^[13] and Qiu et al.^[14], the relationship between thermo-optic coefficient (dn/dT) and volume expansion coefficient (β) can be expressed by the Equation (1):

$$\frac{dn}{dT} = -f(n)\beta \quad (1)$$

with

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

TABLE 1
Optical properties of different content OAAPU

Property	Content of OAAPU (wt%)	2.5	5.0	7.5	10.0
Thermo-optical property	dn/dT ($\times 10^{-4} \text{ } ^\circ\text{C}^{-1}$)	-4.0714	-3.8686	-3.9057	-3.8886
	Correlation coefficient (r)	0.9963	0.9938	0.9958	0.9977
	Standard deviation ($\times 10^{-4}$)	7.3127	9.0246	7.5046	5.5476
Dielectric property	$d\epsilon/dT$ ($\times 10^{-3} \text{ } ^\circ\text{C}^{-1}$)	-1.1600	-1.1000	-1.1200	-1.1200
	Correlation coefficient(r)	0.9965	0.9940	0.9959	0.9979
	Standard deviation ($\times 10^{-3}$)	2.0400	2.5400	2.1200	1.5600
Thermal expansion property	$d\beta/dT$ ($\times 10^{-7} \text{ } ^\circ\text{C}^{-1}$)	9.6000	8.5100	8.4400	8.2700
	Correlation coefficient (r)	0.9954	0.9926	0.9949	0.9969
	Standard deviation ($\times 10^{-2}$)	1.9400	2.1800	1.7930	1.3580

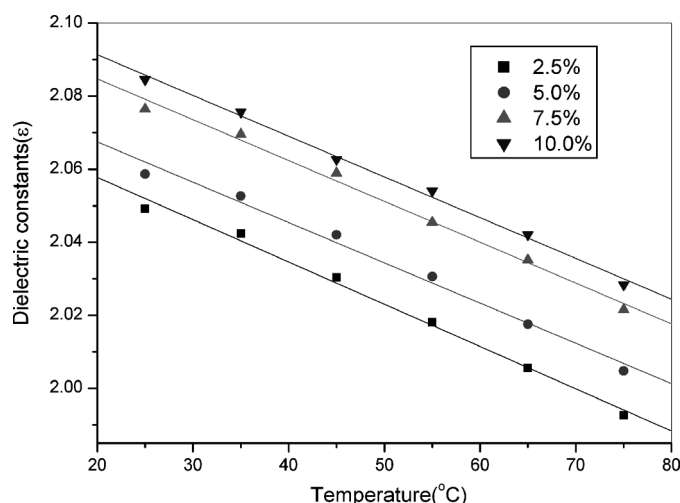


FIG. 6. The dielectric constant of the different content OAAPU.

The volume expansion coefficient (β) of different content OAAPU at different temperature was listed in Figure 7 and Table 1.

The $d\beta/dT$ of OAAPU was $8.27 \sim 9.60 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$. The correlative coefficient was $0.9926 \sim 0.9969$, indicating that dielectric constant and temperature had a good linear correlation in the selected temperature range. The standard deviations were very low.

The results showed that reflective indices and dielectric constants of this system decreased linearly with the increasing of temperature at the same OAAPU weight ratio content, while the volume expansion coefficient increased linearly. Considering the control of refractive index, appropriate temperature and the proper orientation of constant, the material could be used in designing high-performance thermo-optic polymer devices.

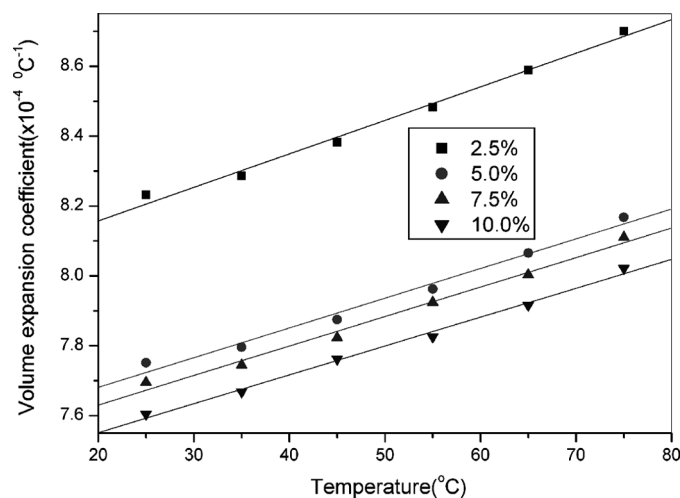


FIG. 7. The volume expansion coefficient of the different content OAAPU.

CONCLUSIONS

Optically active azobenzene polyurethane (OAAPU) was synthesized with high thermal stability. It was dextro-gyric polymer and the optical rotation was $+6.02^\circ$, the melting point was 301°C . The optical switching parameters have been obtained: refractive index n ; thermo-optic constant dn/dT ; dielectric constant (ϵ) and its variation with temperature ($d\epsilon/dT$); volume expansion coefficient (β) and its variation with temperature ($d\beta/dT$). These parameters are of great significance on the optical application of the materials, particularly on the development of optical materials because of the control of their refractive index. The results indicated that the OAAPU polymer could be used in designing thermo-optic switch devices.

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