



## Synthesis, Characterizations, and Thermo-optical Properties of Poly(urethane-imide) Based on Azo-disperse Dye in Its Side Chains

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### ABSTRACT

A new poly(urethane-imide) (PUI) was prepared by a condensation reaction of a -NCO terminated polyurethane prepolymer and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). This prepolymer was prepared by a reaction of azo chromophore (dispersed red 19) containing two hydroxyl functional groups and isophorone diisocyanate (IPDI). The PUI was characterized by common spectroscopic methods such as UV-vis, FTIR and <sup>1</sup>H NMR, and thermal studies using DSC and TGA. The results of DSC and TGA measurements indicated that the PUI exhibits high thermal stability up to its glass-transition temperature ( $T_g$ ) of 201°C and a weight loss of 5% at heat temperature of 238°C, due to introduction of imide components and formation of strong hydrogen bonds. The weight-average molecular weight ( $M_w$ ) was 52600 with a polydispersity of 2.14. The measurement of refractive indices ( $n$ ) was performed using a multi-wavelength light Abbé refractometer with precise temperature control at single wavelength of an attenuated total reflection (ATR) setup. The values of  $n$  and thermo-optic coefficient ( $dn/dT$ ) were used to calculate the dielectric constant ( $\epsilon$ ) and its variation with temperature ( $d\epsilon/dT$ ), volume expansion coefficient ( $\beta$ ) and its variation with temperature ( $d\beta/dT$ ) according to Lorentz-Lorenz equation. The  $dn/dT$  values were from  $-2.45 \times 10^{-4}$  to  $-5.05 \times 10^{-4} \text{ K}^{-1}$  at multiwave-length light and from  $-4.1071 \times 10^{-4}$  to  $-4.3875 \times 10^{-4} \text{ K}^{-1}$  at different single-wavelength lights. The  $d\beta/dT$  values were from  $0.3331 \times 10^{-6}$  to  $1.4668 \times 10^{-6} \text{ K}^{-1}$  at multiwave-length light and from  $0.9449 \times 10^{-6}$  to  $1.1094 \times 10^{-6} \text{ K}^{-1}$  at different single-wavelength lights. The thermo-optic coefficient was recorded as  $10^{-4} \text{ K}^{-1}$  which was nearly ten-fold that of inorganic materials such as  $\text{SiO}_2$  ( $1.1 \times 10^{-5} \text{ K}^{-1}$ ) and  $\text{LiNbO}_3$  ( $4 \times 10^{-5} \text{ K}^{-1}$ ). The results show that PUI may be useful as low loss optical communication devices and optical switches with low driving power.

### Key Words:

poly(urethane-imide);  
refractive index;  
thermo-optic coefficient;  
optical switch;  
thermal stability.

### INTRODUCTION

The refractive index  $n(\lambda, T)$  of an optical medium at a given temperature  $T$  and wavelength  $\lambda$  is an important parameter for characterizing the material. The refractive index, its variation as a function of temperature, i.e., the thermo-optic coefficient ( $dn/dT$ ), and dispersion also are important characteristics of optical glasses and other optical

materials used in high-power laser systems and devices [1-3]. Refractive index measurement is an important process for engineering and science and it has attracted the attention of the many researchers in the last years [4].

Recently polymer-based optical waveguides for fabrication of thermo-optic devices have attracted

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great interest in the telecommunication application areas, such as digital optical switch, Mach-Zehnder interferometer type optical switch, and optical cross-connects [5,6] due to their high thermo-optic coefficient which is one order of magnitude greater than those of silica materials [7]. A large thermo-optic coefficient favours the reduction of power consumption for both the thermal optical switches (TOS) and variable optical attenuators (VOA) since it corresponds to a small temperature change. Thus, a small power input for necessary change in the refractive index of polymer waveguides is required for optical switching or optical attenuation. However, the polymer materials such as, DR1/PMMA and its composite have been studied to a very limited extent. Their thermo-optic (TO) coefficients are not more than  $1.17 \times 10^{-4}$  -  $1.26 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$  [5].

In this paper, a new poly(urethane-imide) with excellent thermal stability was prepared by a condensation reaction of a -NCO terminated polyurethane prepolymer and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) [8]. The -NCO terminated polyurethane prepolymer was prepared by a reaction of azo chromophore (dispersed red 19) containing two hydroxyl functional groups and isophorone diisocyanate (IPDI) [9]. Some important parameters such as refractive index,  $n$ , thermo-optic coefficient,  $dn/dT$ , dielectric constant ( $\epsilon$ ) and its variation with temperature ( $d\epsilon/dT$ ), volume expansion coefficient ( $\beta$ ), and linear thermal expansion coefficient ( $d\beta/dT$ ) have been obtained at multi-wavelength and some single-wavelength lights, respectively. No study has been reported on thermo-optic properties of the PUI material based on IPDI-DR-19-6FDA up to the present time. Moreover, the absolute values of thermo-optic coefficients are much greater than those of inorganic materials such as  $\text{SiO}_2$  ( $1.1 \times 10^{-5} \text{ K}^{-1}$ ) and  $\text{LiNbO}_3$  ( $4 \times 10^{-5} \text{ K}^{-1}$ ). These findings have shown that PUI could be used as low loss optical communication devices and optical switches with low driving power.

## EXPERIMENTAL

### Materials

Dispersed red 19 with chemical formulation of

4-*N,N*-di(2-hydroxyethyl) amino-4'-nitroazobenzene was obtained from the ACROS ORGANICS. The 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) was obtained from TCI Co. and used without further purification. *N,N*-Dimethylformamide (DMF, A.R.) and *N,N*-dimethylacetamide (DMAC) were provided by Shanghai Gaoqiao Petrochemical Co. and stirred over powdered calcium hydride overnight and then distilled under reduced pressure and stored over 4Å molecular sieves. The isophorone diisocyanate (IPDI) was supplied by Huls Co. and was distilled under vacuum prior to use [10].

### Characterization

FTIR spectrum of the prepared PUI was obtained on a KBr pellet using Nicolet AVATAR 360 spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were recorded on NETZSCH STA449C. The programmed heating range was from room temperature to 700°C, at a heating rate of 10°C/min under nitrogen atmosphere. The measurement was taken using 6-10 mg samples. TGA and DSC curves were recorded. The UV-vis spectra of the PUI and DR-19 were analyzed by Shimadzu UV-240 spectrophotometer. The  $^1\text{H}$  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. Molecular weight was determined by gel permeation chromatography (GPC) with a polystyrene standard using a WATERS SEC-244 system at 25°C in THF. The inherent viscosity of PUI was measured by Ubbelohde viscometer at 30°C using DMAc as the solvent and the standard concentration of 1 g/dL.

### Preparation of PUI

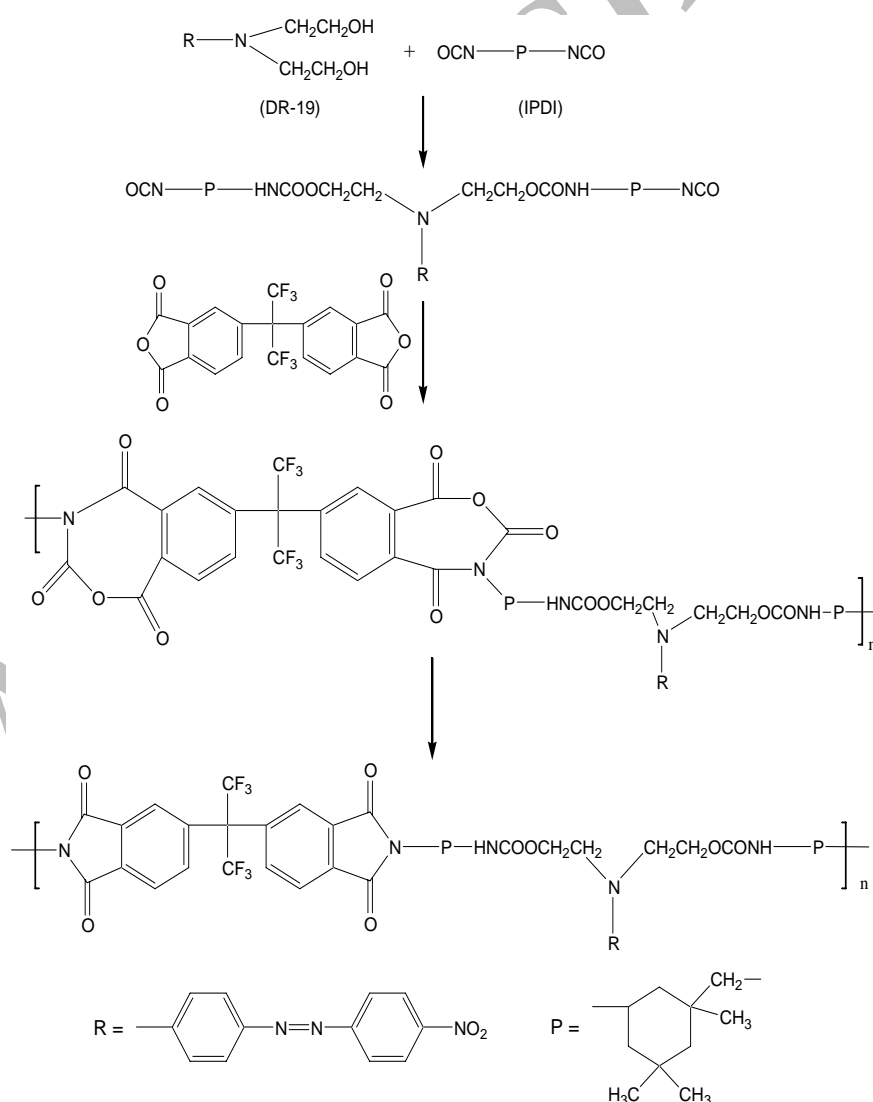
The isophorone diisocyanate (IPDI, 1.5984 g, 7.2 mmol) was dissolved in DMF (15 mL) at room temperature in a 250 mL round-bottom flask equipped with a condenser, mechanical stirrer, nitrogen inlet and a thermometer. DR-19 (1.12 g, 3.4 mmol), dissolved in DMF (15 mL), was added dropwise into the system. To form NCO terminated polyurethane pre-polymer, the temperature was then slowly raised to 40, 75, and 90°C and maintained for

1 h, 1 h, and 2 h, respectively. After cooling to room temperature, the 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, 1.51 g, 3.4 mmol) dissolved in DMAc (30 mL) was added dropwise to the system. The reaction mixture temperature was then increased to 40°C and then to 90°C and maintained for 2 h, respectively. The mixture was refluxed at 160°C for 2 h in order to remove the DMF and DMAc (DMF bp:152°C and DMAc bp:160°C). The red poly(urethane-imide) (PUI) product was precipitated in the mixture of methanol and water (v/v:1/1) and obtained after filtration and drying under vacuum at 60°C in 68% yield. The inherent viscosity  $\eta = 0.21 \text{ dL}\cdot\text{g}^{-1}$ .

Anal. Calcd for  $\text{C}_{57}\text{H}_{60}\text{N}_8\text{O}_{10}\text{F}_6$ : C, 60.53%; H,

5.31%; N, 10.09%. Found: C, 60.48%; H, 5.22%; N, 10.01%. Due to the good solubility of the PUI in THF, the molecular weight can be measured by GPC. The weight-average molecular weight ( $M_w$ ) is 52600 with a polydispersity of 2.14 (polystyrenes as standards).

$^1\text{H}$  NMR (300 MHz, acetone- $d_6$ , ppm)  $\delta$ : 9.0 (-NHCOO-, 2H), 4.21 (-OCH<sub>2</sub>CH<sub>2</sub>-, 4H), 3.71 (-CH<sub>2</sub>CH<sub>2</sub>O-, 4H), 7.09(ArH, 2H), 7.43(ArH, 2H), 7.62(ArH, 2H), 8.06(ArH, 2H), 7.88(ArH, 2H), 8.40(ArH, 2H), 8.38(ArH, 2H), 4.21 (-CH<, 2H), 3.75 (-CH<sub>2</sub>-N-, 4H), 1.80 (-CH<sub>2</sub>-, 4H), 1.45 (-CH<sub>2</sub>-, 4H), 1.21 (-CH<sub>3</sub>, 12H), 1.19 (-CH<sub>3</sub>, 6H), and 1.02 (-CH<sub>2</sub>-, 4H). The synthetic route for PUI is shown in Scheme I.



**Scheme I.** Synthesis of poly (urethane-imide) (PUI).

## RESULTS AND DISCUSSION

### Structure Characterization of PUI

The UV-vis spectra of the prepared material and DR-19 are shown in Figure 1. The content of PUI or DR-19 was  $3.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ . From Figure 1, the absorption peak of DR-19 in DMF is 500 nm, while the absorption peak of PUI in DMF is 455 nm. The result indicated that the absorption peak showed blue shift after polymerization. The two hydroxyl groups in DR-19 formed carbamate ester bond after polycondensation. The electron cloud in azobenzol groups of DR-19 shifted to the ester bond because of the electron acceptance of C=O, which decreased the electron density in azobenzol groups. Thus, absorption band of azobenzol groups would shift to UV region with high energy demand of the electron transfer. Because the absorption peak of PUI was raised by the presence of azobenzol groups in its side-chain, the UV-vis data verified the incorporation of azobenzyl group in polymer side chain.

FTIR spectrum of the prepared PUI was obtained on a KBr pellet using Nicolet AVATAR 360 spectrometer and is shown in Figure 2. This spectrum shows that the band at  $3410 \text{ cm}^{-1}$  is fairly broad and corresponds to the stretching vibration of free and hydrogen-bonded NH groups. Meanwhile, in Figure 2, we can also see that the absorption band at  $1379 \text{ cm}^{-1}$  is characteristic band of the stretch vibration of C-N bond. The absorption bands around  $1782$  and  $1720 \text{ cm}^{-1}$  are assigned to the asymmetric and symmetric stretching vibrations of carbonyl

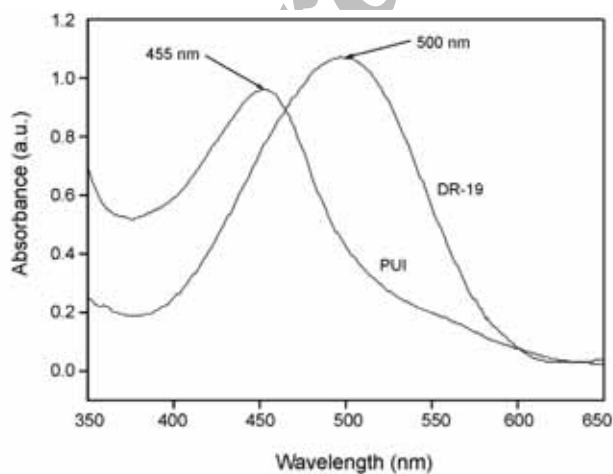


Figure 1. UV-vis spectra of PUI and DR-19.

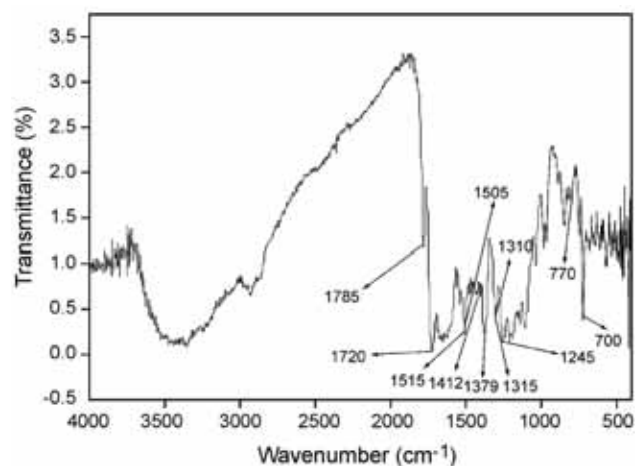


Figure 2. FTIR spectrum of PUI.

groups of imide rings, respectively. The absorption band located at  $1505 \text{ cm}^{-1}$  is the symmetric stretching vibration of  $-\text{N}=\text{N}-$  bond [11]. The characteristic absorption bands of the imide groups are also observed at  $1412$ ,  $1310$ ,  $770$  and  $700 \text{ cm}^{-1}$ . The absorption bands at  $1515 \text{ cm}^{-1}$  and  $1315 \text{ cm}^{-1}$  are assigned to the symmetric and asymmetric stretch vibrations of nitro-group in the side-chain of nonlinear optical chromophore, respectively. Band at  $1245 \text{ cm}^{-1}$  is attributed to the ether (C-O-C) band of DR-19. All the FTIR data verified that the imide groups had been introduced onto PU backbone in our case. Moreover, the absence of the absorption band at  $2270 \text{ cm}^{-1}$  corresponding to the characteristic absorption of isocyanate group indicates that all the monomers had been consumed.

### Thermal Property of PUI

To examine thermal properties and thermal decomposition characteristics of polymer, DSC and TGA experiments were carried out on NETZSCH STA449C with the heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen as shown in Figures 3 and 4, respectively. It can be seen that the glass transition temperature is at  $201^\circ\text{C}$ , which is much higher than that of the corresponding side-chain nonlinear optical (NLO) polyurethanes [12]. Figure 4 shows that the initial decomposition temperature of PUI is at  $200^\circ\text{C}$ , and the 5% weight loss occurs at heating temperature of  $238^\circ\text{C}$ . The results indicated that the obtained polymer possessed excellent thermal stability. The

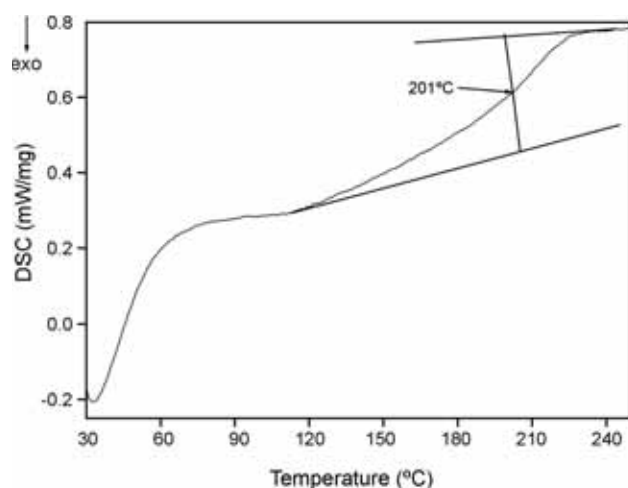


Figure 3. DSC curve of PUI.

reason for this observation could be due to the introduction of imide components and formation of the strong hydrogen bonds between the macromolecular chains of urethane and imide segments, which formed the physical cross-linking network among PUI chains and alleviated the thermal decomposition of PUI and enhanced its thermal stability.

### The Thermo-optic Theory of Polymer

In recent years, some famous international companies and research departments have developed thermo-optic switch and switch arrays by use of the high thermal-effect of organic polymer materials [13-15]. The designation base of this kind of devices is the

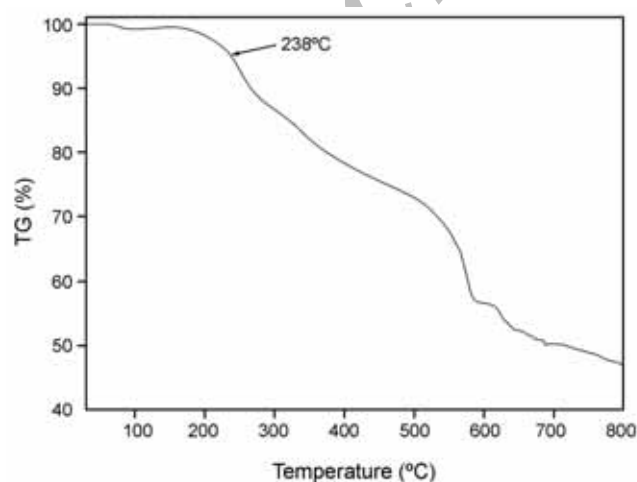


Figure 4. TGA curve of PUI.

thermo-optic coefficient of polymer waveguide. Thus, it is appreciably important to study the thermo-optic effect of polymers in light waveguides applications. Thermo-optic (TO) coefficient ( $dn/dT$ ) is the variation of refractive index as a function of temperature. The thermo-optic coefficient of a polymer is the main factor affecting the driving power and response speed of the optical switch.

In this work, the refractive index  $n$  of the PUI was measured at different temperatures and PUI contents at multi-wavelengths or different single wavelength lights, and then the dielectric constant  $\epsilon$  was calculated according to the relationship between  $n$  and  $\epsilon$ :  $\epsilon = n^2$  for studying the variation of dielectric constant with temperature.

According to Lorentz-Lorenz theory [16], the inter-relationship of factors: refractive index  $n$ , polarizability  $\alpha$ , and density  $\rho$  can be expressed as follows:

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

where,  $M$  is the molar mass of PUI and  $N_A$  is the Avogadro's constant. The polarizability temperature coefficient of the polymer molecular is very small and can be ignored ( $d\alpha/dT \approx 0$ ), thus, from eqn (1) it can be seen that with respect to temperature the refractive index variation ( $dn/dT$ ) is the same as density variation. Therefore, eqn (1) could be changed as follows:

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

according to eqns (1) and (2), it can be written as:

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

In fact, density change with temperature is the coefficient of thermal expansion:

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

if,

$$f(n) = \frac{(n^2 - 1)(n^2 + 2)}{6n} \quad (5)$$

and eqn (3) can be simplified as:

$$\frac{dn}{dT} = -f(n)\beta \quad (6)$$

where,  $\beta$  is the thermal volume expansion coefficient of polymer which could be obtained by measuring the refractive index at different temperatures and calculating  $dn/dT$ . By the same method, the variation of the volume expansion coefficient dependence on the temperature ( $d\beta/dT$ ) could be obtained.

### Thermo-optic Property of PUI Solutions at Multi-wavelength Light

Different concentrations of PUI solution were prepared in DMF with the aid of ultrasonic instrument. Refractive indices of these different polymer solutions were measured in the temperature interval of 298.00-328.00 K at atmospheric pressure using an Abbé refractometer. 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  $\pm 0.01$  K. 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 seven independent records were taken for each sample at each temperature to assure the effectiveness of the measurement. Refractive index values were measured to an accuracy of  $\pm 0.0001$  after the sample mixture was thermostatically at equilibrium. In order to obtain consistent values, we held the temperature constant throughout each set of measurements and repeated every experiment three times under the same conditions [17]. Their refractive indices were measured at different temperatures at the multi-wavelength light (natural light) and dielectric constants and their volume expansion coefficients were calculated and presented in Figures 5-7. At the same time, according to the experimental data, the thermo-optic coefficient of PUI and variations of volume expansion coefficient and dielectric constant based on temperature at different PUI contents were also obtained which are listed in Table 1.

From Figure 5 and Table 1, the slope of the curve,  $dn/dT$  at different PUI contents was from

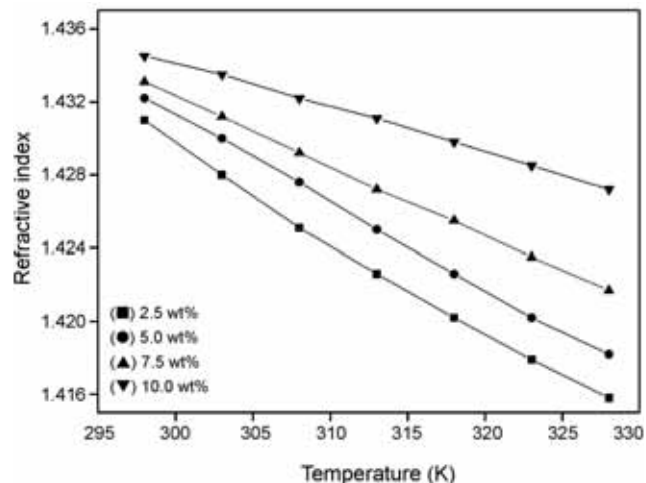


Figure 5. The refractive index at multi-wavelength light.

$-2.4500 \times 10^{-4}$  to  $-5.0500 \times 10^{-4} \text{ K}^{-1}$  at multi-wavelength light. The correlative coefficient was  $\sim 0.9980$ - $0.9998$ , indicating that refractive index and temperature have a good linear correlation in the selected temperature range. The error and standard deviation were very low. The thermo-optic coefficient is in the order of  $10^{-4} \text{ K}^{-1}$  which is nearly ten folds that of inorganic materials such as  $\text{SiO}_2$  ( $1.1 \times 10^{-5} \text{ K}^{-1}$ ) and  $\text{LiNbO}_3$  ( $4 \times 10^{-5} \text{ K}^{-1}$ ). The result has a rather significant effect on developing a new digital optical switch with low driving power and optical communication.

From the Figure 6 and Table 1, it can be seen that the obtained PUI has a low dielectric constant and its  $d\epsilon/dT$  is from  $-0.7011 \times 10^{-3}$  to  $-1.4400 \times 10^{-3} \text{ K}^{-1}$  at

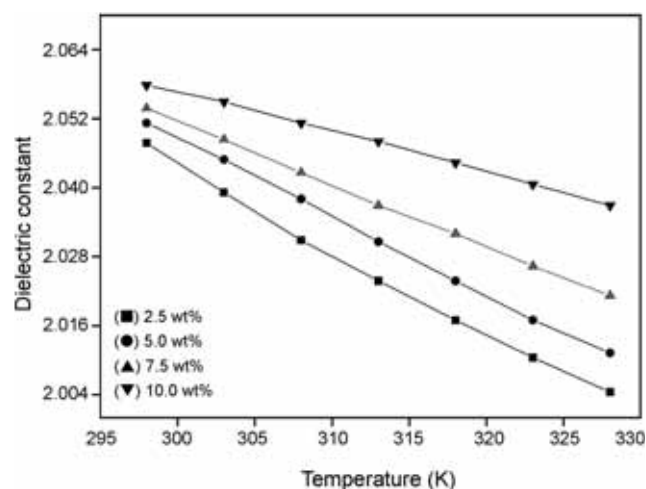


Figure 6. The dielectric constant at multi-wavelength light.

**Table 1.** Optical properties of samples with different PUI contents (at multi-wavelength light).

Optical property	Content of PUI (wt%)	2.5	5.0	7.5	10.0
Thermo-optic property (Figure 5)	$dn/dT(\times 10^{-4} K^{-1})$	-5.0500	-4.7571	-3.8071	-2.4500
	Correlative coefficient (r)	0.9980	0.9996	0.9998	0.9993
	Error( $\times 10^{-5}$ )	0.57853	1.2968	1.0137	0.4907
	SD <sup>a</sup> ( $\times 10^{-4}$ )	1.4340	0.6227	0.3242	0.4028
Dielectric property (Figure 6)	$d\epsilon/dT(\times 10^{-3} K^{-1})$	-1.4400	-1.3600	-1.0900	-0.7011
	Correlative coefficient (r)	0.9979	0.9996	0.9998	0.9994
	Error( $\times 10^{-5}$ )	4.1811	1.8093	0.9614	1.1334
	SD ( $\times 10^{-3}$ )	1.1100	0.4787	0.2543	0.2999
Volume expansion property (Figure 7)	$d\beta/dT(\times 10^{-6} K^{-1})$	1.4668	1.0216	0.8176	0.3331
	Correlative coefficient (r)	0.9986	0.9998	0.9998	0.9992
	Error( $\times 10^{-8}$ )	3.4905	0.7078	0.5664	0.6097
	SD ( $\times 10^{-6}$ )	9.2350	0.1873	0.1499	0.1613

(a) SD: standard deviation

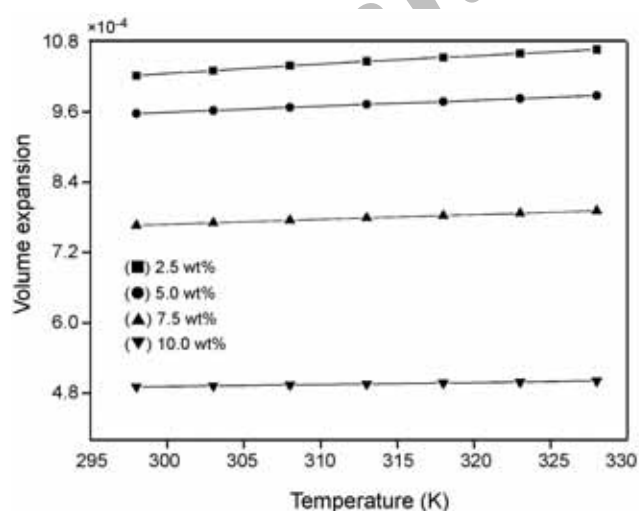
multi-wavelength light. The correlative coefficient is in the range 0.9979-0.9998 indicating that dielectric constant and temperature have a good linear correlation in the selected temperature range. The error and standard deviation are very low. Generally, the dielectric constant of a normal polyimide is between 3.0-3.5 which is difficult to meet the requirement of the transmission speed to produce a high enough signal. Since, the dielectric constant of the PUI with an azo nonlinear optical chromophore in

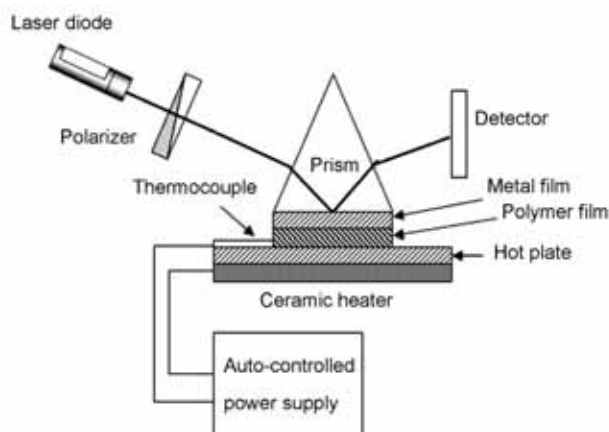
the side-chain is as low as 2.00-2.05 this polymer could be applied in the optical switch and light waveguide facilities. The resulting polymer would be used widely in the microelectronic industry as a dielectric layer. From the Figure 7 and Table 1, it can be concluded that the  $d\beta/dT$  of PUI is in the range of  $0.3331 \times 10^{-6}$ - $1.4668 \times 10^{-6} K^{-1}$  at multi-wavelength light. The correlative coefficient of different contents of PUI is between 0.9986-0.9998 indicating that the volume expansion coefficient and temperature have a good linear correlation in the selected temperature range. The error and standard deviation are very low.

Figures 5-7 also show that the reflective indices and dielectric constants of PUI which have been decreased linearly with increased temperature at the same PUI content, while the volume expansion coefficient has been increased linearly. These observations show that the PUI could be used in designing high-performance thermo-optic polymer devices.

#### Thermo-optic Property of PUI with 2 wt% Concentration at Different Single-wavelength Lights

As shown in Figure 8, measurement of refractive index was conducted in an attenuated-total-reflection index was conducted in an attenuated-total-reflection (ATR) set-up equipped with an auto temperature-control apparatus. In fabrication process, a silver film

**Figure 7.** The volume expansion coefficient at multi-wavelength light.



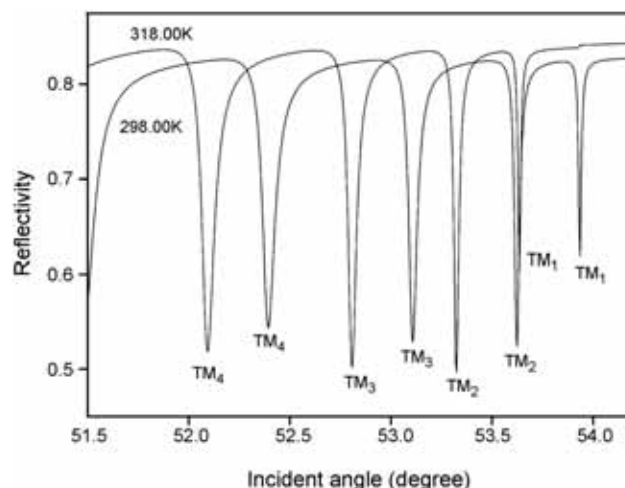
**Figure 8.** Measurement of refractive index.

of about 50 nm thickness was vacuum evaporated on the base of a glass prism, the prepared polymer solution is then spin coated onto the silver film. In this configuration, the silver film served as a coupling layer and the cladding layer of the polymer waveguide as well. The prism-waveguide coupling system was mounted on a brass plate heated by an auto-controlled ceramic heater. Temperature was measured by a thermocouple directly attached to the polymer film.

A collimated light beam from a diode laser passed through a polarizer and then incident occurred on the interface between the prism and the silver film with an appropriate angle. Angular scan was carried out by a  $\theta/2\theta$  computer-controlled goniometer. Reflected light was detected with a silicon photodiode by averaging the output signal.

In the experiment, the goniometer kept rotating to generate the ATR spectrum on the computer screen, a series of dips in reflectivity due to resonant transfer of energy into guide modes were generated on a computer screen and saved in a data file. Variation of refractive index of the polymer film with temperature can be determined through the angle shift of the resonant dips. Temperature during the heating stage, as mentioned above, is measured by a thermocouple directly attached to the polymer film. Temperature stability of the set-up at higher temperatures is ensured by covering the prism-waveguide heating system with a glass cup as temperature shielding.

The error of the measured temperature by the thermocouple is  $\pm 3^\circ\text{C}$ . The speed of ascending



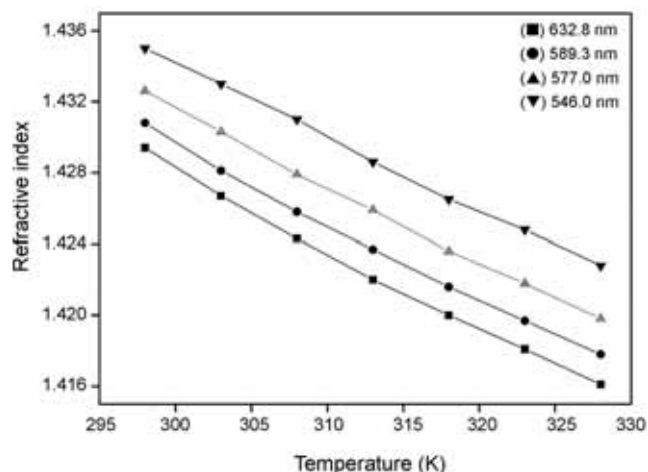
**Figure 9.** The ATR spectra of 2.0 wt% PUI at 298 K and 318 K and 589.3 nm.

temperature is well controlled at  $2^\circ\text{C}/\text{min}$ . Although the measurement errors of the dielectric permittivities of the metal film and the prism exert the influence on the absolute position of the resonant dip, the thermo-optic coefficient only depends on the relative angular shift of the resonant dip. Therefore, the measurement errors of the prism and metal film parameters have less effect on the accuracy of thermo-optic coefficient.

PUI solution of 2.0 wt% in DMF as the solvent was prepared and spin-coated to the film. According to above ATR technique, the ATR spectra at  $T = 298.00\text{ K}$  and  $318.00\text{ K}$  at the wavelength of the D-line of sodium, 589.3 nm, are shown in Figure 9. In these spectra, a series of reflection dips were exhibited in the ATR spectra (Figure 9). Using the Eigen equation of the waveguide modes, the corresponding refractive index of the polymer can be determined from ATR spectrum [18]. Then, changing the laser, the refractive indices of the PUI were measured at different wavelengths and temperatures. The volume expansion coefficients and dielectric constant were calculated with the same methods mentioned above.

Figures 10-12 show the curves of refractive indices, dielectric constants, and volume expansion coefficients of the PUI film in the temperature ranging from 298.00 to 328.00 K at 5.00 K intervals. Thermo-optic coefficient, dielectric constant dependence on the temperature, and the variations of

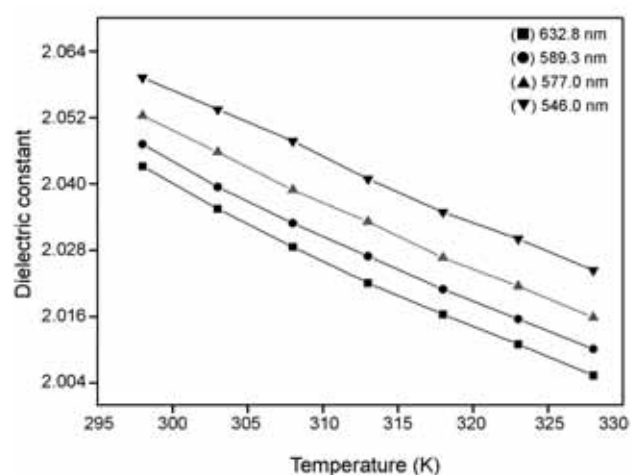




**Figure 10.** The refractive index at single wavelength.

volume expansion coefficient of PUI at different wavelengths are presented in Table 2. Their correlative coefficients are in the range 0.9980-0.9993, 0.9979-0.9993, and 0.9985-0.9994, respectively. The results indicated that based-temperature refractive index, dielectric constant, and volume expansion coefficient have good linear correlations in the selected temperature range. The error and standard deviation are very low, as well.

From the results in the above Figures, it can be deduced that at the same PUI content, the reflective indices and dielectric constants of the polymer decreased linearly with the increasing of the

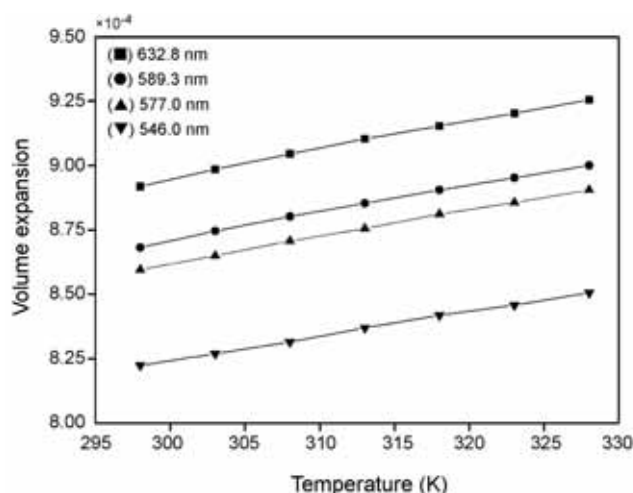


**Figure 11.** The dielectric constant at single wavelength.

wavelength, while the volume expansion coefficients increased linearly. By analogy, with the same wavelength and PUI content, the reflective indices and dielectric constants of the polymer decreased linearly with increased temperature, while the volume expansion coefficients increased linearly. For the samples with the same PUI content, the absolute value of thermo-optic coefficient ( $dn/dT$ ) increased linearly with wavelength increases. But the absolute value in variation of the dielectric constant and volume expansion coefficient based on temperature ( $d\varepsilon/dT$  and  $d\beta/dT$ ) followed the same trend. Differing from inorganic materials, these facts about polymer

**Table 2.** Optical properties at different single-wavelength lights (PUI content: 2.0 wt%).

Optical property	Wavelength (nm)	632.8	589.3	577.0	546.0
Thermo-optic property (Figure 10)	$dn/dT(\times 10^{-4} K^{-1})$	-4.3875	-4.2857	-4.2643	-4.1071
	Correlative coefficient (r)	0.9980	0.9982	0.9991	0.9993
	Error( $\times 10^{-5}$ )	1.2568	1.1499	0.7922	0.6933
	SD ( $\times 10^{-4}$ )	3.3252	3.0426	2.0959	1.8342
Dielectric property (Figure 11)	$d\varepsilon/dT(\times 10^{-3} K^{-1})$	-1.2500	-1.2200	-1.2100	-1.1700
	Correlative coefficient (r)	0.9979	0.9981	0.9991	0.9993
	Error( $\times 10^{-5}$ )	3.6510	3.3476	2.3232	2.0162
	SD ( $\times 10^{-4}$ )	9.6597	8.8570	6.1465	5.3343
Volume expansion property (Figure 12)	$d\beta/dT(\times 10^{-6} K^{-1})$	1.1094	1.0518	1.0317	0.9449
	Correlative coefficient (r)	0.9985	0.9987	0.9994	0.9994
	Error( $\times 10^{-8}$ )	2.7371	2.4113	1.5696	1.4384
	SD ( $\times 10^{-7}$ )	7.2415	6.3797	4.1527	3.8055



**Figure 12.** The volume expansion coefficient at single wavelength.

materials should be explained by the Lorentz-Lorenz relation [16]. It is well known that the refractive index ( $n$ ) of a material depends on the density variation. During the heating process, the thermo-expansion gives rise to the decrease in the density of polymer film. Correspondingly, the refractive index of the polymer film decreases with increase in temperature. Therefore, the PUI polymer could be used in designing high-performance thermo-optic polymer devices.

## CONCLUSION

Polymers are used in fabricating planar waveguide devices deployed in telecommunication systems. In addition to their optical loss and refractive index, the thermo-optic coefficient of the polymers plays a vital role in dictating the device properties. We synthesized a novel poly(urethane-imide) (PUI) with excellent thermal stability and thermo-optic properties, containing azo chromophore (dispersed red 19) in the side-chains. In this paper, we have presented an optical experiment technique to determine the refractive index of the polymer by using Abbé refractometer and thermostatically controlled ATR setup. The following parameters have been obtained according to Lorentz-Lorenz equation: dielectric constant ( $\epsilon$ ) and its variation with temperature ( $d\epsilon/dT$ ), volume expansion coefficient ( $\beta$ ), and linear

thermal expansion coefficient ( $d\beta/dT$ ). The obtained results of the polymer have shown that the thermo-optic coefficient, the dielectric constant, and volume expansion coefficient are related to the PUI content and wavelength. This estimation is useful in the material development and evaluating its possibility in waveguide applications.

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