

Polyamides Containing Thiadiazole Units: Synthesis and Optical Properties^{*}

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Abstract Highly refractive and transparent polyamides containing thiadiazole units have been developed. These polymers were prepared by a polycondensation reaction of 4,4'-(1,3,4-thiadiazole-2,5-thio) bis(methylene) dibenzoyl chloride (TDTBM-DC) and diamine which contained thioether (—S—) and sulfone units. They showed good thermal stabilities such as a relatively high glass transition temperature of 206–233 °C and a 5% weight-loss temperature ($T_{5\%}$) of 376–395 °C. The optical transmittance of the polymer at 450 nm is higher than 83%. The heterocycle units and plural —S— linkages provide the polymer with a high refractive index of 1.716–1.725 at 633 nm and a low birefringence of 0.003–0.004. Also they showed improved solubility in polar aprotic solvents and could form moderate strength films with tensile strength of 72.8–83.1 MPa and storage modulus of 1.0–1.8 GPa (at 200 °C).

Keywords: Synthesis; Optical property; Soluble; Heterocycle.

INTRODUCTION

The refractive index (n) is one of the most important and fundamental characteristic of materials used in optical design and application. High refractive index polymeric materials have been rapidly developed and attract significant interest in recent years. They were used in the areas of ophthalmic lenses, components for charge-coupled devices (CCDs) and complementary metal oxide semiconductor (CMOS) image sensors (CISs) and filters^[1–4] because of their lightweight and processability compared to inorganic materials. The method for increasing the refractive index of polymers is the introduction of substituents with a low molar volume and high molar refraction according to the classic Lorentz-Lorenz equation. The refractive index (n) of a material is related to the molar volume (V_M), polarizability (α) and the molar refractions of functional groups and the backbone repeating unit of the polymer (R_{LL}).

$$\left(\frac{n^2-1}{n^2+2}\right)V_M = \frac{4}{3}\pi N_A \alpha = \sum_i (R_{LL})_i$$

Therefore, according to the molecular design principle, the introduction of substituents with high molar refractions and low-molar volumes can efficiently increase the refractive indices of polymers^[5–10]. For example, aromatic rings, heavy halogen atoms (Cl, Br, I), sulfur atoms and metal atoms are commonly used for this purpose. In particular, the sulfur atom, in view of molar refraction, dispersion chemical stability and facility to

^{*} This work was financially supported by the Youth Fund of Sichuan University (No. 2012SCU11009).

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Received April 17, 2013; Revised June 12, 2013; Accepted June 17, 2013

doi: 10.1007/s10118-014-1407-z

introduce to polymers, is one of an especially effective way to prepare high refractive index polymers. Various kinds of high-*n* polymers containing the sulfur elements were reported, such as epoxies^[11], polyurethanes^[12], polymethacrylates^[13] and polyarylenethioethers^[14]. However, these polymers have relatively low refractive indices in the range of 1.5–1.7 at 633 nm. Recently, aromatic polyimides (PIs)^[15–18] containing sulfur have developed for optical applications, with their advantage of thermal, oxidative, chemical and mechanical properties. Although they exhibit high refractive index in the range of 1.7–1.77, their films have large birefringence and coloration (the coloration of aromatic PIs results from the formation of charge transfer complexes (CTC) between the electron-donating diamine and the electron-accepting carbonyl group), which are the problems of aromatic PIs. Aromatic polyamides containing bulky pendant groups^[19–21], functional groups^[22], phthalazinone groups^[23], non-symmetric groups^[24, 25] and flexible chains such as ethers (—O—)^[26] or ester groups (—COO—)^[27] are high performance engineering polymers. Most of them exhibit excellent optical transparency and solubility^[28]. However, the refractive indices of these polymers are still in the range of 1.6–1.7 at 633 nm. The relatively low refractive index is mainly attributed to the low sulfur content (because the refractive indices of polymers containing sulfur mainly depends on the sulfur content in the repeating unit.) and sterically bulky substituents would endow large free volumes among polymer chains, which lowers the refractive index. Therefore, the breakthrough of the trade-off between the refractive index and optical transparency, birefringence becomes an important subject. Recently, we developed high refractive index polyamides containing phenyl and thioether linkages^[29]. They showed relatively high refractive indices, high transparency and low birefringence. Also it has been reported that N—N=C and C=N—C bonds possess relatively high molar refraction (3.46) and (4.10) as compared to a C=C bond (1.73). Thus, in order to enhance the refractive index and optical transparency, introduction of heterocycles such as thiadiazole units containing —C=N— bonding would be an effective method. On the other hand, the sulfonyl (—SO₂—) group endows polymers with low refractive index dispersion and high transparency due to its low molecular dispersion. On the basis of these considerations, we designed a novel polyamide that contained sulfur, sulfonyl and heterocycles to achieve high refractive index, low birefringence and high optical transparency.

EXPERIMENTAL

Materials

Hydrazine and carbon disulfide (AR, Chengdu, Kelong Chemical Industry Company), 4,4'-dichlorodiphenylsulfone (DCDPS) (AR, Suzhou Yinsheng Chemical Industry Company), 4-fluorobenzoyl chloride (*p*-FBC) (AR, Jiangsu Jintan Lanling chemical industry ltd. Company), 4-aminobenzenthio and 4,4'-thiodianiline (AR, Zhe Jiang Shou Er Fu Chemical Industry Group Co., Ltd.), sodium hydroxide (NaOH) (AR, Sichuan Chengdu Changlian Chemical Reagent Company), 4-chloromethylbenzoic acid (4-CMBA) (AR, Jiangsu Panxi Chemical Industry Company), *N*-methyl-2-pyrrolidone (NMP) (Jiangsu Nanjing Jinlong Chemical Industry Company), 4,4'-diaminodiphenylsulfone (*p*-DDPS) and Me₃SiCl (TMSCl) (AR, Aladdin Reagent Company) were used without further purification. The other reagents and solvents were commercially obtained.

Characterization

The intrinsic viscosity of the polyamides (PA-(a-b)) was obtained in NMP at 30 ± 0.1 °C with 0.500 g of polymer dissolved in 100 mL of NMP, using a Cannon-Ubbelodhe viscometer. The results were obtained by the one-point method (or Solomon-Ciuta equation) as follows:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{c}$$

where $\eta_r = \eta/\eta_0$, $\eta_{sp} = \eta/\eta_0 - 1$.

The number-average molecular weights (M_n) and weight-average molecular weight (M_w) were obtained *via* GPC performed with a Waters 1515 performance liquid chromatography pump, a Waters 2414 differential refractometer (Waters Co., Milford, MA) and a combination of Styragel HT-3 and HT-4 columns (Waters Co., Milford, MA), the effective molecular weight ranges of which were 500–30000 and 5000–800000, respectively. *N,N*-dimethyl formamide (DMF) was used as an eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards were used for calibration. The samples of monomer and PA-(a-b) were measured with an elemental analyzer (EURO EA-3000). The mass spectral analysis was performed on a Bruker-Daltonics ESI instrument. FTIR spectroscopic measurements were performed on a NEXUS670 FTIR instrument. Nuclear magnetic resonance (^1H -NMR) spectra were determined on a BRUKER-600 NMR spectrometer in deuterated chloroform or deuterated dimethyl sulfoxide. The X-ray diffraction (XRD) (Philips X'pert Pro MPD) was used to study the polymer's aggregation structure. The samples were subsequently annealed at 260 °C for 4 h. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC thermal analysis instrument. The heating rate for the DSC measurements was 10 K/min. Thermogravimetric analysis (TGA) measurements were performed on a TGA Q500 V6.4 Build 193 thermal analysis instrument with a heating rate of 20 K/min under nitrogen atmosphere. An Instron Corporation 4302 was used to study the stress-strain behavior of the films (according to GB 13022-91). Dynamic mechanical analysis (DMA) was performed on TA-Q800 apparatus operating in tensile mode at a frequency of 1 Hz in the temperature range from 35 °C to 280 °C, with a heating rate of 5 K/min. The transmittance of the films was determined by UV-Visible spectroscopy (U-2310 II). The out-of-plane (n_{TM}) and in-plane (n_{TE}) refractive indices of the PA films were measured with a SPA-Lite prism coupler (SPA-4000) equipped with a He-Ne laser light source (wavelength: 633 nm). The in-plane (n_{TE})/out-of-plane (n_{TM}) indices and birefringences (Δn) were calculated with the following equation: $\Delta n = n_{\text{TE}} - n_{\text{TM}}$. The average refractive index was calculated according to the following equation: $n_{\text{AV}} = [(2 n_{\text{TE}}^2 + n_{\text{TM}}^2)/3]^{1/2}$ [31]. Dielectric constants were estimated from the optical data based on an empirical relation: $\epsilon_{\text{Calculated}} = 1.1 n_{\text{AV}}^2$ [32, 33]. The water absorption of the samples was measured according to GB/T17037.3-2003. Dielectric constants were measured on a TH2819A instrument in a frequency region of 0.1 kHz –100 kHz at 25 °C. The solubility of polymers in various solvents was tested at room temperature and the boiling point of the solvents.

Monomer Synthesis

2,5-Dimercapto-1,3,4-thiadiazole (DMTD)

$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (20 g, 0.4 mol), NaOH (32 g, 0.8 mol), triethylamine (0.11 g, 0.001 mol) and water (150 mL) were added into a 500 mL round bottom three-necked flask. The mixture was stirred at 5–6 °C and carbon disulfide (68.4 g, 0.9 mol) was added dropwise within 2 h. Then the reaction solution was heated to 80 °C (The gas overflowed from reaction system was absorbed with sodium hydroxide) and reacted for another 4 h. The excess carbon disulfide was distilled under vacuum. The reaction solution was acidified with concentrated HCl (60 mL) to precipitate a white crude product under stirring. The crude product was then washed three times with hot water, dried, then recrystallized from alcohol. That afforded DMTD as light yellow crystallites.

Yield: 46.8 g, 78%.

Elemental analysis (%): Found: C, 16.23 (15.99); H, 1.34 (1.34); N, 18.87 (18.65) (data in brackets are calculated).

FTIR (KBr, cm^{-1}): 2474 (S—H), 1504 (—C=N), 1450, 1263 (1,3,4-thiadiazole ring), 1075 (C—S).

^{13}C -NMR (600 MHz, DMSO- d_6 /TMS, δ): C_1 , 151.511.

4,4'-(1,3,4-Thiadiazole-2,5-thio) bis(methylene) dibenzoyic acid (TDTBM-DA) (shown in Scheme 1)

TDTBM-DA was prepared according to the following procedure: 200 mL of water, DMTD (15.2 g, 0.11 mol) and K_2CO_3 (27.6 g, 0.40 mol) were added into a 500 mL three-necked flask equipped with a water segregator, reflux condenser, mechanical stirrer and thermometer. 4-CMBA (34.1 g, 0.2 mol) was added into the flask when the reaction solution was clear. Then the reactor was heated to 100 °C and maintained for 12 h. The reaction solution was then poured into water and filtered. The filter liquor was acidified with 1 mol/L HCl to precipitate a

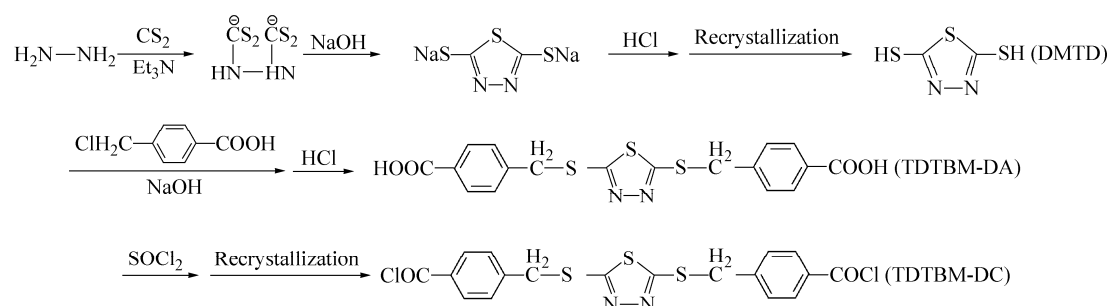
cottony white product under stirring. The crude product was then washed three times with hot water to remove possible residual salts. Next, the purified product was filtered, dissolved in a solution of NaHCO_3 , filtered, acidified with hydrochloric acid and then filtered again. This process was repeated for two times. The material was then vacuum-dried at $100\text{ }^\circ\text{C}$ for more than 12 h to yield a white powder.

Yield: 39.8 g, 95.3%.

Elemental analysis (%): Found: C, 52.03 (51.66); H, 3.38 (3.37); N, 6.76 (6.69) (data in brackets are calculated).

FTIR (KBr, cm^{-1}): 3071 (C—H aromatic ring), 2928, 2851 ($-\text{CH}_2-$), 2661, 2534 (1,3,4-thiadiazole ring), 1686 ($-\text{COOH}$), 1609, 1574, 1508 ($\text{C}=\text{C}$ aromatic ring), 1123 (C—S—C), 834 (para-substituent of aromatic ring).

$^1\text{H-NMR}$ (600 MHz, $\text{DMSO-d}_6/\text{TMS}$, δ): 4.580 (s, 4H, H_1), 7.520–7.534 (d, 4H, H_2), 7.889–7.903 (d, 4H, H_3), 12.972 (s, 2H, H_4).



Scheme 1 Synthesis routes of TDTBM-DA and TDTBM-DC

4,4'-(1,3,4-Thiadiazole-2,5-thio) bis(methylene) dibenzoyl chloride (TDTBM-DC)

A mixture of TDTBM-DA (16.7 g, 0.04 mol), thionyl chloride (SOCl_2 , 80 mL) and dry pyridine (0.6 mL) were added into a 250 mL round-bottom flask. The mixture was stirred at room temperature under N_2 in darkness for 3 h, then refluxed for 12 h. The solvent and unreacted raw materials were removed by vacuum distillation. The residue was extracted repeatedly at $90\text{ }^\circ\text{C}$ with dry petroleum ether ($b.p.$ = $90\text{--}120\text{ }^\circ\text{C}$). Next, the extraction solution was gradually cooled to precipitate yellow crystal powder, which was filtered and dried under vacuum at $56\text{ }^\circ\text{C}$.

Yield: 16.8 g, 92.6%, m/z (M^+): 456.41.

Elemental analysis (%): Found: C, 47.98 (47.47); H, 2.73 (2.66); N, 6.20 (6.15), data in brackets are calculated.

FTIR (KBr, cm^{-1}): 3069 (C—H aromatic ring), 2933 ($-\text{CH}_2-$), 2663, 2530 (1,3,4-thiadiazole ring), 1769, 1736 ($-\text{COCl}$), 1602, 1573, 1502 ($\text{C}=\text{C}$ aromatic ring), 1123 (C—S—C), 830 (para-substituent of aromatic ring).

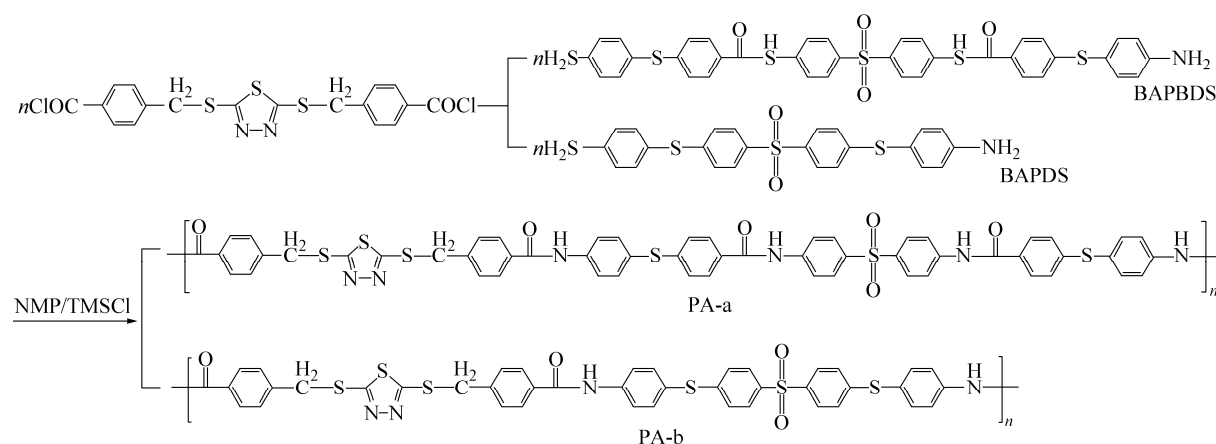
$^1\text{H-NMR}$ (600 MHz, chloroform- d /TMS, δ): 4.563 (s, 4H, H_1), 7.557–7.571 (d, 4H, H_2), 8.067–8.081 (d, 4H, H_3).

4,4'-bis(4-(4-aminophenylthio)benzamido)diphenyl sulfone (BAPBDS) was prepared according to our previous report^[29]. 4,4'-bis(4-aminophenylthio)diphenylsulfone (BAPDS) was prepared with a similar method as that of BAPBDS^[30].

Polymer Synthesis (PA-a)

A typical polymerization was performed as shown in Scheme 2. In a 100 mL three-necked flask fitted with a mechanical stirrer and thermometer, BAPBDS (7.02 g, 0.01 mol) and Me_3SiCl (TMSCl) (0.66 g, 0.006 mol) were dissolved in 60 mL of NMP. After BAPBDS had completely dissolved, TDTBM-DC (4.55 g, 0.01 mol) was added. The mixture was stirred at $0\text{ }^\circ\text{C}$ for 2 h, then stirred at room temperature for 12 h to yield a viscous pale-yellow solution. Next, the reaction solution was poured into water to obtain a fibrous precipitate, which was

washed with water and ethanol and dried under vacuum. The fibrous precipitate was pulverized to powder and washed with water and ethanol again. After drying under vacuum at 100 °C for 12 h, 10.4 g (95.6%) of PA-a was obtained.



PA-a: elemental analysis (%), Found: C: 62.01 (61.97); H: 3.89 (3.71); N: 7.56 (7.74), data in brackets are calculated. FTIR (casting film, cm^{-1}): 3433, 1655 ($-\text{CO}-\text{NH}-$), 2932 ($-\text{CH}_2-$), 2671 (1,3,4-thiadiazole ring), 1587, 1519, 1494 ($\text{C}=\text{C}$ aromatic ring), 1308, 1147 ($-\text{SO}_2-$), 1104 ($\text{C}-\text{S}-\text{C}$), 829 (para-substituent of aromatic ring). $^1\text{H-NMR}$ (600 MHz, $\text{DMSO}-d_6/\text{TMS}$, δ): 4.606 (s, 4H, H_1), 7.231–7.251 (d, 4H, H_2), 7.500–7.520 (d, 4H, H_3), 7.572–7.92 (d, 4H, H_4), 7.801–7.900 (m, 16H, H_5-H_8), 7.973–7.995 (d, 4H, H_9), 10.419 (s, 2H, H_{10}), 10.580 (s, 2H, H_{11}).

PA-b was prepared following a similar procedure as that of PA-a. We also synthesized the polyamide which has no sulfone groups (PA-s: the polyamide of TDTBM-DC and 4,4'-thiodianiline) to compare its transmittance with PA-(a-b).

PA-b: 7.79 g, Yield: 92.1%. Elemental analysis (%), Found: C: 60.03 (59.55); H: 3.89 (3.57); N: 6.97 (6.61), data in brackets are calculated. FTIR (casting film, cm^{-1}): 3423, 1652 ($-\text{CO}-\text{NH}-$), 2931 ($-\text{CH}_2-$), 2670 (1,3,4-thiadiazole ring), 1609, 1575, 1494 ($\text{C}=\text{C}$ aromatic ring), 1309, 1151 ($-\text{SO}_2-$), 1109 ($\text{C}-\text{S}-\text{C}$), 817 (para-substituent of aromatic ring). $^1\text{H-NMR}$ (600 MHz, $\text{DMSO}-d_6/\text{TMS}$, δ): 4.598 (d, 4H, H_1), 7.170–7.189 (d, 4H, H_2), 7.442–7.463 (d, 4H, H_3), 7.545–7.565 (d, 4H, H_4), 7.754–7.774 (d, 4H, H_5), 7.831–7.914 (m, 8H, H_6-H_7), 10.471 (s, 2H, H_8).

RESULTS AND DISCUSSION

Monomers

Monomer synthesis

The synthetic routes of TDTBM-DC are shown in Scheme 1. TDTBM-DC was synthesized through the reaction of hydrazine, carbon disulfide and 4-CMBA. First, hydrazine reacted with carbon disulfide to form DMTD, which reacted with 4-CMBA and K_2CO_3 under nitrogen to prepare TDTBM-DA. Then, TDTBM-DA was converted to TDTBM-DC through reaction with SOCl_2 . This procedure must be anhydrous, or the yield would be very low.

Characterization of TDTBM-DA and TDTBM-DC

The chemical structure of the monomers was confirmed by FTIR and $^1\text{H-NMR}$. The FTIR spectrum of TDTBM-DA (Fig. 1) showed the characteristic absorptions of $-\text{COOH}$ near 1690 cm^{-1} , and the absorption of $-\text{S}-$ near 1120 cm^{-1} . The $^1\text{H-NMR}$ spectrum (Fig. 2) of TDTBM-DA showed four groups of peaks. The proton signal

of $-\text{COOH}$ was present obviously at high frequency area ($\delta = 12.972$). The characteristic absorptions of $-\text{COCl}$ and $-\text{S}-$ at 1769 , 1736 and 1130 cm^{-1} were found in the TDTBM-DC FTIR spectrum (Fig. 1). The $^1\text{H-NMR}$ spectrum (Fig. 2) of TDTBM-DC showed three groups of peaks (ranged from 4.563 to 8.081). The ratio of the corresponding integral curves was about $1:1:1$. Combining the results of the FTIR and mass spectral analyses suggested that we had synthesized TDTBM-DC as shown in Scheme 1.

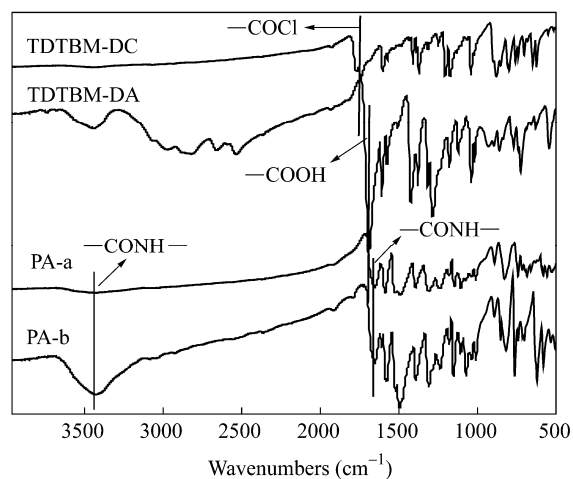


Fig. 1 FTIR spectra of TDTBM-DA, TDTBM-DC and PA-(a-b)

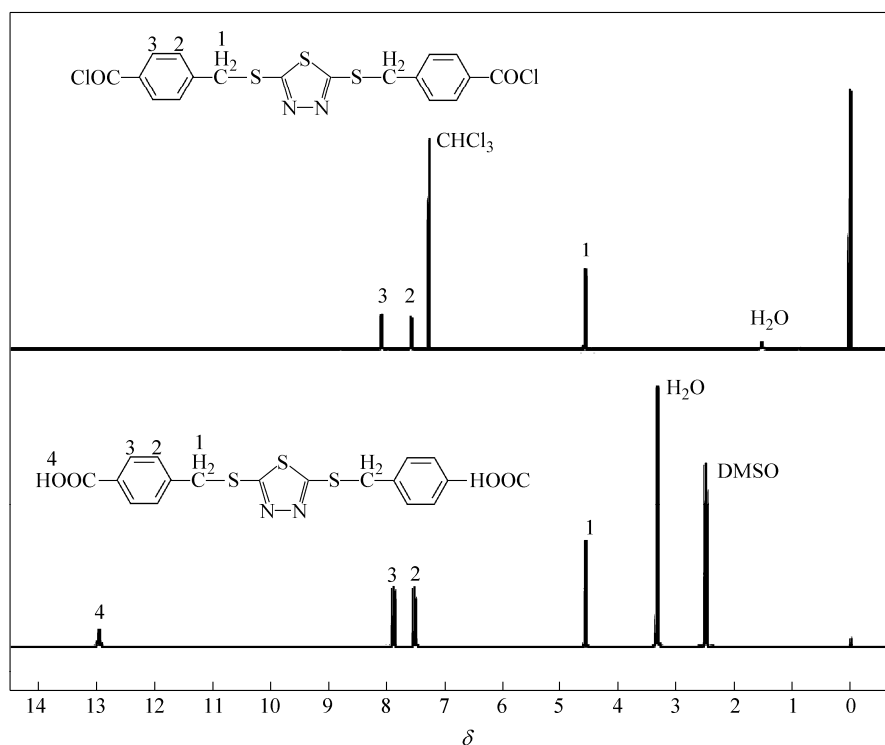


Fig. 2 $^1\text{H-NMR}$ spectra of TDTBM-DA and TDTBM-DC

Polymers

Polymer synthesis

The polycondensation reaction of the diamine (BAPBDS) and TDTBM-DC was conducted in the presence of TMSCl as a catalyst in NMP. Silylation of the diamine is an efficient activation method to obtain high molecular weight polymers^[34–36]. Due to the strong affinity of Si for oxygen, the carbonyl oxygen of the acid chloride is attracted to the Si atom in the amine derivatives, which in turn facilitates nucleophilic attack of the N atom of the N-silylated amine at the carbonyl carbon.

The intrinsic viscosity ($[\eta]$) and molecular weights of PA-(a-b)

The molecular weights of the polyamides were measured by $[\eta]$ and GPC. As shown in Table 1, the $[\eta]$ values of PA-(a-b) were in the range of 0.40–0.51 dL/g. PA-(a-b) showed M_n values in the range of 3.7×10^4 – 4.6×10^4 and M_w values in the range of 7.8×10^4 – 9.1×10^4 , respectively. The polydispersity indices (PDIs) of PA-(a-b) were 2.0 and 2.1, respectively. The results indicate that the polyamides had moderate molecular weight.

Table 1. Intrinsic viscosity, molecular weights and thermal properties of PA-(a-b)

Samples	$[\eta]$ (dL/g)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	T_g (°C)	$T_{5\%}$ (°C)	Char yield (%)
PA-a	0.51	4.6×10^4	9.1×10^4	2.0	206	395	43.6
PA-b	0.40	3.7×10^4	7.8×10^4	2.1	233	376	43

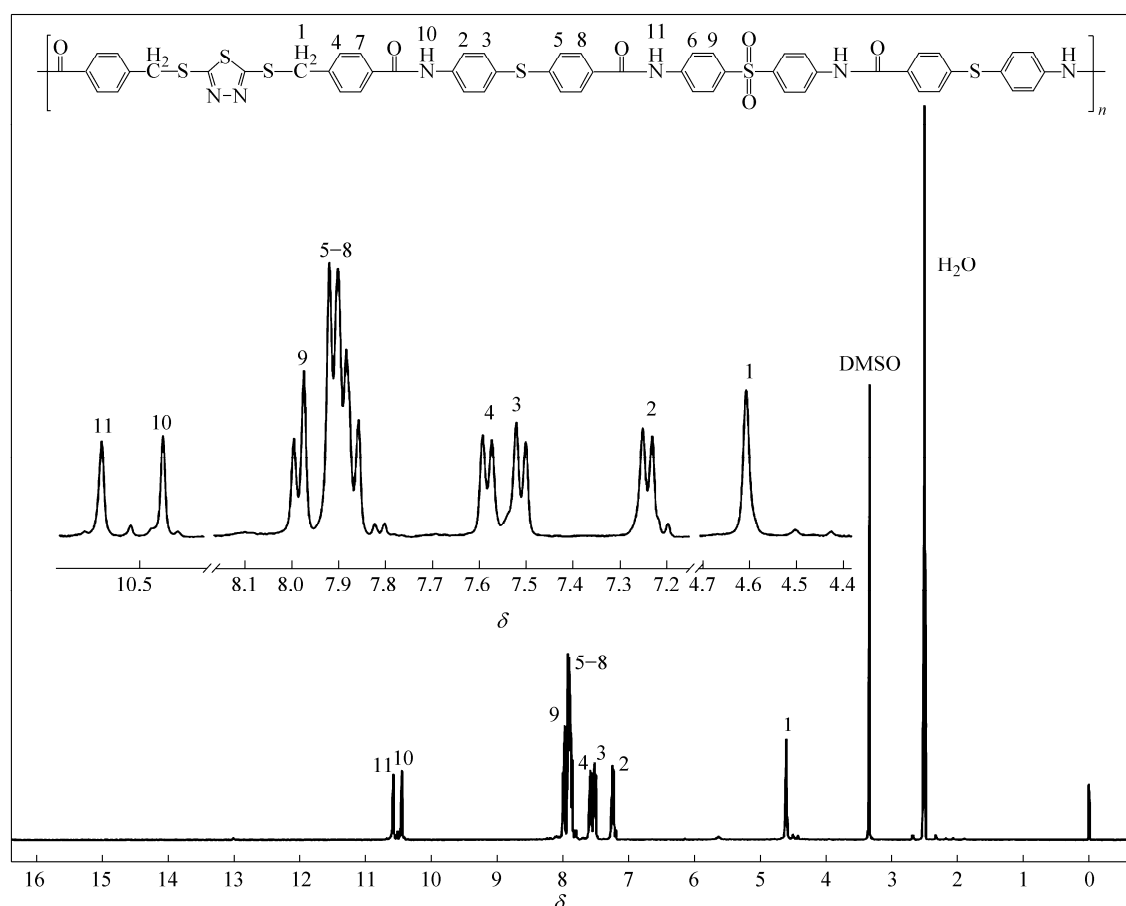


Fig. 3 ^1H -NMR spectrum of PA-a (polyamide of TDTBM-DC and BAPBDS)

The FTIR and ^1H -NMR spectra of PA-(a-b)

From the FTIR spectra of PA-(a-b) (Fig. 1) we can find the characteristic absorptions of the amide group ($-\text{CONH}-$) near 3400 and 1650 cm^{-1} , the sulfone group ($-\text{SO}_2-$) near 1320 cm^{-1} , 1150 cm^{-1} and the $-\text{S}-$ group near 1100 cm^{-1} . In comparison with the monomers (TDTBM-DC), the absorptions of $-\text{COCl}$ (1770 and 1740 cm^{-1}) disappeared. It indicates that the amino and carboxyl chloride had reacted. Figure 3 shows the ^1H -NMR spectra of PA-a. Eight groups of peaks appeared in the ^1H -NMR spectrum of PA-a. The calculated result should have eleven group peaks and the ratio of corresponding integral curves was 2:2:2:2:2:2:2:2:1:1, but the chemical shifts of H_5 - H_8 were largely overlapped so that they can not be easily separated. The signals at 4.606, 10.419 and 10.580 were assigned to the methylene and amide groups. The aromatic protons were observed at about $\delta = 7.231$ – 7.995 . The ratio of corresponding integral curves was $\text{H}_1:\text{H}_2:\text{H}_3:\text{H}_4:(\text{H}_5-\text{H}_8):\text{H}_9:\text{H}_{10}:\text{H}_{11} = 2:2:2:2:8:2:1:1$. In combination with the FTIR and elemental analysis results, these eight groups of peaks were ascribed to H_1 , H_2 , H_3 , H_4 , H_5 , H_6 , H_7 , H_8 , H_9 , H_{10} and H_{11} , as shown in Fig. 3. The structure of PA-b was characterized by the ^1H -NMR spectrum (Fig. 4), FTIR spectra and elemental analysis also. These finding suggests that the polymers were prepared as shown in Scheme 2.

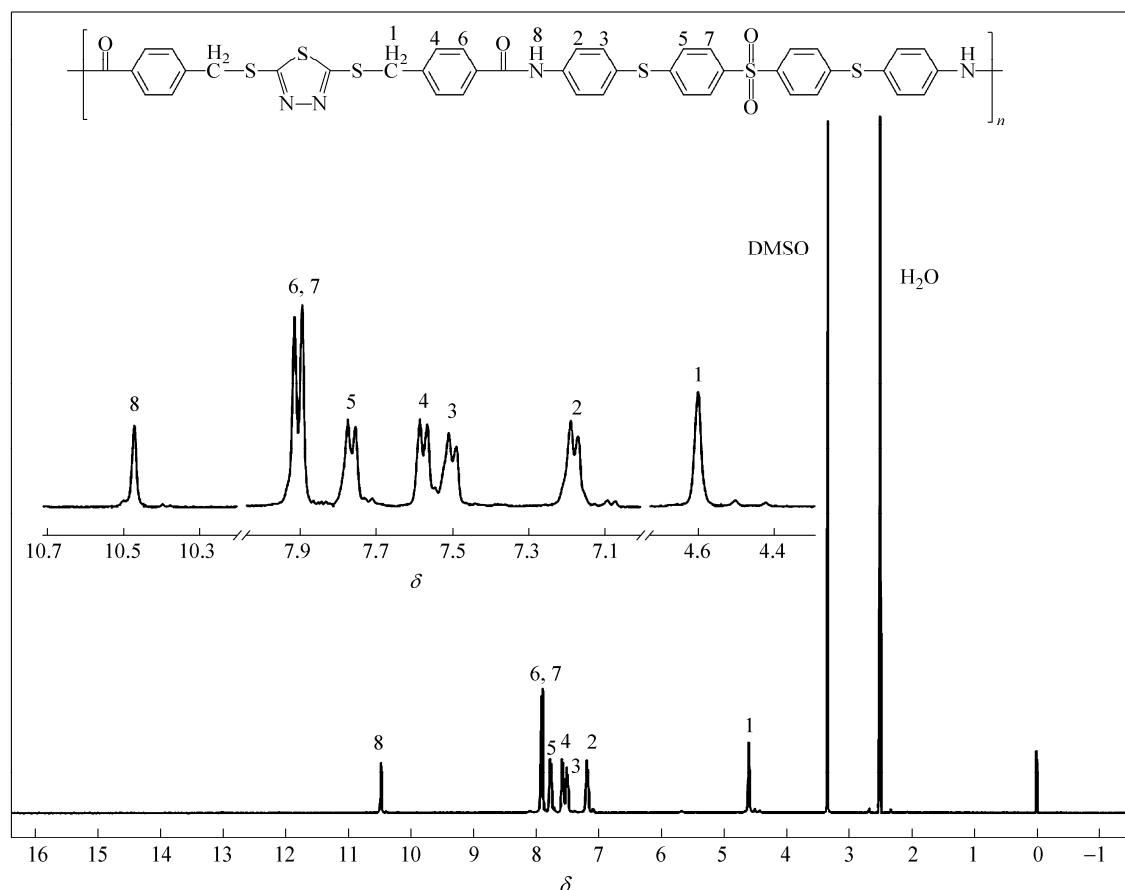


Fig. 4 ^1H -NMR spectrum of PA-b (polyamide of TDTBM-DC and BAPDS)

The X-ray diffraction analysis of PA-(a-b)

Figure 5 was the X-ray diffraction patterns of PA-(a-b) (annealed at $260\text{ }^\circ\text{C}$). As manifested in Fig. 5, PA-(a-b) had no crystalline peaks. That suggests PA-(a-b) are amorphous. The polymer mainchain locomotion was limited by the strong polarity sulfone group, so the molecular chains could not arrange in order.

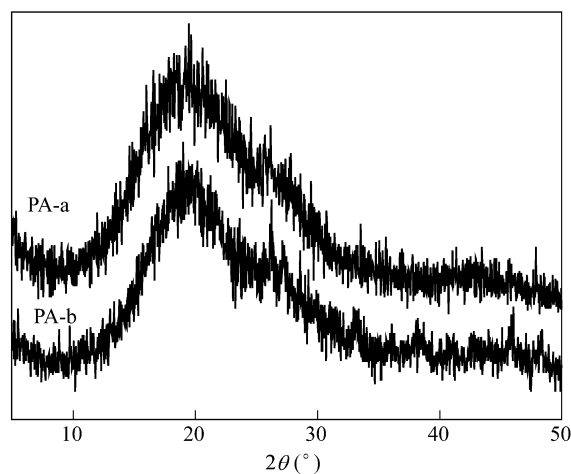


Fig. 5 XRD profiles of PA-(a-b) annealed at 260 °C for 4 h

Thermal properties of PA-(a-b)

The thermal properties of PA-(a-b) were examined by DSC and TGA. As shown in Fig. 6, the T_g values of PA-(a-b) were 206–233 °C (in Table 1). The DSC curves of PA-(a-b) showed no endothermic melting peak. Thus DSC measurements also revealed that the amorphous nature of PA-(a-b). That was consistent with the results of XRD. From the DSC curves we found that PA-a had about 30 K higher T_g than PA-b, the main reason was the existence of higher content hydrogen bonds in the main chain of PA-a. As shown in Fig. 7, the initial degradation temperatures of PA-(a-b) in nitrogen ($T_{5\%-\text{nitrogen}}$) were 395 °C and 376 °C, respectively. They provided about 40% char yield at 800 °C in nitrogen (Table 1). The TGA data also suggested that these polymers had a good thermal performance.

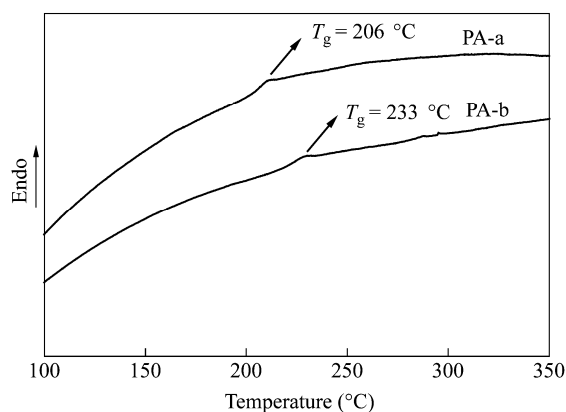


Fig. 6 DSC curves of PA-(a-b) at a heating rate of 10 K/min in N_2

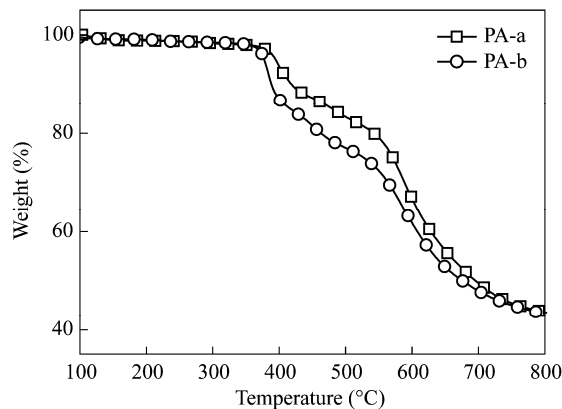


Fig. 7 TGA curves of PA-(a-b) at a heating rate of 20 K/min in N_2

Tensile properties

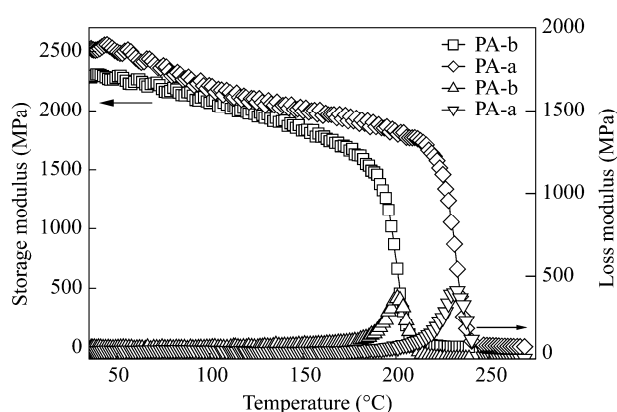
The mechanical properties of the casting films of the polyamides (PA-(a-b)) are given in Table 2 (treated at 120–140 °C for 10 h, 180 °C for 10 h). As shown, the average tensile strengths and the Young's modulus values of PA-(a-b) were 83.1–72.8 MPa and 2.1–1.7 GPa, respectively. That suggests the polyamides had excellent mechanical properties. While the elongation at break was less than 5%, suggesting that the toughness of the polymers need to be further improved.

Table 2. Tensile properties of PA-(a-b)

Polymers	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Storage modulus at 200 °C (GPa)	Glass transition temperature ^a (°C)
PA-a	83.1	2.1	3.4	1.8	202
PA-b	72.8	1.7	4.2	1.0	232

^a detected by dynamic mechanical analysis (DMA)*Dynamic mechanical analysis*

Figure 8 is the storage modulus curves of PA-(a-b). As shown in Fig. 8, PA-(a-b) showed a storage modulus about 1–1.8 GPa at 200 °C. This finding indicates that these polyamides had good mechanical properties. An obvious transition behavior was observed. The temperatures of α relaxation of PA-(a-b) were 202 °C and 232 °C (these results were close to the DSC data). With incorporating high content of amide bonds in the polymeric backbone, the glass transition temperature increased.

**Fig. 8** The storage modulus and loss modulus curves of PA-(a-b)*Water absorption*

The water absorption of PA-(a-b) was measured according to GB/T17037.3-2003. The results are listed in Table 3. The water absorptions of PA-(a-b) were 0.24% and 0.23%. In comparison with the aliphatic polyamide (such as PA6), it indicates that PA-(a-b) have low water absorption. That is good for their dimensional and mechanical stability.

Table 3. Dielectric constant of PA-(a-b)

Polymers	Thickness (μm)	Water absorption (%)	Dielectric constant			
			0.1 (kHz)	1 (kHz)	10 (kHz)	100 (kHz)
PA-a	92	0.24	4.32	4.08	3.76	3.69
PA-b	81	0.23	4.28	3.87	3.60	3.63

Dielectric constants

The dielectric constants of PA-(a-b) are listed in Table 3. They showed low dielectric constants of 3.69–3.63 at 100 kHz, which are almost identical to that of “Aramid1313 (3.3–3.6)”. The low dielectric constants may be attributed to low water absorption and rigid molecular chain of the polymers. That is important to the application of photo-electronic materials.

Optical properties

Figure 9 shows the optical transmittance spectra of PA-(a-b) and PA-s. The cut-off wavelengths (λ_{cutoff}) of the PA-(a-b) films were 350 nm and 358 nm, respectively. The transmittances of the films measured at 450 nm were much higher than 80% (film thicknesses: 7–10 μm). In order to compare the effect of the sulfone group, we tested the optical transparency of PA-s which had no sulfone groups (PA-s: the polymer of TDTBM-DC and 4,4'-thiodianiline). We observed that the transmittance (at 450 nm) was about 33.2% (shown in Fig. 9). This

finding indicates that incorporating the sulfone group into the polymer chain is beneficial for improving the optical transmittance of the polymer film. The optical properties of the PA films, such as the cut-off wavelengths, in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices, average refractive indices (n_{av}) and birefringences (Δn) are listed in Table 4. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of PA-(a-b) were in the range of 1.717–1.726 and 1.715–1.722, respectively. The n_{TE} values are slightly higher than those of the n_{TM} ones for all PA films since the molecular chains are preferentially oriented in the film plane. The n_{av} values of PA-(a-b) measured at 633 nm were 1.716 and 1.725, respectively. The n_{av} depended on several factors, such as sulfur content, molecular chain flexibility and molar volume. The refractive index of PA-b is higher than that of PA-a. This finding was mainly attributed to PA-b's higher sulfur content compared to that of PA-a. In addition, we found that PA-a exhibits similar refractive index value (1.716) in spite of having lower sulfur content than PA-R^[30]. This result clearly indicates that the thiadiazole moiety endows high polarizability and high refractive index compared to a phenyl ring. Also PA-(a-b) showed lower Δn values of 0.003–0.004 than aromatic PI (0.006–0.0076)^[37]. All of the results suggest that the introduction of thiadiazole units is an effective way to endow PAs with a high refractive index. The dielectric constants ($\epsilon_{\text{Calculated}}$) of the PA films estimated from the average refractive indices using the modified Maxwell equation: $\epsilon_{\text{Calculated}} = 1.1 n_{\text{AV}}^2$ are shown in Table 4. The PA films are expected to show the slightly lower ϵ values of 3.23–3.27 compared with the measured results (shown in Table 4).

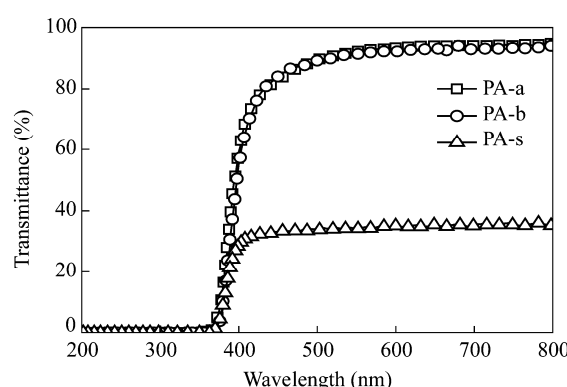


Fig. 9 UV-Vis spectra of PA-(a-b) and PA-s films

Table 4. Optical properties of the polyamide films

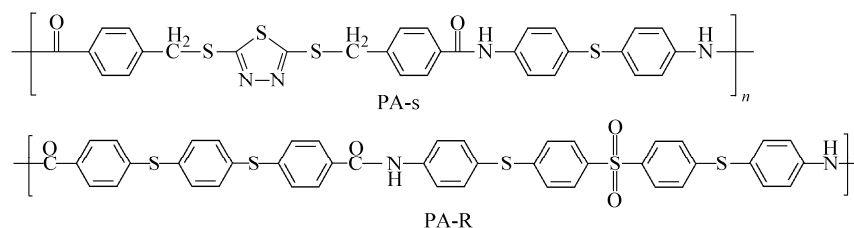
Polymers	Sc (%)	λ_{cutoff} (nm)	T_{450} (%)	633 nm				$\epsilon_{\text{Calculated}}$
				n_{TE}	n_{TM}	n_{AV}	Δn	
PA-a	17.73	350	83	1.717	1.714	1.716	0.003	3.23
PA-b	22.71	358	84	1.726	1.722	1.725	0.004	3.27
PA-s ^b	21.42	370	33.2	—	—	—	—	—
PA-R	19.77	364	96.3	1.718	1.711	1.716	0.007	3.24
Polymers	1310 nm				1550 nm			
	n_{TE}	n_{TM}	n_{AV}	Δn	n_{TE}	n_{TM}	n_{AV}	Δn
PA-a	1.686	1.682	1.685	0.004	1.681	1.677	1.680	0.004
PA-b	1.697	1.693	1.696	0.004	1.693	1.688	1.691	0.005

^b The polyamide of TDTBM-DC and 4,4'-thiodianiline

Sc: the content of S; T_{450} : the transmittance of films at 450 nm; ϵ : dielectric constant;

n_{TE} : the in-plane refractive index; n_{TM} : the out-of-plane refractive index;

Δn : birefringence; $\epsilon_{\text{Calculated}} = 1.1 n_{\text{AV}}^2$; —: not detected.



Solubility experiments

Through the solubility experiments (Table 5), we found that the polyamides (PA-(a-b)) were soluble in NMP, DMF, DMSO and concentrated sulfuric acid at room temperature. However, these polyamides were not soluble in hydrochloric acid (6 mol/L), formic acid, NaOH (1 mol/L) and acetone and so on. In comparison to alkyl-polyamide (PA6, PA66), these polymers showed better corrosion resistance. Thus, they can be processed using following methods, such as electro-spinning and solution casting.

Table 5. Solubility behavior of PA-(a-b)

Solvent	Polymers	
	PA-a	PA-b
concentrated sulfuric acid	++	++
formic acid	—	—
NMP	++	++
DMF	++	++
pyridine	+-	+-
hydrochloric acid (6 mol/L)	—	—
acetone	—	—
chloroform	—	—
DMSO	++	++
1, 4-dioxane	—	—
toluene	—	—
cyclohexanone	—	—

* ++: soluble at room temperature; +: soluble at solvents boiling point;
+-: swelling with heating; —: insoluble with heating.

CONCLUSIONS

Aromatic dibenzoyl chloride with high sulfur content and thiadiazole was designed and synthesized to develop high-*n* polyamides. The resultant polyamides showed good thermal stabilities, such as T_g of 206–233 °C, $T_{5\%}$ of 376–395 °C and mechanical properties. The polyamides exhibited good optical performance. The transmittance of polyamides films with about 10 μm thickness is around 83% at 450 nm. The polymers exhibited refractive indices about 1.716–1.725 at 633 nm and low birefringence of 0.003–0.004. It can be concluded that the high refractive indices are caused by high sulfur contents and heterocyclic units, while keeping the solubility of polymers in organic solvents, such as NMP, DMF and so on. Moreover, the synthesis of the TDTBM-DA is more facile and affordable than the other monomers reported for sulfur-containing polymers. Thus, the polyamides can be good candidates as components for advanced optical device applications, such as optical wave guides for CMOS image sensor.

REFERENCES

- 1 Suwa, M., Niwa, H. and Tomikawa, M., J. Photopolym. Sci. Technol., 2006, 19: 275
- 2 Geiger, F., Stoldt, M., Schweizer, H., Bauerle, P. and Umbach, E., Adv. Mater., 1993, 5: 922
- 3 Kunugi, Y., Miller, L., Maki, T. and Canavesi, A., Chem. Mater., 1997, 9: 1061

- 4 Kitamura, K., Okada, K., Fujita, N., Nagasaka, Y., Ueda, M., Sekimoto, Y. and Kurata, Y., *Jpn. J. Appl. Phys.*, 2004, 43: 5840
- 5 Matsuda, T., Funae, Y., Yoshida, M., Yamamoto, T. and Takaya, T., *J. Appl. Polym. Sci.*, 2000, 76: 45
- 6 Liu, J.G., Nakamura, Y., Ogura, T., Shibasaki, Y., Ando, S. and Ueda, M., *Chem. Mater.*, 2008, 20: 273
- 7 You, N.H., Nakamura, Y., Suzuki, Y., Higashihara, T., Ando, S. and Ueda, M., *J. Polym. Sci. Part A: Polym. Chem.*, 2009, 47: 4886
- 8 You, N.H., Fukuzaki, N., Suzuki, Y., Nakamura, Y., Higashihara, T., Ando, S. and Ueda, M., *J. Polym. Sci. Part A: Polym. Chem.*, 2009, 47: 4428
- 9 Matsuda, T., Funae, Y., Yoshida, M., Takaya and T., *J. Macro. Sci. Pure Appl. Chem.*, 1999, 36: 1271
- 10 Sawada, T. and Ando, S., *Chem. Mater.*, 1998, 10: 3368
- 11 Lu, C.L., Cui, Z.C., Wang, Y.X., Yang, B. and Shen, J.C., *J. Appl. Polym. Sci.*, 2003, 89: 2426
- 12 Nebioglu, A., Leon, J.A. and Khudyakov, I.V., *Ind. Eng. Chem. Res.*, 2008, 47: 2155
- 13 Terraza, C.A., Liu, J.G., Nakamura, Y., Shibasaki, Y. and Ando, S., *J. Polym. Sci. Part A: Polym. Chem.*, 2008, 46: 1510
- 14 Seesukphronrarak, S., Kawasaki, S., Kobori, K. and Takata, T., *J. Polym. Sci. Part A: Polym. Chem.*, 2007, 45: 3073
- 15 Liou, G.S., Lin, P.H., Yen, H.J., Yu, Y.Y. and Chen, W.C., *J. Polym. Sci. Part A: Polym. Chem.*, 2010, 48: 1433
- 16 Liu, J.G., Nakamura, Y., Terraza, C.A., Shibasaki, Y., Ando, S. and Ueda, M., *Macromol. Chem. Phys.*, 2008, 209: 195
- 17 Fukuzaki, N., Higashihara, T., Ando, S. and Ueda, M., *Macromolecules*, 2010, 43: 1836
- 18 Huang, X.H., Huang, W., Fu, L.C. and Yan, D.Y., *J. Polym. Res.*, 2012, 19(2): 9790
- 19 Wang, W.C., Ong, G.T., Lim, S.L., Vora, R.H., Kang, E.T. and Neoh, K.G., *Ind. Eng. Chem. Res.*, 2003, 42: 3740
- 20 Kyung, H.C. and Jin, C.J., *Macro. Mater. Eng.*, 2004, 289: 737
- 21 Liu, M.H., Shen, G.Y., Xu, W.J. and Shen, G.L., *Polym. Int.*, 2007, 56: 1432
- 22 Mehdipour-Ataei, S. and Babanzadeh, S., *React. Funct. Polym.*, 2007, 67: 883
- 23 Liu, P.T., Wang, J.Y., Liu, C. and Jian, X.G., *Macromol. Chem. Phys.*, 2006, 207: 1610
- 24 Hajipour, A.R., Habibib, S. and Ruohoa, A.E., *Polym. Int.*, 2009, 58: 630
- 25 In, I. and Kim, S.Y., *Polymer*, 2006, 47: 547
- 26 Zhang, G., Huang, G.S., Li, D.S., Wang, X.J., Long, S.R. and Yang, J., *Ind. Eng. Chem. Res.*, 2011, 50: 7056
- 27 Hsiao, S.H. and Leu, W.T., *Polym. Int.*, 2005, 54: 392
- 28 José, M., García, F.C., García, F.S., José, L. and Dela, P., *Prog. Polym. Sci.*, 2010, 35: 623
- 29 Zhang, G., Huang, G.S., Wang, X.J., Long, S.R. and Yang, J., *J. Polym. Res.*, 2011, 18: 1261
- 30 Zhang, G., Li, D.S., Huang, G.S., Wang, X.J., Long, S.R. and Yang, J., *React. Funct. Polym.*, 2011, 71: 775
- 31 Liu, J.G., Nakamura, Y., Shibasaki, Y., Ando, S. and Ueda, M., *Polym. J.*, 2007, 39: 543
- 32 Hougham, G., Tesoro, G., Viehbeck, A. and Chapple-Sokol, J.D., *Macromolecules*, 1994, 27: 5964
- 33 Hougham, G., Tesoro, G., Viehbeck, A. and Shaw, J., *Macromolecules*, 1994, 27: 3642
- 34 Oishi, Y., Kakimoto, M.A. and Imai, Y., *Macromolecules*, 1988, 21: 547
- 35 Oishi, Y., Kakimoto, M.A. and Imai, Y., *J. Polym. Sci. Part A: Polym. Chem.*, 191, 29: 1925
- 36 Mehdipour-Ataei, S., Tadjarodi, A. and Babanzadeh, S., *Eur. Polym. J.*, 2007, 43: 498
- 37 You, N.H., Higashihara, T., Ando, S. and Ueda, M., *J. Polym. Sci. Part A: Polym. Chem.*, 2010, 48: 656