Polymer 54 (2013) 601-606

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis of highly refractive and transparent poly(arylene sulfide sulfone) based on 4,6-dichloropyrimidine and 3,6-dichloropyridazine

Gang Zhang^a, Hao-hao Ren^b, Dong-sheng Li^a, Sheng-ru Long^{a,**}, Jie Yang^{a,c,*}

^a Institute of Materials Science & Technology, Analytical & Testing Center, Sichuan University, Chengdu 610064, PR China
^b College of Physical Science and Technology of Sichuan University, Chengdu 610065, PR China
^c State Key Laboratory of Polymer Materials Engineering (Sichuan University), Chengdu 610065, PR China

ARTICLE INFO

Article history: Received 12 September 2012 Received in revised form 21 November 2012 Accepted 1 December 2012 Available online 6 December 2012

Keywords: Synthesis Optical property Heterocycle

ABSTRACT

A highly refractive and transparent poly(arylene sulfide sulfone) (PASS) containing pyrimidine (or pyridazine) unit has been developed. The polymer was prepared by a polycondensation reaction of 4,4'dimercaptodiphenyl sulfone (DMDPS) and 4,6-dichloropyrimidine (DCPM) (or 3,6-dichloropyridazine (DCPD)). They showed good thermal stabilities such as a relatively high glass transition temperature of 193–202 °C and a 5% weight loss temperature ($T_{5\%}$) of 370–372 °C. The optical transmittance of the polymer at 450 nm is higher than 81%. The heterocycles unit and plural –S– linkages provides the polymer with a high refractive index of 1.737–1.743 at 633 nm and a low birefringence of 0.003–0.004. © 2012 Elsevier Ltd. All rights reserved.

1. Introduction

High refractive index polymeric materials have been rapidly developed and attract significant interest in recent years. They were used in lenses, prisms, components for charge-coupled devices [1] and complementary metal oxide semiconductor image sensors [2–4] because of their lightweight, impact resistance, processability, and dying ability compared to inorganic glasses. A general approach 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 $(V_{\rm M})$, polarizability (α) and the molar refractions of functional groups and the backbone repeating unit of the polymer (R_{LL}) [5]. Among these high refractive index substituents (Cl, Br, I, sulfur atoms and metallic elements), the sulfur element is commonly selected because of its high polarizability, stability, and facility to introduce to polymers.

$$\left(\frac{n^2-1}{n^2+1}\right)V_{\rm M} = \frac{4}{3}\pi N_{\rm A}\alpha = \sum_i \left(R_{\rm LL}\right)_i$$

Various kinds of high-n polymers containing sulfur elements were reported, such as epoxies [6], polyurethanes [7], polymethacrylates [8], and polyarylenethioethers [9]. However, the polymers have relatively low refractive indices in the range of 1.5–1.7 at 633 nm. Recently, aromatic polyamides (PAs) [10,11] and polyimides (PIs) [12–18] containing sufur have been 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 (That is resulted into coloration of aromatic PIs for its formation charge transfer complexes (CTC) between the electron-donating diamine and the electron-accepting carbonyl group), which are the problems of aromatic PAs and PIs.

Poly(aryl thioether)s, such as in poly(phenylene sulfide), poly(phenylene sulfide ketone) [19], and poly-(phenylene sulfide sulfone) [20–23] are of well-known high performance engineering thermoplastics. They all have excellent processability, mechanical, thermal, and antioxidant properties. Recently, fluorene and sulfone substituents have been introduced into the poly(aryl thioether)s mainchain to form soluble and thermal stable optical resins [9,24,25]. Most of them exhibit excellent optical transparency and low birefringence. 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 sulfur containing polymers mainly depends on the sulfur content in the repeating unit.) and sterically bulky substituents such as fluorene groups would endow





^{*} Corresponding author. Institute of Materials Science & Technology, Analytical & Testing Center, Sichuan University, Chengdu 610064, PR China. Fax: +86 28 8541 2866.

^{**} Corresponding author. Fax: +86 28 8541 2866.

E-mail addresses: lsrhome@163.com (S.-r. Long), ppsf@scu.edu.cn (J. Yang).

^{0032-3861/\$ –} see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.polymer.2012.12.008

Table 1

The molar refraction of common atoms and groups.

| Group | Molar Refraction (R) | Group | Molar Refraction (R) |
|-------|-------------------------|---|-------------------------|
| Н | 1.100 | Phenyl(C ₆ H ₅) | 25.463 |
| С | 2.418 | Naphthyl(C ₁₀ H ₇) | 43.00 |
| C=C | 1.733 | Cl | 5.967 |
| C≡C | 2.398 | Br | 8.865 |
| C=0 | 2.211 | Ι | 13.900 |
| -C-O- | 1.643 | -SH | 7.69 |
| F | 0.95 | -S-S- | 8.11 |
| N–N=C | 3.46 | C-N=C | 4.10 |

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. From Table 1, we can find that N–N=C and C=N–C bonds possess relatively high molar refraction (3.46) and (4.10) as compared to C=C bond (1.73) [26]. Thus, in order to enhance the refractive index and optical transparency. introduction of aromatic heterocycles such as pyridazine and pyrimidine units containing -C=N- bonding would be an effective method [15]. On the other hand, the sulfonyl (-SO₂-) group endows polymers with low refractive index dispersion and high transparency. On the basis of these considerations, we designed a novel polymer that contained sulfur, sulfonyl and aromatic heterocycles to achieve high refractive index, low birefringence and high optical transparency. This article reports the synthesis and properties of the pyridazine and pyrimidine ring containing PASSs prepared from 4,6-dichloropyrimidine (DCPM) (or 3.6dichloropyridazine (DCPD)) and 4,4'-dimercaptodiphenylsulfone (DMDPS). The obtained PASSs exhibited high refractive indices in the range of 1.737-1.743, a low birefringence of 0.003-0.004, and high optical transparency over 81% at 450 nm.

2. Experimental

2.1. Materials

Commercially available 4,6-dichloropyrimidine (DCPM) and 3,6-dichloropyridazine (DCPD) (99%, Quzhou, Rainful Chemical Industry Company), 4,4'-dichlorodiphenylsulfone (DCDPS) (AR, Suzhou Yinsheng Chemical Industry Company), 1,3-dimercaptobenzene (m-DMB) (97%, Alfa Aesar Chemical Company Ltd.), 1,4-dimercaptobenzene (p-DMB) (98%, Zhe Jiang Shou Er Fu Chemical Industry Group Company Ltd.), sodium hydroxide (NaOH) (AR, SiChuan ChengDu ChangLian Chemical Reagent Company), sodium sulfide (Na₂S·xH₂O, Na₂S% \approx 60%) (Nafine Chemical Industry Group Co., Ltd.), N-methyl-2-pyrrolidone (NMP) (JiangSu NanJing JinLong Chemical Industry Company), sodium benzoate,

sodium 4-methylbenzenesulfonate (AR, Aladdin Reagent Company) and other reagents and solvents were commercially obtained.

2.2. Monomer synthesis

4,4'-dimercaptodiphenylsulfone (DMDPS) (shown in Scheme 1). We prepared DMDPS following a similar procedure as earlier reports [27]. We carried out the reaction with sodium sulfide as reagent. Also we used sodium benzoate and sodium 4-methylbenzenesulfonate to assist the dissolution of the sodium sulfide [28].

Polymer synthesis (DMDPS-DCPM) (shown in Scheme 1).

A typical polymerization was performed as shown in Scheme 1. In a 250 ml three-necked flask fitted with a mechanical stirrer and thermometer, DMDPS (14.1 g, 0.05 mol), DCPM (7.45 g, 0.05 mol), potassium carbonate (10.4 g, 0.075 mol), toluene (30 ml) and NMP (100 ml) were added. The mixture was stirred at 130–150 °C for 1 h to remove water; then stirred at 160 °C for 6 h to yield a viscous pale-yellow solution. Next, the reaction solution was poured into water to obtain a white fibrous precipitate, which was washed with water and ethanol; then 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, 16.5 g (92.3%) of DMDPS-DCPM was obtained.

DMDPS-DCPM: elemental analysis (%), Found: C: 53.8 (53.6); H: 2.87 (2.79); N: 7.61 (7.82) (data in brackets are calculated). FT-IR (casting film, cm⁻¹): 3081 (C–H aromatic ring), 1539, 1499 (C=C aromatic ring), 1395 (C–N), 1331, 1155 ($-SO_2$ –), 1091 (C–S–C), 835 (para-substituent of aromatic ring). ¹H NMR (600 MHz, DMSO-d₆/TMS, ppm): 7.259 (s, 1H, H₁), 7.819–7.841 (d, 4H, H₂), 8.034–8.056 (d, 4H, H₃), 8.599 (s, 1H, H₄). DMDPS-DCPD was prepared following a similar procedure as that of DMDPS-DCPM.

DMDPS-DCPD: 16.3 g, Yield: 91%, elemental analysis (%), Found: C: 54.0 (53.6); H: 2.85 (2.79); N: 7.56 (7.82) (data in brackets are calculated). FT-IR (casting film, cm⁻¹): 3090 (C–H aromatic ring), 1595, 1482 (C=C aromatic ring), 1379 (C–N), 1323, 1147 ($-SO_2-$), 1075 (C–S–C), 820 (para-substituent of aromatic ring). ¹H NMR (600 MHz, DMSO-d₆/TMS, ppm): 7.588 (s, 2H, H₁), 7.711–7.748 (d, 4H, H₂), 7.983-8.018 (d, 4H, H₃).

We also synthesized comparative samples which had no aromatic herocycles (m-DMB-DCDPS: the polymer of m-DMB and DCDPS, p-DMB-DCDPS: the polymer of p-DMB and DCDPS) under 190 °C to compare their optical properties with DMDPS-DCPM and DMDPS-DCPD.

2.3. Characterization

Limiting viscosity and molecular weights analysis: the limiting viscosities $\left(\left[\eta \right] = \lim_{c \to 0} \frac{\eta_{sp}}{C} \right)$ of PASSs were obtained by one-point



Scheme 1. Synthesis routes of DMDPS and polymers.

method at 30 ± 0.1 °C with 0.500 g of polymer dissolved in 100 ml of NMP, using a Cannon-Ubbelhode viscometer:

$$[\eta] = \frac{\sqrt{2(\eta_{\rm sp} - \ln\eta_{\rm r})}}{C}$$

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

The number-average molecular weights (M_n) and weightaverage 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 500-30,000 and 5000-800,000, 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. Elemental analysis: the samples of monomer and polymers were measured with an elemental analyzer (EURO EA-3000). Chemical structure analysis: FT-IR spectroscopic measurements were performed on a NEXUS670 FT-IR instrument. Nuclear magnetic resonance (¹H NMR) spectra were determined on a BRUKER-600 NMR spectrometer in deuterated chloroform or deuterated dimethyl sulfoxide. Thermal analysis: differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC thermal analysis instrument. The heating rate for the DSC measurements was 10 °C/min. Thermogravimetric analysis (TGA) measurements were performed on a TGA Q500 V6.4 Build 193 thermal analysis instrument with a heating rate of 10 °C/min under nitrogen atmosphere. Mechanical testing: 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 30 to 250 °C, with a heating rate of 5 °C/min. Optical analysis: the transmittance of the films was determined by UV-Visible spectroscopy (U-2310II). The out-ofplane $(n_{\rm TM})$ and in-plane $(n_{\rm TE})$ refractive indices of the PASSs films were measured with a SPA-Lite prism coupler (SPA-4000) at the wavelength of 633, 1310 and 1550 nm. The in-plane $(n_{\text{TE}})/\text{out}$ 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: $n_{\text{AV}} = [(2 n_{\text{TE}}^2 + n_{\text{TM}}^2)/3]^{1/2}$ [29]. Experiment of solubility: The solubility of polymers in various solvents was tested at room temperature and the boiling point of the solvent.

3. Results and discussion

3.1. Synthesis of monomers

In this study, the monomer (DMDPS) containing a sulfone group and sulfur content of 34.06% was prepared with the nucleophilic substitution reaction in the presence of sodium benzoate and sodium 4-methylbenzenesulfonate. It is better to control the temperature of vacuum-drying below 35 °C, or DMPDS may be oxidized to disulfide compounds. The structure of DMDPS was characterized by elemental analysis, FT-IR and ¹H NMR spectroscopies (see Supplementary data).

| Table 2 | |
|--|--|
| Limiting viscosity $([\eta])$, molecular weights and thermal properties of PASSs. | |

| Polymers | $[\eta] (dL/g)$ | M _n (g/mol) | M _w (g/mol) | PDI (M_w/M_n) |
|------------|-----------------|------------------------|------------------------|-----------------|
| DMDPS-DCPM | 0.82 | $8.1 	imes 10^4$ | 1.47×10^5 | 1.8 |
| DMDPS-DCPD | 0.64 | $6.3 	imes 10^4$ | 1.16×10^5 | 1.84 |



Fig. 1. FT-IR spectra of DMDPS-DCPM and DMDPS-DCPD.

3.2. Synthesis and characterization of polymers

The polycondensation reaction was carried out by nucleophilic substitution polymerization using potassium carbonate as the catalyst. The reaction temperature was about 160 °C, it is lower as that of polyethersulfone (PES: 180–200 °C). The most reason is that the strong electron withdrawing effect of -N=N- and -C=N-, then it is easy for the Ar–S⁻ to attack the positively charged carbon atoms which linked to chloride atoms. The molecular weights of the polymers were measured by limiting viscosity and GPC. As shown in Table 2, the [η] values of DMDPS-DCPM and DMDPS-DCPD were 0.82 and 0.64 dL/g, the M_n values were 8.1 × 10⁴ and 6.3 × 10⁴, M_w values were 1.47 × 10⁵ and 1.16 × 10⁵, respectively. The polydispersity indices (PDIs) of polymers DMDPS-DCPM and DMDPS-DCPD were 1.8 and 1.84.

The structures of the resultant polymer were characterized by elemental analysis, FT-IR and ¹H NMR spectroscopies. The FT-IR



Fig. 2. ¹H NMR spectra of DMDPS-DCPM.



Fig. 3. ¹H NMR spectra of DMDPS-DCPD.

spectra (Fig. 1) of polymers exhibit the characteristic -C-N- and thioether stretching at 1323–1331 and 1075–1091 cm⁻¹, respectively. The absorptions near 1320, 1150 cm⁻¹ were attributed to the sulfone group. Comparing with the spectrum of DMDPS, the characteristic absorption around 2560 cm⁻¹ (–SH) has disappeared. Fig. 2 shows the ¹H NMR spectra of DMDPS-DCPM. The signals of protons on bezene ring are shifted to low field because of the deshielding effects of unit of -C=N- compared to monomer DMDPS. The signals at 7.259 and 8.599 were assigned to the pyrimidine units. The ratio of corresponding integral curves was 1:4:4:1. Combined with the FT-IR and elemental analysis results suggest that the polymerization proceeds as descript in Scheme 1. The structures of DMDPS-DCPD were also characterized by the ¹H NMR (Fig. 3), FT-IR spectra and elemental analysis.

3.3. Thermal properties of polymers

The thermal properties of polymers were evaluated by TGA, DSC and DMA measurements. The results of weight loss temperatures ($T_{5\%}$) and glass transition temperatures are summarized in Table 3. As shown in Fig. 4 (TGA), the polymers show good thermal stability, such as 5% weight loss were 370–372 °C (It attributed to the thermal decomposition of pyrimidine and pyridazine ring [15]). They provided about 48% char yield at 800 °C in nitrogen. The glass transition temperatures (T_{gS}) of the polymers estimated by DSC (Fig. 5) and DMA (Fig. 6) exhibit similar values. The resultant polymers show high T_{gS} of more than 190 °C. In particular, DMDPS-DCPD has 10 °C higher T_{g} than those of DMDPS-DCPM because of the rigid structure of the pyridazine ring. Also from the DSC curves

Table 3

Tensile properties of PASSs.



Fig. 4. TGA curves of polymers at a heating rate of 10 °C/min in N₂.

we had not find the endothermic melting peak of polymers. It suggests the amorphous nature of the resultant polymers. That is beneficial for the polymers' transparency. In additionally, DMA analysis were carried out under nitrogen at a heating rate of 5 °C/min. Fig. 6 illustrates the variations in the storage modulus (E') and loss modulus (E'') at different temperatures. It can be seen from Fig. 6 that the storage modulus remained constant or decreased slightly on heating over a wide temperature range up to 190 °C. They were kept above 1.0 GPa at 200 °C. The $T_{\rm g}$ s determined as the peak temperatures of the E'' method, are nearly the same as those obtained by the DSC method. The slight differences are mainly attributed to the different responses of the polymers to these two measurements.

3.4. Tensile properties

The average tensile strengths of the casting films of the polymers treated at 120-140 °C for 10 h, then at 180 °C for 10 h, are given in Table 3. As shown in Table 3, the average tensile strengths and the Young's modulus values of the films were 88-104 MPa and 2.0-2.5 GPa, respectively. That suggests the polymers had good mechanical properties. While the elongation at break was more than 5%, suggesting the films have better toughness than that of earlier reported by our group [10,11].

3.5. Optical properties

The optical properties of PASSs films and comparative samples (m-DMB-DCDPS and p-DMB-DCDPS), such as the cutoff wavelength (λ_{cutoff}), the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices measured at 633, 1310, 1550 nm, the average refractive indices (n_{av}) and birefringence (Δn) are summarized in Table 4. Fig. 7 displays the optical transmission spectra of PASSs films and comparative samples (9–11 µm thick) at the region of 200–800 nm.

| Polymers | $T_{\rm g}(^{\circ}{ m C})$ | <i>T</i> _{5%} (°C) | Char yield (%) | Tensile strength (MPa) | Young's modulus (GPa) | Elongation at break (%) | Storage modulus at 200 °C (GPa) | Glass transition Temperature (°C) ^a |
|------------|-----------------------------|-----------------------------|----------------|---------------------------|--------------------------|----------------------------|------------------------------------|---|
| DMDPS-DCPM | 193 | 372 | 48.2 | 104 | 2.0 | 6.8 | 1.3 | 196 |
| DMDPS-DCPD | 202 | 370 | 48.8 | 88 | 2.5 | 5.3 | 1.1 | 214 |

^a Detected by dynamic mechanical analysis (DMA).



Fig. 5. DSC curves of polymers at a heating rate of 10 °C/min in N₂.

The cutoff wavelengths (λ_{cutoff}) of DMDPS-DCPM, DMDPS-DCPD, m-DMB-DCDPS and p-DMB-DCDPS films were 341, 356, 346 and 349 nm, respectively. The transparencies of the films measured at 400 and 450 nm were almost 68.6-78.8% and 81-85%, respectively. Comparing m-DMB-DCDPS and p-DMB-DCDPS, it suggests that the introduction of pyrimidine and pyridazine units do not significant deteriorate the optical transparency of polymers. Also we find the PASSs have better transparency than aromatic polyimides containing pyrimidine and pyridazine units [15]. As listed in Table 4, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of DMDPS-DCPM and DMDPS-DCPD at 633 nm were in the range of 1.738-1.744 and 1.735-1.740, respectively. The n_{TF} values are slightly higher than those of the $n_{\rm TM}$ ones for PASSs films since the molecular chains are preferentially oriented in the film plane. The nav values of DMDPS-DCPM, DMDPS-DCPD, m-DMB-DCDPS and p-DMB-DCDPS measured at 633 nm were 1.737, 1.743, 1.723 and 1.726, respectively. The n_{av} depended on several factors, such as sulfur content, molecular chain flexibility and molar volume. The refractive index of DMDPS-DCPD is slightly higher than that of DMDPS-DCPM. In addition, we found that PASSs exhibits higher refractive index value in spite of having lower sulfur content than m-DMB-DCDPS, p-DMB-DCDPS and PES [30,31]. This result clearly indicates



Fig. 6. The storage modulus and loss modulus curves of polymers.

| able | 4 | |
|------|---|--|
| | | |

| Opti | cal p | roper | ties o | of PA | ASSs' | films. |
|------|-------|-------|--------|-------|-------|--------|
|------|-------|-------|--------|-------|-------|--------|

| Polymers | Sc (%) | λ_{cutoff} | T_{400} | T_{450} | 633 nm | | | | |
|-------------|-----------------|--------------------|-----------------|------------|-----------------|-----------------|-----------------|------------|--|
| | | (nm) | (%) | (%) | n _{TE} | n _{TM} | n _{AV} | Δn | |
| DMDPS-DCPM | 26.82 | 341 | 68.6 | 83.4 | 1.738 | 1.735 | 1.737 | 0.003 | |
| DMDPS-DCPD | 26.82 | 356 | 72.4 | 81.2 | 1.744 | 1.740 | 1.743 | 0.004 | |
| m-DMB-DCDPS | 27.06 | 346 | 78.8 | 85.4 | 1.724 | 1.721 | 1.723 | 0.003 | |
| p-DMB-DCDPS | 27.06 | 349 | 78.0 | 84.3 | 1.727 | 1.724 | 1.726 | 0.003 | |
| Polymers | 1310 n | 1310 nm | | | 1550 nm | | | | |
| | n _{TE} | n _{TM} | n _{AV} | Δn | n _{TE} | n _{TM} | n _{AV} | Δn | |
| DMDPS-DCPM | 1.706 | 1.702 | 1.705 | 0.004 | 1.701 | 1.697 | 1.700 | 0.004 | |
| DMDPS-DCPD | 1.708 | 1.703 | 1.706 | 0.005 | 1.703 | 1.698 | 1.701 | 0.005 | |

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.

that the heterocycles moiety endows high polarizability and high refractive index compared to aliphatic chain and phenyl ring. Fig. 8 is the wavelength-dependent refractive indices of polymers at 633, 1310 and 1550 nm, as shown in Fig. 8, the n_{av} at 1310 and 1550 nm was near 1.7, the dispersion of n_{av} with wavelength is well.



Fig. 7. UV–Vis spectra of polymers' (DMDPS-DCPM, DCPD) films.



Fig. 8. The wavelength-dependent refractive indices of polymers at 633, 1310 and 1550 nm.

Table 5

Solubility behavior of polymers.

| Solvents | Polymers | | | | |
|----------------------------|------------|------------|--|--|--|
| | DMDPS-DCPM | DMPDS-DCPD | | | |
| concentrated sulfuric acid | ++ | ++ | | | |
| formic acid | _ | - | | | |
| NMP | ++ | ++ | | | |
| DMF | ++ | ++ | | | |
| pyridine | +- | _ | | | |
| acetone | _ | - | | | |
| chloroform | +- | - | | | |
| DMSO | ++ | ++ | | | |
| 1, 4-Dioxane | - | - | | | |
| toluene | _ | - | | | |
| cyclohexanone | - | - | | | |
| Phenol + tetrachloroethane | + | +- | | | |

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

The PASSs show lower Δn in the range of 0.003–0.004 at 633 nm than aromatic PA and PI (0.006–0.0076) [32]. These relatively low Δn values of the polymers can be attributed to the highly flexible phenyl-sulfanyl-phenyl linkages in the main chains. All of the results suggest that the introduction of high content of thioether and heterocyclic units is an effective way to endow PASSs with a high refractive index.

3.6. Solubility experiments

Through the solubility experiments (Table 5), we found that the polymers were soluble in NMP, DMF, DMSO and concentrated sulfuric acid at room temperature. Thus, they can be processed using following methods, such as electro-spinning and solution casting. As listed in Table 5, these polymers were not soluble in toluene, formic acid and acetone and so on. Thus, these polymers showed good balance between the solubility and corrosion resistance.

4. Conclusions

Aromatic dithiol (DMDPS) with a sulfone unit and high sulfur content was synthesized to develop high-n PASSs. The PASSs were prepared by the nucleaphilitic polycondensation of DCPM and DCPD with DMDPS. The resultant PASSs showed good thermal stabilities, such as T_{gs} higher than 190 °C, a $T_{5\%}$ around 370 °C and mechanical properties. The PASSs exhibited good optical performance. The transmittance of PASSs films with about 11 µm thickness is around 81% at 450 nm. The polymers exhibited refractive indices about 1.74 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 DMDPS is more facile and affordable than the other monomers reported for sulfur containing polymers. Thus, the PASSs can be good candidates as components

for advanced optical device applications, such as optical wave guides for CMOS image sensor.

Acknowledgment

This work was supported by research grants from the Youth Fund of Sichuan University (Grant No.: 2012SCU11009).

Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.polymer.2012.12.008.

References

- [1] Geiger F, Stoldt M, Schweizer H, Bauerle P, Umbach E. Advan Mater 1993;5: 922–5.
- 2] Regolini JL, Benoit D, Morin P. Microelectron Reliab 2007;47:739-42.
- [3] Kunugi Y, Miller L, Maki T, Canavesi A. Chem Mater 1997;9:1061-2.
- [4] Kitamura K, Okada K, Fujita N, Nagasaka Y, Ueda M, Sekimoto Y, et al. Jpn J Appl Phys 2004;43:5840–4.
- [5] Yang CJ, Jenekhe SA. Chem Mater 1995;7:1276-85.
- [6] Lu CL, Cui ZC, Wang YX, Yang B, Shen JC. J Appl Polym Sci 2003;89:2426-30.
- [7] Nebioglu A, Leon JA, Khudyakov IV. Ind Eng Chem Res 2008;47:2155–9.
- [8] Terraza CA, Liu JG, Nakamura Y, Shibasaki Y, Ando S. J Polym Sci Part A Polym Chem 2008;46:1510–20.
- [9] Seesukphronrarak S, Kawasaki S, Kobori K, Takata T. J Polym Sci Part A Polym Chem 2007;45:3073–82.
- [10] Zhang G, Hu JJ, Yang HW, Wang XJ, Long SR, Yang J. Polym Intern 2012;61: 800–9.
- [11] Zhang G, Li DS, Huang GS, Wang XJ, Long SR, Yang J. React Funct Polym 2011; 71:775–81.
- [12] Liou GS, Lin PH, Yen HJ, Yu YY, Chen WC. J Polym Sci Part A Polym Chem 2010; 48:1433–40.
- [13] Liu JG, Nakamura Y, Terraza CA, Shibasaki Y, Ando S, Ueda M. Macromol Chem Phys 2008;209:195–203.
- [14] Fukuzaki N, Higashihara T, Ando S, Ueda M. Macromolecules 2010;43: 1836–43.
- [15] You NH, Nakamura Y, Suzuki Y, Higashihara T, Ando S, Ueda M. J Polym Sci Part A Polym Chem 2009;47:4886–94.
- [16] You NH, Higashihara T, Oishi Y, Ando S, Ueda M. Macromolecules 2010;43: 4613-5.
- [17] Shockravi A, Javadi A, Kamali M, Hajavi S. J Appl Polym Sci 2012;125:1521-9.
 [18] Suzuki Y, Liu JG, Nakamura Y, Shibasaki Y, Ando S, Ueda M. Polym J 2008;40: 414-20.
- [19] Yang J. PAS resin and its application. China: Chemical Industry Press; 2006.
- [19] Yang J. FAS resin and its application. China: Chemical industry Fress, 200 [20] Xu SX, Yang J. Long SR, Chen YR, Li GX. Polym Bull 2005;54:251–61.
- [20] Au SA, Faing J, Eong SK, Citch TR, El GA, Folym Bull 2009, 54:251–01.
 [21] Liu Y, Bhatnagar A, Ji Q, Riffile JS, McGrath JE, Geibei JF, et al. Polymer 2000;41: 5137–46.
- [22] Wang HD, Yang J, Long SR, Wang XJ, Yang Z, Li GX. Polym Degrad Stab 2004; 83:229–35.
- [23] Yang J, Wang HD, Xu SX, Li GX, Huang YJ. J Polym Res 2005;12:317-23.
- [24] Matsumura S, Kihara N, Takata T. J Appl Polym Sci 2004;92:1869-74.
- [25] Kawasaki S, Yamada M, Kobori K, Jin F, Kondo Y, Hayashi H, et al. Macromolecules 2007;40:5284–9.
- [26] Speight JG. Lange's handbook of chemistry. 16th ed. McGraw-Hill; 2005.
- [27] Ding Y, Hay AS. Macromolecules 1996;29:6386–92.
- [28] Yang J, Zhang G, Long SR, Wang XJ. CN patent 101429279; 2009.
- [29] Liu JG, Nakamura Y, Shibasaki Y, Ando S, Ueda M. Polym J 2007;39:543-50.
- [30] Okutsu Rie, Suzuki Yasuo, Ando Sinji, Ueda Mitsuru. Macromolecules 2008; 41:6165-8.
- [31] Suzuki Y, Higashihara T, Ando S, Ueda M. Macromolecules 2012;45:3402-8.
- [32] You NH, Higashihara T, Ando S, Ueda M. J Polym Sci Part A Polym Chem 2010; 48:656–62.