A facile approach towards optically isotropic, colorless, and thermoplastic polyimidothioethers with high refractive index

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A series of novel optically isotropic, transparent, and thermoplastic polyimidothioethers (PITEs) with high refractive index were prepared *via* Michael polyaddition from commercially available bismaleimides and dithiols. These polymers were readily soluble in various organic solvents and showed useful thermal stability associated with high glass-transition temperatures. In addition to the useful thermal processing window up to 190 °C, these PITEs also exhibit a high refractive index and ultra-low birefringence of 1.6763 and 0.0002, respectively.

Introduction

High refractive index polymers have been widely proposed in recent years for their potential in advanced optoelectronic applications.[1-4] In addition to the basic parameter of the refractive index, other parameters such as birefringence, Abbe's number, optical transparency, processability, and thermal stability are often taken into consideration. Regarding the encapsulants for organic light-emitting diodes (OLEDs),[2] commercial applications require materials with high refractive index, low birefringence, high optical transparency, and a long-term ultraviolet light and thermal stability. Furthermore, the melt-processable polymers will be in high demand for the future LEDs encapsulation due to the advantages of molding techniques. Therefore, to achieve a good combination of the above-mentioned parameters is a crucial and on-going issue.[5] Recently, systematic work by Ueda *et al.* revealed the influence of sulfur groups and related structures on the refractive index and optical dispersion of the resulted polyimides.[6-9] The incorporation of a sulfur atom into polymer systems could enhance the refractive index and optical transparency due to its large atomic refraction.[10-12] It is also well known that the thermoset polyimides derived from bismaleimides (BMIs) exhibit excellent thermal and mechanical properties, thus making them extremely popular for advanced composites and electronics. However, thermoplastic BMI-type optical polyimides have so far not been the subject of detailed investigation. Therefore, the development of highly transparent thermoplastics based on BMIs for optoelectronic applications is a challenging and interesting project. In the present study we describe a facile synthesis of optical transparent and thermoplastic polyimidothioethers (PITEs) with high refractive index and ultra-low birefringence values from BMI-type monomers which are commercially available and much simpler than the other starting materials derived from multi-step procedure approaches.

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Experimental section

Materials

4,4′-(Diaminodiphenylsulfide)bismaleimide (**S–BMI**)[13] (mp: 187 °C) and 4,4′-(diaminodiphenylsulfone)bismaleimide (**SO$_2$–BMI**)[14] (mp: 252 °C) were readily synthesized by reacting the respective diamines with maleic anhydride according to the reported procedure. Commercially available monomers such as 4,4′-(diaminodiphenylmethane)bismaleimide (**CH$_2$–BMI**), 1,2-ethanedithiol (**DT–C$_2$**) and 4,4′-thiobisbenzenethiol (**DT–S**) were used as received. All other reagents were used as received from commercial sources.

Polymer synthesis

The synthesis of PITE **SSO$_2$–C$_2$** was used as an example to illustrate the general synthetic route used to produce the PITEs. The bismaleimides **S–BMI** (0.872 g; 2.3 mmol) and **SO$_2$–BMI** (0.946 g; 2.3 mmol) were dissolved in 11.5 mL of *m*-cresol, **DT–C$_2$** (0.397 ml; 4.6 mmol) was added to the mixture and stirred for 10 min. Then, 23 μL of triethylamine were added slowly and the polymerization proceeded at room temperature for 4 h. During the polymerization, the solution viscosity increased gradually, and the obtained polymer solution was then poured slowly into 300 mL acidified methanol giving rise to a white fiber-like precipitate which was collected by filtration, washed thoroughly with methanol, and dried under vacuum at 100 °C. Precipitations from DMAc into methanol were carried out twice for further purification. The inherent viscosity of the obtained PITE **SSO$_2$–C$_2$** was 0.34 dL g^{-1} (measured at a concentration of 0.5 g dL^{-1} in DMAc at 30 °C). ^{1}H NMR (DMSO-d$_6$, δ, ppm): 2.63–3.63 (m, 6H), 4.14–4.26 (m, 2H), 7.29 (d, 2H), 7.46 (d, 2H), 7.57 (d, 2H), 8.12 (d, 2H). ^{13}C NMR (DMSO-d$_6$, δ, ppm): 30.7, 30.9, 34.5, 36.2, 37.5, 128.1, 128.4, 131.1, 131.5, 134.8, 136.9, 140.2, 173.8, 174.1, 175.6, 175.9. Anal. Calcd. (%) For (C$_{22}$H$_{18}$N$_2$O$_5$S$_3$)$_n$ (486.59)$_n$: C, 54.30; H, 3.73; N, 5.76; S, 19.77. Found: C, 53.49; H, 4.08; N, 6.25; S, 19.25. The other PITEs were prepared from the corresponding bismaleimide and dithiol by similar procedure as described above.
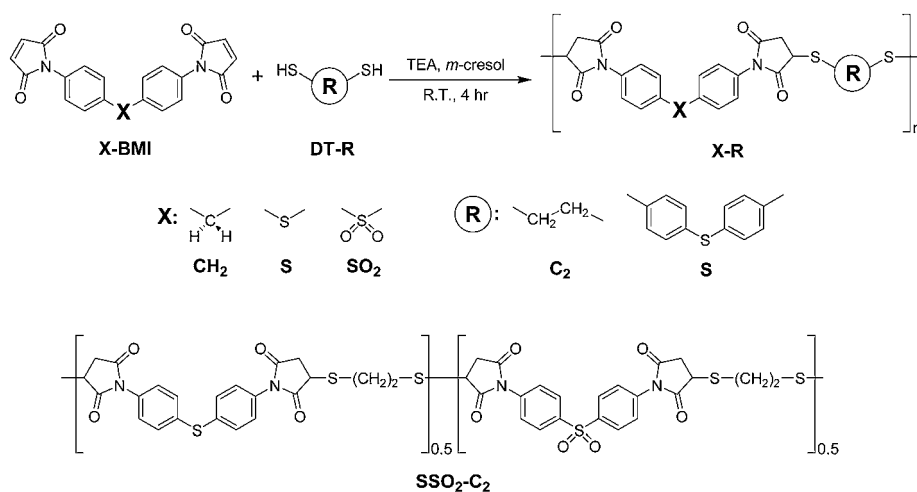
Scheme 1 Michael polyaddition of polyimidothioethers.

Preparation of the PITE Films

NMP solutions of the PITEs were drop-coated onto fused silica (amorphous SiO₂) or glass substrates and dried at 80 °C for 6 h, and then 150 °C for 8 h under vacuum. Finally, PITE films with thicknesses of 20 μm were obtained and used for solubility tests, refractive index, transmittance, and thermal analyses.

Measurements

Elemental analyses were run using a Heraeus VarioEL-III CHNS elemental analyzer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-AL 300 MHz spectrometer in DMSO-d₆, using tetramethylsilane as an internal reference, and peak multiplicity was reported as follows: d, doublet; m, multiplet. The inherent viscosities were determined at 0.5 g dL^{-1} concentration using a Tamson TV-2000 viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a Perkin-nElmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm³ min^{-1}) at a heating rate of 20 °C min^{-1}. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 10 °C min^{-1} in flowing nitrogen (20 cm³ min^{-1}). Ultraviolet-visible (UV-vis) spectra of the polymer films were recorded on a Hitachi U-4100 UV-vis-NIR spectrophotometer. The film thickness, in-plane (n_{TE}), and out-of plane (n_{TM}) refractive indices of the films formed on the silica substrates were measured using a prism coupler (Metricon, PC-2000) at wavelengths of 632.8, 845, and 1324 nm at room temperature. The mean refractive indices (n_{av}) were calculated as $n_{av}^2 = (2n_{TE}^2 + n_{TM}^2)/3$. The in-plane/out-of-plane birefringence (Δn) was calculated as $\Delta n = n_{TE} - n_{TM}$. The refractive indices at infinite wavelength (n_{∞}) were estimated from the curve fitting using the simplified Cauchy's formula, $n_{\lambda} = n_{\infty} + (D/\lambda^2)$, where n_{∞} is the estimated refractive index at infinite wavelength and D is the coefficient of wavelength dispersion.

Results and discussion

Polymer synthesis

According to the Michael polyaddition technique described by Crivello,[15] a series of new PITEs (except CH₂–C₂[16] and S–S[17])

with high refractive index and optical transparency were synthesized from the readily obtainable BMIs and dithiols (Scheme 1). The Michael polyaddition was chosen as it is an attractive reaction for the synthesis of step-growth polymers with high molecular weights from BMIs and dithiols, and the reaction was carried out at room temperature for 4 h in the presence of a catalytic amount of triethylamine as a basic catalyst in m-cresol. The polymerization proceeded homogeneously throughout the procedure and afforded clear, viscous polymer solutions in high yields with no evolution of volatile molecules. All the polymers precipitated in a white fiber-like form when slowly pouring the resulting polymer solutions into acidified methanol. The obtained PITEs had inherent viscosities in the range 0.32–0.50 dL g^{-1} (Table 1). Elemental analysis and NMR spectroscopic techniques were used to identify structures of PITEs. Fig. 1 shows the NMR spectra of PITEs in DMSO-d₆, where the spectrum of copolymer SSO₂–C₂ agreed well with the corresponding individual molecular structure of S–C₂ and SO₂–C₂. Furthermore, the elemental composition of the polymer was confirmed by elemental analysis.

Basic characterization

The PITEs were readily soluble in polar aprotic organic solvents such as N-methyl-2-pyrrolidinone (NMP), N,N-dimethylaceta-mide (DMAc), N,N-dimethylformamide (DMF), and dimethyl

Table 1 Solubility behavior of polyimidothioethers

Code	Solubility in various solvents[a]						
	NMP	DMAc	DMF	DMSO	m–Cresol	THF	CHCl₃
CH₂–C₂	++	++	++	++	++	−	−
CH₂–S	++	++	++	++	++	−	−
S–C₂	++	++	++	++	++	−	−
S–S	++	++	++	++	++	−	−
SO₂–C₂	++	++	++	++	++	−	−
SO₂–S	++	++	++	++	++	−	−
SSO₂–C₂	++	++	++	++	++	−	−

[a] The solubility was determined with a 50 mg sample in 1 mL of a solvent. ++ = soluble at room temperature; − = insoluble even on heating.
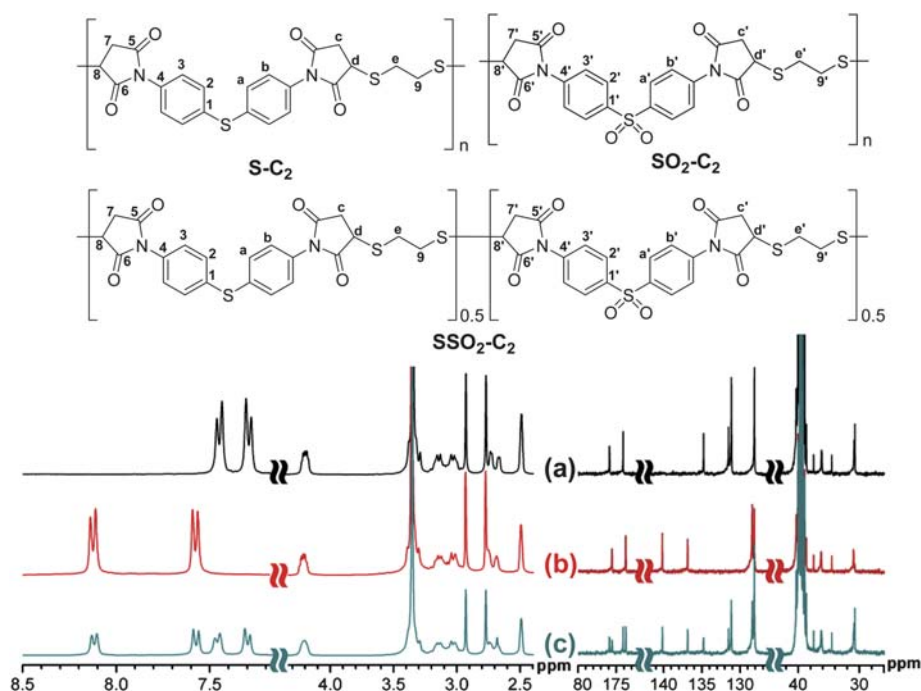
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Fig. 1 ^{1}H NMR (left) and ^{13}C NMR (right) spectra of PITE (a) **S–C$_2$** (b) **SO$_2$–C$_2$**, and (c) **SSO$_2$–C$_2$** in DMSO-d$_6$.

sulfoxide (DMSO), and the results are listed in Table 1. Furthermore, the PITEs could be solvent cast into flexible, transparent, and tough films (Fig. 2). Therefore, these novel high performance thin films could be prepared by spin-coating or inkjet-printing processes for optical practical applications.

Thermal properties

The thermal properties of PITEs were examined by TGA and DSC, and the results are summarized in Table 2. All the prepared PITEs exhibited good thermal stability with insignificant weight loss up to 340 °C under nitrogen atmosphere. The glass-transition temperatures (T_g) of PITEs could be easily measured in the DSC thermograms; they were observed in the range 151–189 °C,

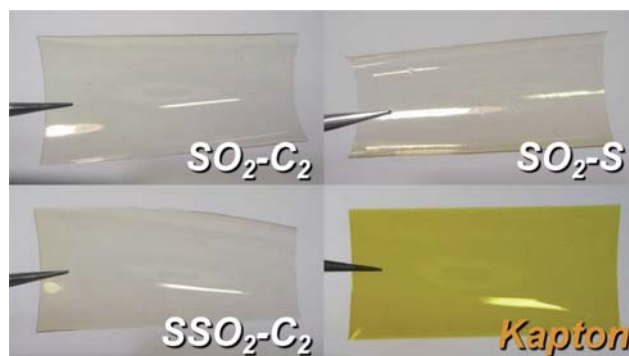**Fig. 2** Flexible transparent representative PITE and Kapton films (thickness ≈ 20 µm).

Table 2 Properties of polyimidothioethers

Index	η_{inh}[a]/dL g^{-1}	Thermal properties/°C			Optical properties				
		T_g[b]	T_d[c]	ΔT[d]	λ_0[e]/nm	n_{av}[f]	Δn[g]	n_∞[h]	V_{NIR}[i]
CH$_2$–C$_2$	0.39	159	338	169	328	1.6243	0.0013	1.5995	32.17
CH$_2$–S	0.48	169	347	178	353	1.6403	0.0006	1.6089	25.86
S–C$_2$	0.32	151	342	191	333	1.6476	0.0018	1.6169	25.27
S–S	0.50	167	358	191	351	1.6763	0.0002	1.6384	20.10
SO$_2$–C$_2$	0.37	180	359	179	320	1.6271	0.0011	1.5994	30.01
SO$_2$–S	0.43	189	367	178	353	1.6546	0.0030	1.6227	26.31
SSO$_2$–C$_2$	0.34	163	350	187	331	1.6398	0.0008	1.6087	26.27
Kapton					457	1.6873	0.0770	1.6395	18.23

[a] Measured at a polymer concentration of 0.5 g dL^{-1} in DMAc at 30 °C. [b] Midpoint temperature of baseline shift on the heating DSC trace. [c] Initial decomposition temperature recorded by TGA. [d] The melting-process window (ΔT) was calculated as $\Delta T = T_d - T_g$. [e] The cutoff wavelength (λ_0) from the UV-vis transmission spectra of polymer films (thickness ≈ 20 µm). [f] The average refractive indices measured at 632.8 nm, which were calculated as $n_{av}^2 = (2n_{TE}^2 + n_{TM}^2)/3$. [g] The in-plane/out-of-plane birefringence (Δn) was calculated as $\Delta n = n_{TE} - n_{TM}$. [h] The refractive indices at infinite wavelength (n_∞) was estimated from the curve fitting using the simplified Cauchy's formula. [i] Abbe's number is given by $V_{NIR} = (n_{845} - 1)/(n_{633} - n_{1324})$.
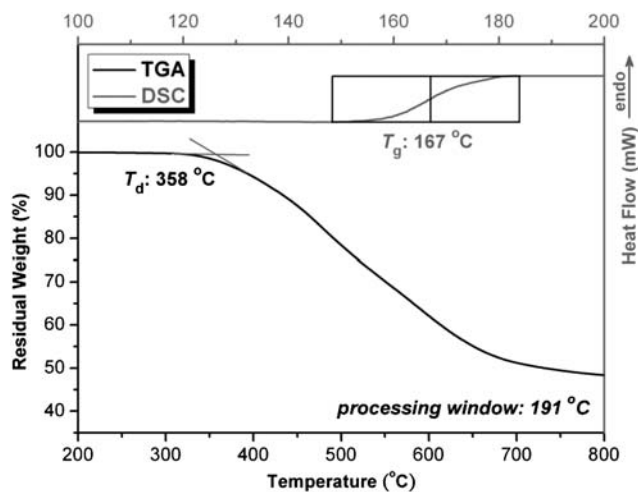
Fig. 3 TGA and DSC traces of PITE **S–S** measured under nitrogen atmosphere.

depending upon the stiffness of the polymer chain. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms, which supports the amorphous nature of these PITEs. Typical TGA and DSC curves of the representative PITE **S–S** under nitrogen atmospheres were shown in Fig. 3. The melting-process window (ΔT) termed as the region between the glass-transition temperatures (T_g) and the initial decomposition temperature (T_d) for these materials were in the range 169–191 °C, exhibiting great potential for injection molding processes.

Optical properties

The UV-visible (UV-vis) absorption spectra of PITE films (thickness: 20 μm) are shown in Fig. 4. All of the polymer films exhibited high transparency (>85%) in the visible region (wavelengths: 450–800 nm). The coefficients of n_{av}, Δn, n_∞, and V_{NIR} are presented in Table 1. The wavelength dispersion of refractive indices are depicted in Fig. 5 with a fitted curve using the simplified Cauchy's equation.[17] The values of n_{av} and Δn having potential for optical applications are 1.6763 and 0.0002 for PITE **S–S**, respectively, whereas the (n_{av}, Δn) values for Kapton are

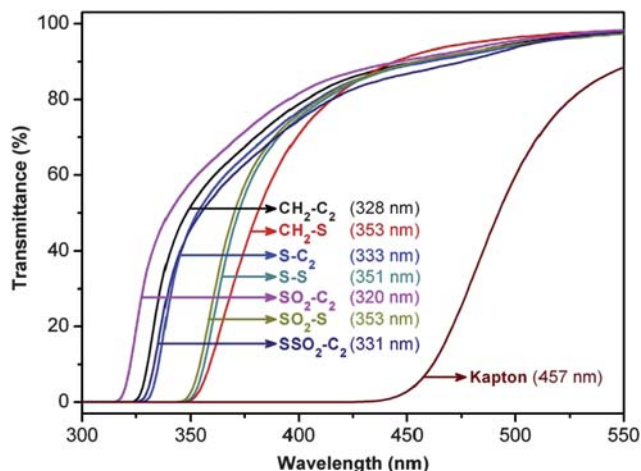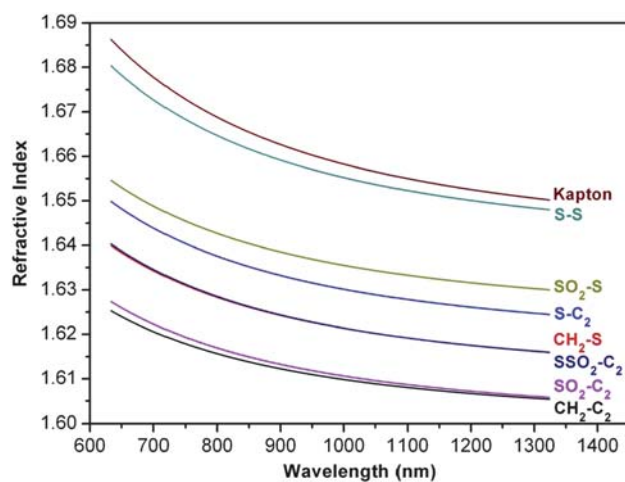**Fig. 4** Optical transmission spectra of PITEs (thickness ≈ 20 μm).

Fig. 5 Wavelength dispersion of the experimental refractive indices of PITEs. The experimental refractive indices were measured at three wavelengths (632.8, 845, and 1324 nm), and the dispersion is fitted by the simplified Cauchy's formula.

(1.6873, 0.0770). It is a notable result to the best of our knowledge that these new PITEs revealed optically isotropic characteristic with the ultra-lowest birefringence values in the range of 0.0002 to 0.0030 compared with other high refractive index polyimides.[5] Because of the combination of low optical wavelength dispersion, higher molecular refraction, and larger volume of the sulfonyl group comparing to the sulfide group,[18] and the concept of the material design and structure–property relationship which support present significant optical performance of these polymer materials were also reported.[5,19] Therefore, PITE **SO₂–C₂** showed higher V_{NIR}, lower Δn and n_{av} values, and better optical transparency compared with PITE **S–C₂**. In addition, the copolymer of **SSO₂–C₂** could also be prepared from SO₂– and S–BMIs to obtain polyimides with high optical transparency and to tune the optical properties such as n_{av}, V_{NIR}, and Δn values for the requirements of applications.

Conclusion

Using this facile approach, a series of thermoplastic PITEs could be readily prepared from the BMIs and dithiols *via* Michael polyaddition. The obtained polymers showed a useful thermal processing window up to 190 °C. All of the amorphous polymers exhibited high optical transparency with cutoff wavelength in the range 323–353 nm, and revealed high refractive indices and Abbe's numbers, in the range 1.6763 to 1.6243 and 20.1 to 32.2, respectively. Moreover, the lowest birefringence of 0.0002 could also be achieved. Thus, these novel optically isotropic thermoplastic PITEs exhibiting well-balanced optical properties are promising candidates for optical waveguide or encapsulant materials in advanced optical applications for both solution casting and injection molding techniques.

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References and Notes

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