

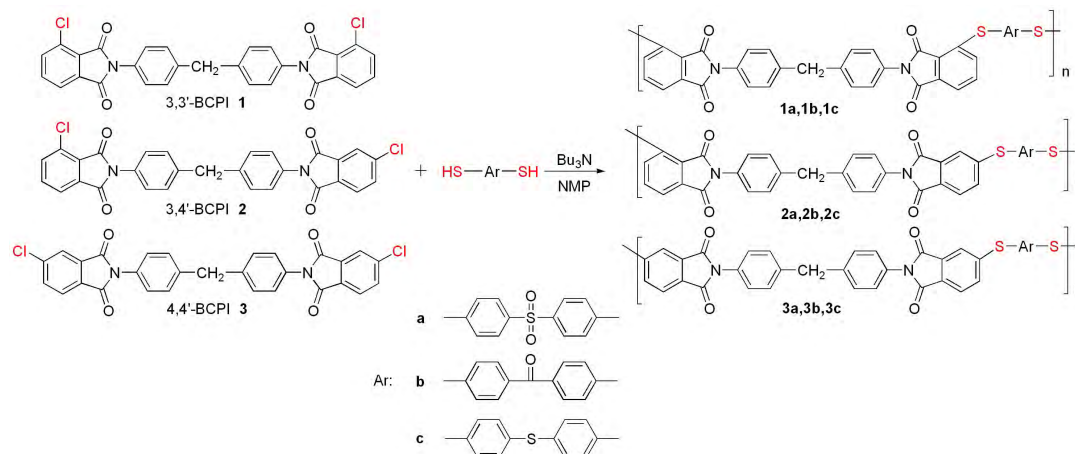
Preparation, characterization, and properties of poly(thioether imide)s from isomeric bis(chlorophthalimide)s and bithiophenols

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Introduction

The last few decades have seen an enormous proliferation of research into aromatic polyimides (PIs) which have a unique property combination, such as outstanding thermal stability, excellent mechanical properties, low dielectric constant, etc.. These characteristics make them useful for special applications in aerospace field, microelectronic area, photonics industry, and national defense industry.^[1-3] However, the main obstacles on the way to applications of PI materials are their poor solubility and high melt viscosity for solution or melt processing. Interestingly, isomeric polyimides, which possess geometrically asymmetric and noncoplanar moieties, were found to be endowed with good solubility, low melt viscosity, and comparable thermal and mechanical properties.^[4] Very recently, our group has been focused on isomeric poly(thioether imide)s (PTIs) and found that the introduction of isomeric moieties and flexible thioether linkage into polymer main chain could be an effective way to obtain good solubility and melt processability without sacrificing other excellent properties.^[5-8] Here, we synthesized a series of isomeric PTIs with a high content of flexible linkages in the polymer backbone based on the aromatic nucleophilic substitution of the isomeric bis(chlorophthalimide)s (BCPIs) and bithiophenols with sulfone, ketone and sulphur structural unit, respectively. The thermal, mechanical, and rheological properties of isomeric PTIs were investigated.



Scheme 1. Synthesis of isomeric PTIs from bithiophenols and isomeric BCPIs.

Results and discussion

Isomeric BCPIs (**1-3**) were prepared in laboratory according to our previous work.^[8] As shown in **Scheme 1**, a series of isomeric PTIs were synthesized from the aromatic nucleophilic substitution of bithiophenols and isomeric BCPIs in NMP using tributylamine as catalyst at 160 °C. As a result of the high nucleophilic reactivity of bithiophenols, the inherent viscosities of isomeric PTIs were between 0.39 and 0.88 dL/g, indicating the formation of high molecular weight polymers.

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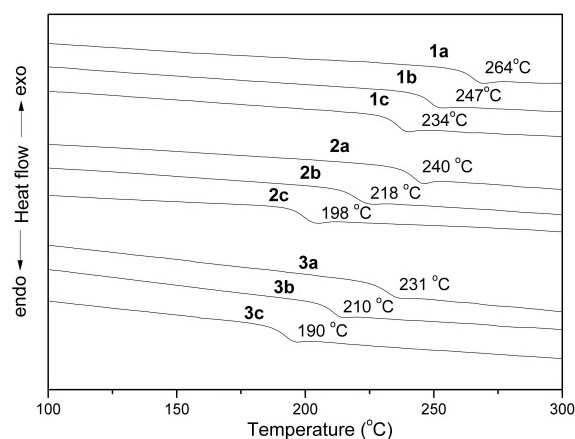


Figure 1. DSC curves of isomeric PTIs in nitrogen at 20 °C/min rate.

As shown in **Table 1**, for a given BCPI isomer, the T_g s of isomeric PTIs from three bisthiophenols increased in the order of **c** < **b** < **a** (**Fig. 1**), which could be ascribed to the rigidity of the polymer according to the order containing the following linkage: **c** (sulphur) < **b** (ketone) < **a** (sulfone). Furthermore, for a given bisthiophenol, the T_g s of the PTIs from three BCPI isomers increased in the order of 4,4'-BCPI < 3,4'-BCPI < 3,3'-BCPI. Higher T_g values were caused by more difficult chain rotation of polymers, so this phenomenon could mainly be attributed to the rotational freedom around the carbon-sulfur bonds of 3-substituted phthalimide, which is partially restricted by the steric effect of the ortho-carbonyl substituent, leading to the higher T_g value.^[6,7]

Table 1. Thermal and mechanical properties of isomeric PTIs.

PTIs	η_{inh} (dL/g) ^a	T_g (°C)		$T_{5\%}$ (°C) ^d		Char Yield (%) ^e	Strength at Break (MPa)	Tensile Moduli (GPa)	Elongation at Break (%)
		DSC ^b	DMTA ^c	N ₂	Air				
1a	0.57	264	261	441	472	54.46	121	2.6	8.0
1b	0.86	247	242	485	513	60.63	117	2.5	9.3
1c	0.88	234	229	474	509	59.07	106	2.3	10.1
2a	0.44	240	238	457	475	56.53	113	2.5	8.2
2b	0.60	218	209	491	518	60.97	103	2.4	10.3
2c	0.41	198	201	483	511	59.68	96	2.3	11.4
3a	0.39	231	230	479	477	57.06	103	2.4	9.4
3b	0.46	210	208	508	520	61.39	98	2.3	10.7
3c	0.44	190	196	492	514	60.38	91	2.1	11.9

^a Inherent viscosity measured with 0.5 g/dL at 30 °C in NMP.

^b Obtained from DSC at a heating rate of 20 °C/min in nitrogen.

^c Obtained from DMTA at heating rate of 3 °C/min at 1Hz.

^d $T_{5\%}$ =5% weight loss temperature (obtained by TGA at a heating rate of 10 °C/min in nitrogen or air).

^e Residual weight (%) at 800 °C in nitrogen.

As summarized in **Table 1**, the thermal decomposition and stability of the PTIs were evaluated by TGA. The $T_{5\%}$ values of PTIs in air stayed in the range 472-520 °C, which were slightly higher than that in nitrogen 441-508 °C. Furthermore, the thermal oxidative resistance of polymers can also be testified by the char yield. For a given BCPI isomer, the char yield of isomeric PTIs increased in the order of **a** < **c** < **b**, the high char yield indicated good thermal oxidative

resistance.^[6] We also found that the $T_{5\%}$ values increased in the order of 3,3'-BCPI < 3,4'-BCPI < 4,4'-BCPI. The inferior thermal stability of the PTIs derived from 3,3'-BCPI may be ascribed to the structural stress caused by nonplanar configuration of the 3-substituted phthalimide moiety.^[5]

The mechanical properties of PTIs films were listed in **Table 1**. The PTI films about 20 μm thickness exhibited moderate mechanical properties with tensile strength of 91-121 MPa, elongation at break of 8.0-11.9 %, and tensile moduli of 2.1-2.6 MPa.

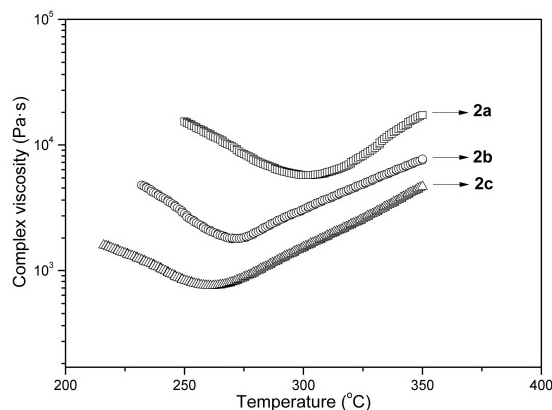


Figure 2. Rheological behavior of isomeric PTIs (**2a-2c**) as a function of temperature.

The rheological properties of isomeric PTIs having very close molecular weight with inherent viscosities about 0.40 dL/g were carefully obtained and studied in detail. For a given bithiophenol, the minimum complex viscosity of isomeric PTIs from three BCPI isomers decreased in the order of 3,3'-BCPI > 4,4'-BCPI > 3,4'-BCPI. This rheological behavior of isomeric PTIs was attributed to the geometrically asymmetric and noncoplanar structure of 3,4'-BCPI, which hindered the packing of the macromolecule and weakened the intermolecular interaction, whereas the 4,4'-BCPI and 3,3'-BCPI are symmetric.^[8] The rigid chain structure of PTIs from 3,3'-BCPI makes the melt viscosity larger than PTIs from 4,4'-BCPI. PTIs from 3,4'-BCPI possesses more rigid chains than PTIs from 4,4'-BCPI, but its asymmetrical structure contributes to the much weaker intermolecular interaction so the minimum melt viscosity is obtained.^[9] **Fig. 2** shows the rheological behavior of isomeric PTIs (**2a-2c**), as for a given BCPI isomer, the minimum complex viscosity of isomeric PTIs from three bithiophenols decreased in the order of **a** (sulfone) > **b** (ketone) > **c** (sulphur), which could be ascribed to the flexibility of the polymer resulted from different linkages.

As presented in **Fig. 3**, the melt stability of PTIs (**2c**) was also characterized by the isothermal viscosity sweeps. The range of the complex viscosity at 280 °C was below 1000 Pa·s and maintained for a long period of time about 60 min, which showed good melt stability and processability. This complex viscosity range was appropriate for extrusion and injecting molding.^[5]

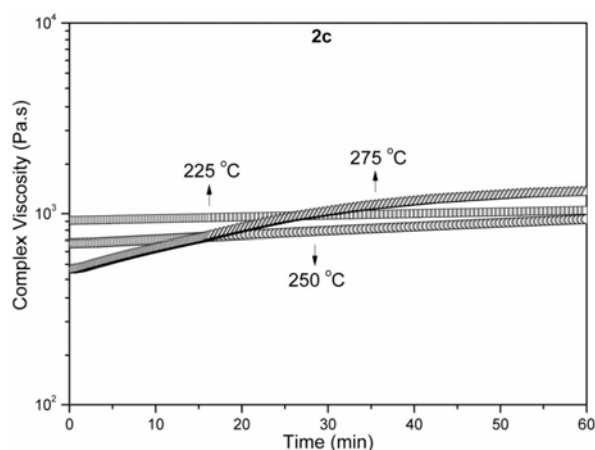


Figure 3. The complex viscosity of isomeric PTIs (**2c**) at different temperatures.

Conclusions

A series of isomeric PTIs were successfully obtained from isomeric BCPIs and bithiophenols. Several important conclusions are summarized as follows:

(1) For a given bithiophenol, the T_g s of isomeric PTIs from three BCPI isomers increased in the order of 4,4'-BCPI < 3,4'-BCPI < 3,3'-BCPI, while the $T_{5\%}$ values increased in the order of 3,3'-BCPI < 3,4'-BCPI < 4,4'-BCPI.

(2) For a given BCPI, the T_g s of isomeric PTIs from three bithiophenols increased in the order of **c** (sulphur) < **b** (ketone) < **a** (sulfone).

(3) For a given BCPI, the minimum complex viscosity decreased in the order of **a** (sulfone) > **b** (ketone) > **c** (sulphur). For a given bithiophenol, the minimum complex viscosity decreased in the order of 3,3'-BCPI > 4,4'-BCPI > 3,4'-BCPI.

These data demonstrated that this kind of novel isomeric PTIs endowed with moderate mechanical property, moderate T_g s, good thermal stability and processability can be served as high performance engineering thermoplastic materials where the T_g and melt viscosity can be tailored by controlling different BCPI isomers and bithiophenols.

References

- [1] Sroog, C. E. *J. Polym. Sci. Macromol. Rev.* **1976**, *11*, 161.
- [2] Sroog, C. E. *Prog. Polym. Sci.* **1991**, *16*, 561.
- [3] Hasegawa, M.; Horie, K. *Prog. Polym. Sci.* **2001**, *26*, 259.
- [4] Ding, M. X. *Prog. Polym. Sci.* **2007**, *32*, 623.
- [5] Wei, H. B.; Pei, X. L.; Fang, X. Z. *J Polym. Sci. Part A Polym. Chem.* **2011**, *49*, 2484.
- [6] Wei, H. B.; Fang, X. Z.; Han, Y.; Hu, B. L.; Yan Q. *Eur. Polym. J.* **2010**, *46*, 246.
- [7] Wei, H. B.; Wu, X. S.; Hu, B. L.; Fang, X. Z. *Polym. Adv. Technol.* **2011**, *22*, 2488.
- [8] Liu, J. T.; Chen, G. F.; Fang, X. Z. *Polym. Adv. Technol.* **2014**, *25*, 329.
- [9] Li, Q. X.; Fang, X. Z.; Wang, Z.; Gao, L. X.; Ding, M. X. *J Polym. Sci. Part A Polym. Chem.* **2003**, *41*, 3249.