Comparative Studies on Melt Processable Polyimides Derived from 3,4'-Oxydiphthalic Anhydride and 3,4'-Thioetherdiphthalic Anhydreide

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Introduction

The melt stability and thermal properties of thermoplastic polyimides(TPIs) are closely related to their structures. Recent studies showed that it is possible to develop high performance TPIs by use of isomeric polyimides(PIs) derived from dianhydride isomers. So study on the structure-property relations of isomeric TPIs plays an important role for the development of new type TPIs. At present, 2,3,3′,4′-oxydiphthalic anhydride (3,4′-ODPA) and 2,3,3′,4′-thioetherdiphthalic anhydride (3,4′-TDPA) are the two most important common bridged isomeric dianhydrides. Based on the two dianhydrides, two similar molecular weight thermoplastic polyimides were synthesized [Scheme 1], and their melt processability and thermal properties were comparatively studied. In order to better understand the structure-property relations, the corresponding model compounds were also prepared [Scheme 2], and their experimental and computational simulation data were used to explain the performance differences of corresponding polyimides.

Results and Discussion

As shown in Table 1, the close molecular weight polyimides derived from 3,4′-ODPA, 3,4′-TDPA and ODA, were successfully obtained. **PI-1** had T_g value of about 15 ^{o}C higher than that of **PI-2**, and the minimum complex viscosity of **PI-2** was lower about an order of magnitude than that of **PI-1** from rheology curve [Figure 1(a)]. Furthermore, **PI-2** showed better melt stability than **PI-1** [Figure 1(b)], and the melt index (MI) at 330 ^{o}C of **PI-1** was one-tenth of **PI-2**'s MI. These results revealed that **PI-2** had better melt processability and wider processable window than PI-1. Moreover, the **PI-2** exhibited better thermo-oxidative stability at the temperature below 430 °C [Figure 2]. According to the computational simulation data of the corresponding model compounds [Table 2], model compound **2** showed the smaller electronic density and energy gap than that of **1**.

Conclusions

Two thermoplastic polyimides with similar Mw from 3,4′-ODPA and 3,4′-TDPA with ODA were prepared by a one-step, high-temperature solution polycondensation method. It was found that **PI-2** showed much better melt processability and wider processable window than **PI-1**, which might be related to unique chain flexibility of **PI-2** having the thioether unit. The 5% weight loss temperatures in both air and nitrogen atmospheres of the two polyimides were close, while the long-term thermo-oxidative stability of **PI-2** at the temperatures below 430 °C was better than that of **PI-1**. The thermal stability difference of polyimides could be explained by the computational simulation data of the corresponding model compounds.

Reference

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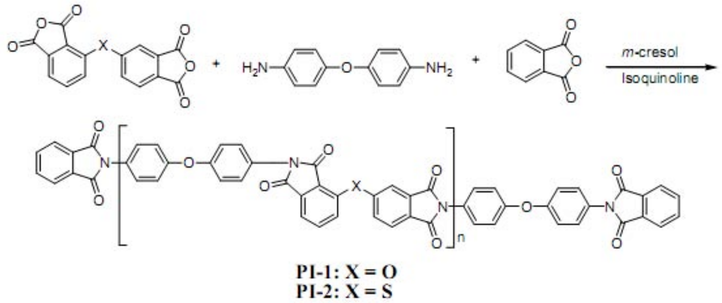
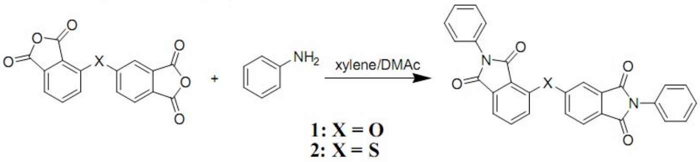


Scheme 1. Synthesis of polyimides derived from 3,4′-ODPA and 3,4′-TDPA with ODA.



Scheme 2. Synthesis of model compounds derived from 3,4′-ODPA and 3,4′-TDPA with ODA.

Table 1. Molecular weight, thermal properties and melt index of polyimides

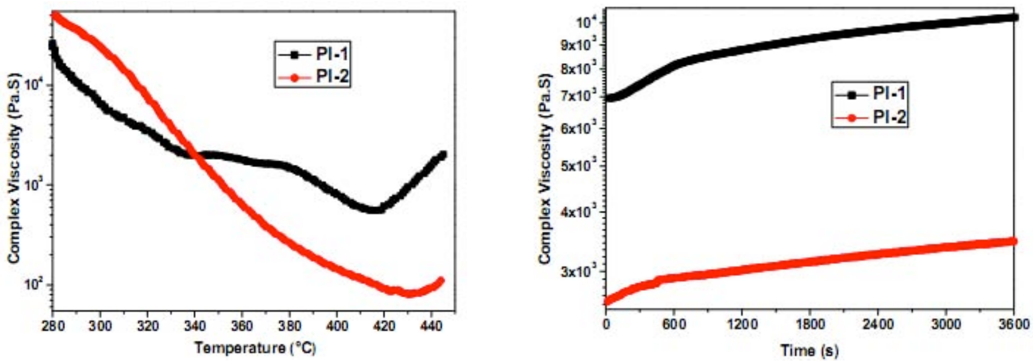
Polymer	η_{inh}[a] (dL/g)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_g[b] (℃)	$T_{5\%}$[c] (℃) N$_2$	$T_{5\%}$[c] (℃) Air	MI[d] (g/10min)
PI-1	0.44	13600	31700	2.33	273	537	531	3.1
PI-2	0.45	11200	21800	1.94	258	532	525	0.31

[a] Measured at a concentration of 0.5 g/dL in *m*-cresol at 30 °C. [b] Obtained from DSC at a heating rate of 20 °C/min in nitrogen. [c] Temperature at 5% weight loss were recorded by TGA at a heating at 10 °C/min.
[d] measured at a load of 12.5 kg at 330 °C.

Table 2. Computational simulation data of model compounds[a]

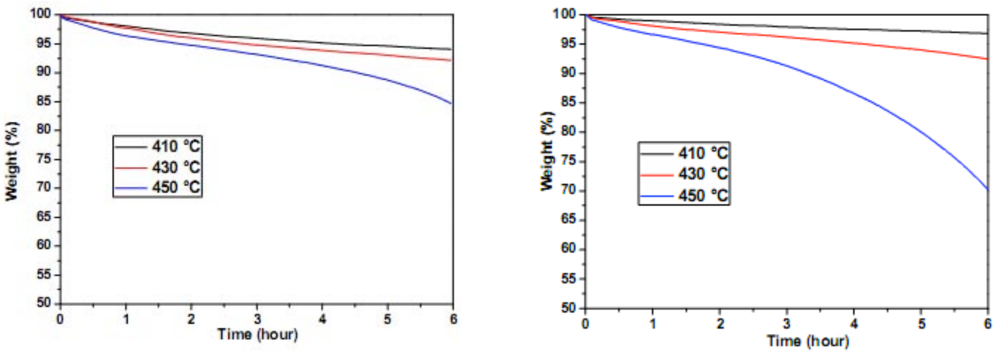
Model Compound	Electronic density	ε_{HOMO}	ε_{LUMO}	$\Delta\varepsilon$
1	-0.491	-0.24983	-0.10523	0.145
2	0.388	-0.24784	-0.11025	0.137

[a] Calculated by density functional theory in quantum chemistry.



(a) (b)

Figure 1. Complex viscosity of polyimides as a function of (a) temperature, and (b) time in air at 340 °C.



(a) (b)

Figure 2. Isothermal weight loss curves of (a) PI-1 and (b) PI-2 for 6 h at different temperatures in air.