Colorless Polyimides Derived from Alicyclic Dianhydrides

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1. Introduction

Polyimides have been widely used in modern industry because of their excellent thermal resistance, electrical and mechanical properties. However, polyimides still suffer from the drawbacks of insolubility in some common organic solvents and the light or dark color caused by intra- and inter- molecular charge transfer interactions, which limits their applications in flexible substrates and liquid crystal display devices.[1,2] Thus, many efforts have been aimed at the development of polyimides with high optical transparence and good solubility. Efficient approaches include the introduction of bulky substituents[3] or asymmetric units[4], the addition of fluorine atoms,[5] the incorporation of alicyclic and aliphatic dianhydrides or diamines.[6] By these approached, the solubility and optical properties of the resulting polyimides are greatly improved due to the loose chain packing, disrupted conjugation, and reduced molecular density and polarity.

Despite their high transparency, low dielectric constants and good solubility,[7] alicyclic and aliphatic polyimides usually exhibit higher in-plane coefficient of thermal expansion (in-plane CTE) and lower glass transition temperature (T_g) compared with wholly aromatic counterparts. High CTE could give rise to delamination and curliness due to the CTE mismatch between PI layers and metal substrates. In this work we synthesize colorless polyimides derived from three novel alicyclic dianhydrides with relatively symmetrical, rigid, regular-shape structures, namely, dicyclohexyl-2,3,3’4’-tetracarboxylic acid dianhydride (3,4’-HBPDA), dicyclohexyl-2,3,2’3’-tetracarboxylic acid dianhydride (3,3’-HBPDA) and 2,5,7,10-naphthanetetracarboxylic dianhydride (HNTDA). The structure-property relationship of these polymers was also elucidated.

2. Results and discussion

The dianhydride monomers dicyclohexyl-2,3,3’4’-tetracarboxylic acid dianhydride (3,4’-HBPDA), dicyclohexyl -2,3,2’3’-tetracarboxylic acid dianhydride (3,3’-HBPDA) and 2,5,7,10-naphthanetetracarboxylic dianhydride (HNTDA) were synthesized through the hydrogenation of their corresponding aromatic precursors. The structures of these three monomers were confirmed by ^{1}H NMR spectra. Then corresponding polyimides were synthesized via a conventional one-step method in *m*-cresol as depicted in Scheme 1.

The properties of colorless polyimides in this study are summarized in Table 1 and 2. The T_g values of HBPDA-based polyimides were higher than 200 ^{o}C. Polyimide from 3,4’-HBPDA and *p*-PDA owned the highest T_g of 321 ^{o}C, amongst HBPDA-based polyimides. For a given diamines, the T_g values of HNTDA-based polyimides were much higher than those of HBPDA-based one. Moreover, HNTDA-based polyimides possessed better thermal stability and lower in-plane CTE, which can be attributed to the higher rigidity of bulky naphthane ring. Similarly, because of its high rigidity, HNTDA-based PIs showed higher tensile strength and modulus compared with the HBPDA-based PIs. The UV-vis spectra of HBPDA- and HNTDA-based polyimides were displayed in Fig. 1. HBPDA- and HNTDA-based polyimides were colorless due to the inhibition of the formation of charge transfer complex originating from the alicyclic structure.

3. Conclusions

In this work, a series of colorless polyimides were prepared using isomeric HBPDAs, HNTDA and various diamines as the monomers. Due to their higher structural rigidity, HNTDA-based PIs showed better thermal and mechanical properties than HBPDA-based ones. These colorless polyimides showed great potential in the applications of optical films due to an excellent combination of high T_g, good thermal stability, favorable mechanical properties, and excellent optical transparency.

References

[1]Wen, Y.; Liu, H.; Yang, S.; Fan, L. *J. Appl. Polym. Sci.* **2015**, *132* (44), 1–11.

[2] Choi, M.; Kim, Y.; Ha, C. *Prog. Polym. Sci.* **2008**, *33*, 581–630.

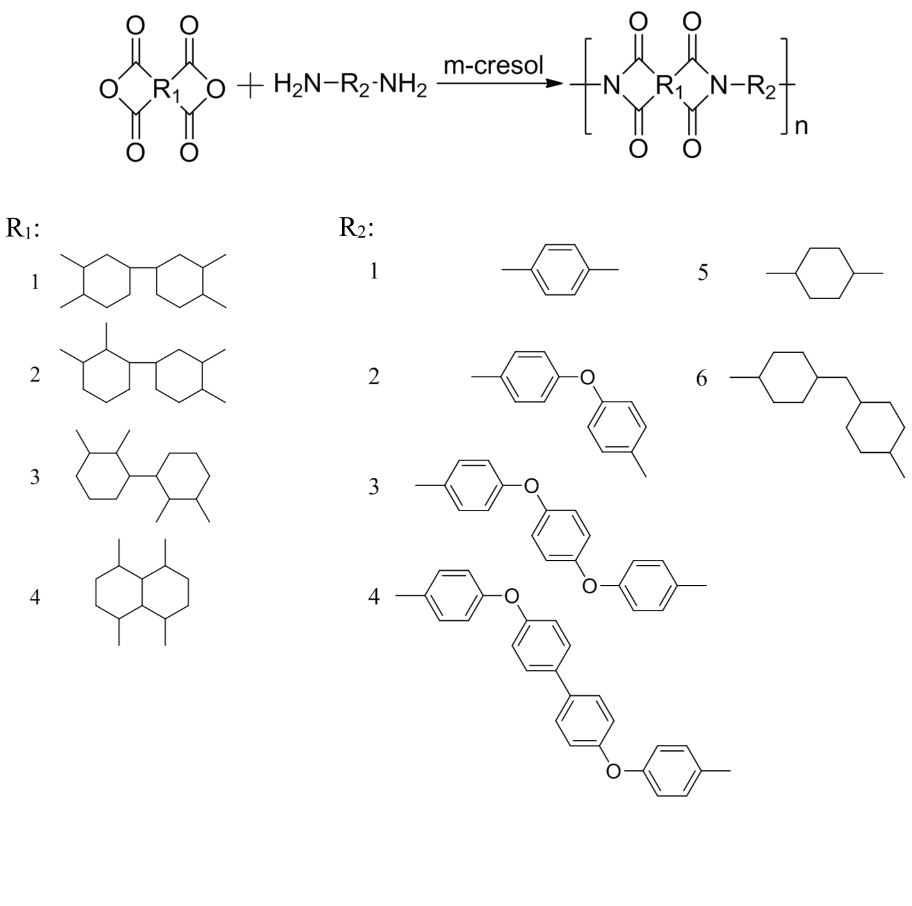
[3] Tapaswi, P. K.; Choi, M.; Jeong, K.; Ando, S.; Ha, C. *Macromolecules* **2015**, *48* (11), 3462–3474.

[4]Banihashemi, A.; Abdolmaleki, A. *Eur. Polym. J.* **2004**, *40* (8), 1629–1635.

[5] Guan, Y.; Wang, D.; Song, G.; Dang, G.; Chen, C.; Zhou, H.; Zhao, X. *Polymer* **2014**, *55* (16), 3634–3641.

[6] Ji, X.; Wang, Z.; Yan, J.; Wang, Z. *Polymer* **2015**, *74*, 38–45.

[7] Liaw, D.; Wang, K.; Huang, Y.; Lee, K.; Lai, J.; Ha, C. *Prog. Polym. Sci.* **2012**, *37* (7), 907–974.



Scheme 1. Synthesis of colorless polyimides

Table 1. Thermal and mechanical properties of isomeric HBPDA-based polyimides

Polyimides	Code	T_g (℃)	T_d^5 (℃) N$_2$	TS (MPa)	TM (GPa)	EB (%)	CTE (ppm/K)[a]
4, 4’-HBPDA/4, 4’-ODA	PI-1-2	256	468	88	2.1	13.8	41.4
4, 4’-HBPDA/1, 4, 4-APB	PI-1-3	230	473	84	1.9	17.6	43.0
4, 4’-HBPDA/4, 4’, 4-BAPB	PI-1-4	240	470	86	1.9	36.6	44.0
4, 4’-HBPDA/*t*-CHDA	PI-1-5	272	462	58	1.9	4.2	46.5
4, 4’-HBPDA/4MBCHA	PI-1-6	241	455	73	1.8	7.6	48.0
3, 4’-HBPDA/*p*-PDA	PI-2-1	321	446	106	2.5	21.3	32.6
3, 4’-HBPDA/4, 4’-ODA	PI-2-2	274	447	87	2.0	46.5	38.0
3, 4’-HBPDA/1, 4, 4-APB	PI-2-3	237	450	105	2.2	98.0	39.4
3, 4’-HBPDA/4, 4’, 4-BAPB	PI-2-4	249	465	91	1.8	87.0	43.4
3, 4’-HBPDA/*t*-CHDA	PI-2-5	293	448	78	2.5	9.9	44.3
3, 4’-HBPDA/4MBCHA	PI-2-6	245	439	75	2.3	10.4	44.9
3, 3’-HBPDA/4, 4’-ODA	PI-3-2	297	438	89	2.0	12.0	34.8
3, 3’-HBPDA/1, 4, 4-APB	PI-3-3	272	444	89	2.1	26.7	37.0
3, 3’-HBPDA/4, 4’, 4-BAPB	PI-3-4	290	445	87	2.0	9.6	33.1
3, 3’-HBPDA/*t*-CHDA	PI-3-5	301	428	71	2.2	4.7	41.0
3, 3’-HBPDA/4MBCHA	PI-3-6	241	429	74	2.2	5.8	43.6

Table 2. Properties of HNTDA-based polyimides

Polyimides	Code	η_{inh} (dL/g)[a]	T_g (°C)	$T_d^5(N_2)$ (°C)	TS (MPa)[b]	TM (GPa)[c]	EB (%)[d]	CTE (ppm/K)	n_{av}	Δn_{th}
HNTDA/4,4'-ODA	HNTDA-1	0.74	418	479	106	3.9	6.7	20.0	1.6018	0.0347
HNTDA/1,4,4-APB	HNTDA-2	0.77	357	482	115	3.5	18.6	29.7	1.6108	0.0281
HNTDA/4,4',4-BAPB	HNTDA-3	0.69	358	489	111	3.4	14.8	26.4	1.6353	0.0483
HNTDA/MBCHA	HNTDA-4	0.51	312	461	88	3.1	4.4	30.8	1.5489	0.0060
HPMDA/4,4'-ODA	HPMDA-1	0.99	346	471	83	2.6	7.9	36.5	1.6142	0.0103
HPMDA/1,4,4-APB	HPMDA-2	1.62	295	473	80	2.2	20.7	44.5	1.6271	0.0188
HPMDA/MBCHA	HPMDA-4	0.65	267	446	68	2.1	5.9	45.7	1.5490	0.0031

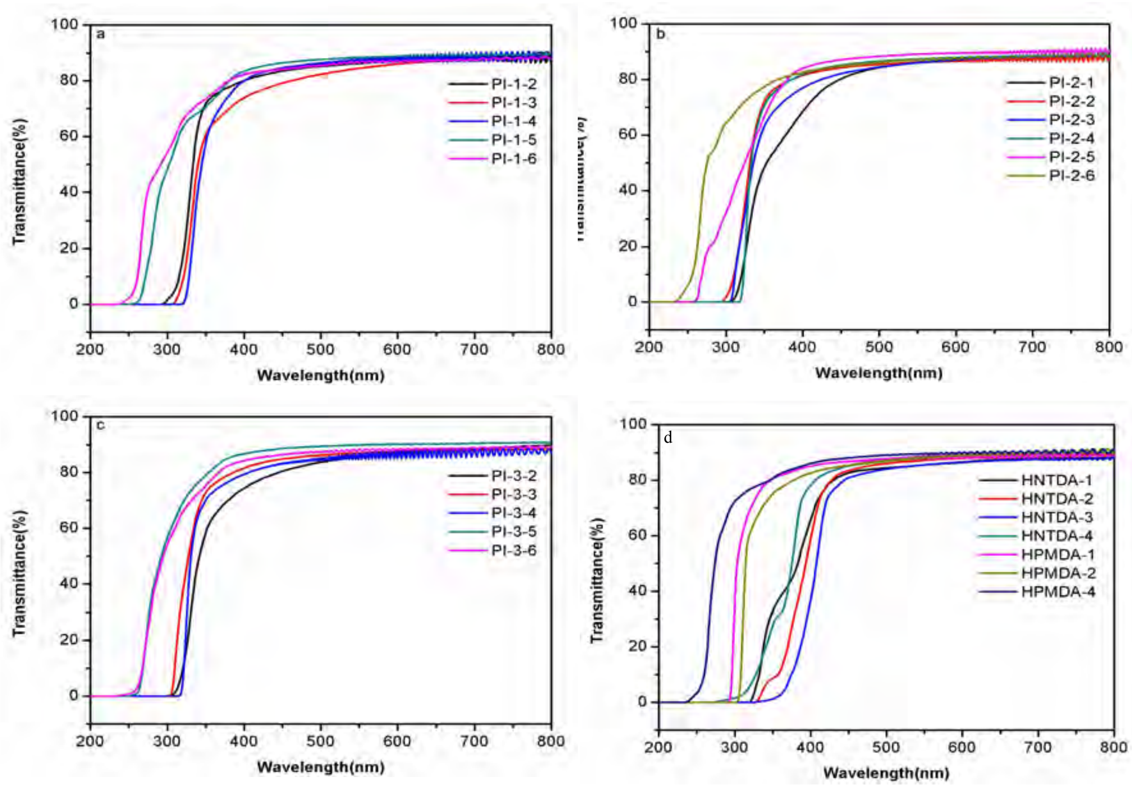


Figure 1. UV-vis spectra of colorless polyimides

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