Organo-soluble semi-alicyclic PIs: A low-cost route from tetralin alicyclic dianhydrides and aromatic diamines

Jin-gang Liu,* Yuan-zheng Guo, Hai-xia Yang, Ai-jun Hu, Shi-yong Yang*
Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China
*Tel: +86-10-62529173; Fax: +86-10-62569562 * E-mail: liujg@iccas.ac.cn; shiyang@iccas.ac.cn*

Alicyclic polyimides (PIs) have attracted much attention over the past decades due to their superior optical transparency, lower dielectric constants ,dissipation factors and acceptable thermal stability as compared with their all-aromatic analogues [1,2]. Now alicyclic PIs have found applications in many newly-arising industries, such as advanced opto-electronic fabrication, flexible display and the information industry [3]. However, the high cost of the alicyclic dianhydrides has greatly hindered the wide applications of alicyclic PIs due to the synthetic difficulties for the monomers. Severe reaction conditions, including photo-irradiation or high-pressure oxidation with nitric acid or ozone are often used in the synthesis of the common alicyclic dianhydrides [4]. Thus, a low-cost synthetic route for alicyclic dianhydride monomers is highly desired to develop high performance alicyclic PIs.

In the present work, a series of novel alicyclic dianhydrides, including 3,4-dicarboxy-1,2,3,4-tetrahydro-6-methyl-1-naphthalene succinic dianhydride (MTDA), 3,4-dicarboxy-1,2,3,4-tetrahydro-6-*tert*-butyl-1-naphthalene succinic dianhydride (TTDA), 3,4-dicarboxy-1,2,3,4-tetrahydro-6-fluoro-1-naphthalene succinic dianhydride (FTDA), and 3,4-dicarboxy-1,2,3,4-tetrahydro-6-chloromethyl-1-naphthalene succinic dianhydride (CMTDA) have been developed with a yield higher than 70% via a low-cost route with maleic anhydride and substituted-styrene compounds as the starting materials, as shown in **Scheme 1**. The chemical structures were characterized by DSC, FTIR,NMR and elemental analysis measurements. The melting points measured by DSC are shown in **Fig.1**, in which the single and sharp endothermic peaks indicated the good purity of the derived monomers. The two-dimensional ^{1}H-^{13}C heteronuclear single-quantum coherence (HSQC) NMR spectrum of the typical FTDA dianhydride presented in **Fig. 2** further confirmed the chemical structures of the monomers.

As illustrated in **Scheme 2**, a series of alicyclic PIs were synthesized from the newly-developed alicyclic dianhydrides, including MTDA (II), TTDA (III), FTDA (IV) and aromatic diamines, such as 4,4'-oxydianiline (ODA), 1,4-bis(4-aminophenoxy)benzene (APB), 2,2-bis[(4-aminophenoxy)- phenyl]propane (BAPP) and 2,2-bis[(4-amino-phenoxy)phenyl]hexafluoropropane (BDAF), respectively. For comparison, the PIs derived from the commercially available tetralin dianhydride, 3,4-dicarboxy-1,2,3,4-tetrahydro-1-naphthalene succinic dianhydride (TDA, I, from TCI, Japan) and the same diamines were also prepared.

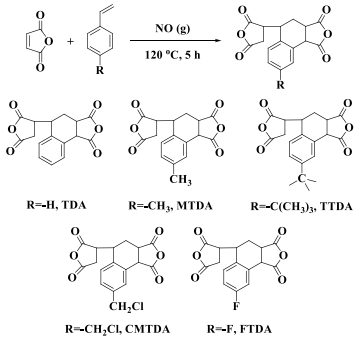
As tabulated in **Table 1**, the intrinsic viscosities of the resulting PIs were in the range of 0.43 to 1.03 dL/g measured at 25 ^{o}C in NMP. This result reveals that the developed tetralin dianhydrides possessed good reactivity when polymerizing with aromatic diamines. The derived PIs had moderate to high molecular weights. The solubility of the PIs was determined in seven typical solvents and the results are shown in **Table 1**. All the PIs exhibited good solubility in the tested solvents except in butyl cellosolve . They were wholly soluble in NMP, DMAc, g-butyrolactone and *m*-cresol at a concentration of 15 wt% at room temperature. The TTDA-PIs (PI-III$_a$~PI-III$_d$) exhibited the best solubility in the PI series. .

Flexible, tough and transparent PI films were cast from their NMP solution at elevated temperatures (80~250 ^{o}C), as shown in **Fig. 3**. The cutoff wavelengths of the PI films were around 300 nm and the transmittance values of the films at 400 nm reached or exceeded 75%. PI films derived from fluoro-containing diamine BDAF and the tetralin dianhydrides, exhibited the best optical transparency with transmittances over 80% at 400 nm and yellow indices as low as 6.07 (**Fig.4** and **Table 2**). The thermal and mechanical properties of the PIs were evaluated and the results are tabulated in **Table 3**. All the PIs showed initial thermal decomposition temperatures ($T_{5\%}$) at around 400 ^{o}C. The PI films exhibited tensile strength (T_s) values higher than 60 MPa..

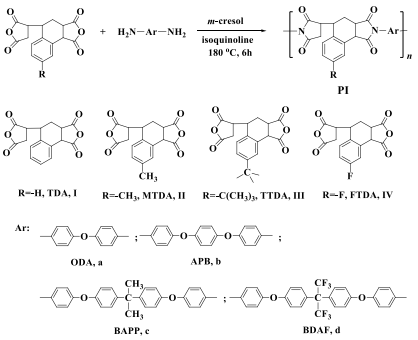
Acknowledgements. Financial support from the National Natural Science Foundation of China (51173188) is gratefully acknowledged.

References

1. Matsumoto T, Mikami D, Hashimoto T, Kaise M, Takahsshi R, Kawabata S. *J Phys: Conf Ser*, **187**, 012005(2009).
2. Mathews AS, Kim I, Ha CS. *Macromol Res* , **15**, 114-128(2007).
3. Liaw DJ, Wang KL, Huang YC, Lee KR, Lai JY, Ha CS. *Prog Polym Sci* , **37**, 907-974(2012).
4. Matsumoto, T. *J Synth Org Chem Jpn* , **62**, 776-786(2000).



Scheme 1. Synthesis of tetralin dianhydrides.



Scheme 2. Synthesis of alicyclic PIs

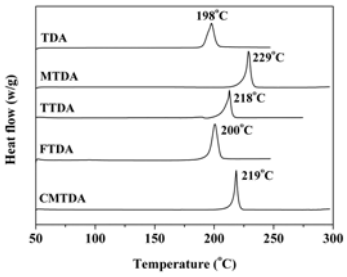


Fig.1. Melting points of dianhydride monomers.

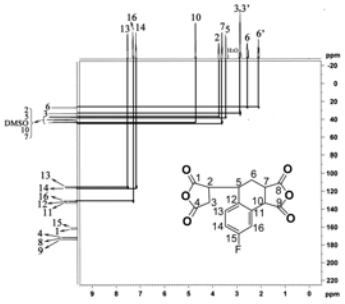


Fig.2. ^{1}H-^{13}C COSY NMR spectrum of FTDA.

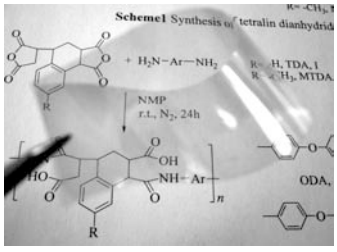


Fig.3. Appearance of PI-II$_d$ film (MTDA-BDAF).

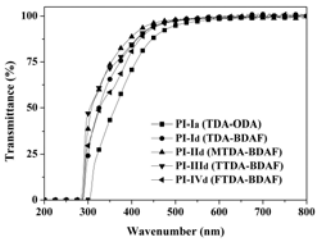


Fig.4. UV-Vis spectra of PIs derived from

Table 2. Optical transparency and yellow indices of PI-III and PI-IV films*.

PI	λ (nm)	T_{400} (%)	d (μm)	YI (b^*)
PI-III$_a$	274	78.9	43	40.98
PI-III$_b$	279	79.4	45	38.47
PI-III$_c$	289	81.7	47	37.77
PI-III$_d$	281	84.6	45	28.20
PI-IV$_a$	287	75.6	ND	ND
PI-IV$_b$	294	76.5	26	29.08
PI-IV$_c$	289	77.3	35	30.60
PI-IV$_d$	285	80.8	35	6.07

* λ: cutoff wavelength; T_{400}: transmittance at 400 nm; YI: yellow index; ND: not detected.

Table 1. Inherent viscosities and solubility of the PIs*.

PI	$[\eta]_{inh}$ (dL/g)	Solvent			
		NMP,DMAc, γ-BL or *m*-cresol	BC	THF	CH_2Cl_2
PI-I$_a$		++	—	—	—
PI-I$_b$	0.69	++	—	+	—
PI-I$_c$	0.63	++	—	++	+
PI-I$_d$	0.55	++	—	++	+
PI-II$_a$	0.68	++	—	—	+
PI-II$_b$	0.62	++	—	—	—
PI-II$_c$	0.54	++	—	++	++
PI-II$_d$	0.43	++	—	++	++
PI-III$_a$	1.03	++	—	+	+
PI-III$_b$	0.95	++	—	+	++
PI-III$_c$	0.85	++	—	++	++
PI-III$_d$	0.65	++	—	++	++
PI-IV$_a$	0.89	++	—	—	—
PI-IV$_b$	1.02	++	—	—	—
PI-IV$_c$	0.79	++	—	+	+
PI-IV$_d$	0.64	++	—	++	++

* $[\eta]_{inh}$: inherent viscosities measured with a PI resin at a concentration of 0.5 g/dL in NMP at 25 °C; ++: Wholly soluble at room temperature; +: Partially soluble; —: Insoluble; BC: butyl cellosolve.

Table 3. Thermal properties of PI films*

PI	T_g (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_S (MPa)	T_M (GPa)	E_b
PI-I$_a$	255	395	405	91	2.7	4.9
PI-I$_b$	235	405	416	ND	ND	ND
PI-I$_c$	217	388	400	ND	ND	ND
PI-I$_d$	227	401	411	ND	ND	ND
PI-II$_a$	271	404	412	84	2.5	6.4
PI-II$_b$	232	387	407	79	2.2	5.4
PI-II$_c$	207	392	409	80	2.2	5.2
PI-II$_d$	207	393	408	81	2.4	4.8
PI-III$_a$	278	438	452	ND	ND	ND
PI-III$_b$	260	440	455	83	2.4	5.8
PI-III$_c$	210	436	453	61	2.3	5.3
PI-III$_d$	240	434	447	73	1.9	5.4
PI-IV$_a$	271	402	431	ND	ND	ND
PI-IV$_b$	231	412	434	81	2.3	4.1
PI-IV$_c$	226	440	462	83	2.3	5.6
PI-IV$_d$	236	436	456	84	2.3	5.3

* T_g: glass transition temperature; $T_{5\%}$, $T_{10\%}$: temperatures at 5% and 10% weight loss, respectively; T_S: tensile strength; T_M: tensile modulus; E_b: elongation at break; ND: not detected.