Organo-Soluble Asymmetrical Fluorinated Poly(amide-imide)s Derived from 2,3,3′,4′-Biphenyltetracarboxylic Dianhydride, 2,4,5-Trifluoro-3-aminobenzoic Acid and Various Aromatic Diamines

*Jin-gang Liu**, *Zhuo-Li, Xiao-juan Zhao, Hai-xia Yang, Lin-Fan, Shi-yong Yang**

(Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China)

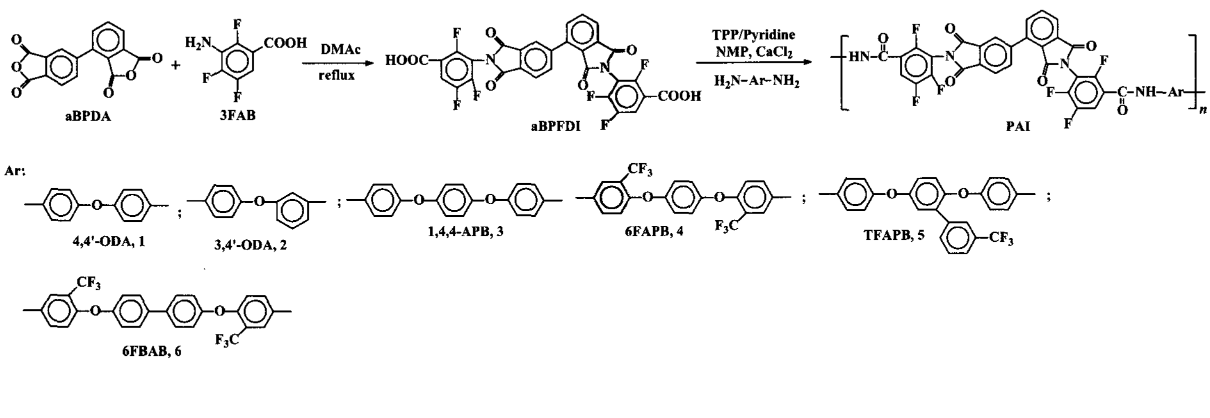
Tel: 86-10-62529173; Fax: 86-10-62569562; E-mail: liujg@iccas.ac.cn

Abstract: An aromatic fluoro-containing asymmetric dicarboxylic acid, 2,3,3′,4′-biphenyltetracarboxylic-*N,N*′-bis(3-carboxyl-2,5,6-trifluorophenyl) diimide (a-BPFDI) had been synthesized from 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA) and 3-amino-2,4,5-trifluorobenzoic acid. A series of poly(amide imide)s (PAIs) were prepared from a-BPFDI and various aromatic diamines via Yamazaki-Higashi reaction with *N*-methyl-2-pyrrolidone (NMP) as the solvent, triphenyl phosphite (TPP) and pyridine as the condensing agents, and calcium chloride as the catalyst. Among the synthesized PAIs, those derived from a-BPFDI and fluorinated aromatic diamines showed good solubility in polar aprotic solvents. The PAI films exhibited good thermal stability with the glass transition temperatures of 250-280 °C and 10% weight loss temperatures higher than 460 °C in nitrogen. In addition, the PAI films showed acceptable transparency with the cutoff wavelengths of 330-380 nm and transmittances higher than 60% at 450 nm.

Key words: poly(amide-imide); asymmetry; fluorine; solubility; transparency

Fluorinated poly(amide-imide)s (PAIs) are well known for their good combined properties, including good tensile properties, thermal stability, dielectric strength, low dielectric constant, and low color. The versatile properties cover their applications from conventional insulating areas to more recent high-tech optoelectronic fields. In this paper, we reported a series of PAIs with high fluorine contents.

The synthesis procedure is shown in Scheme 1. First, the dicarboxylic acid compound aBPFDI was prepared and then polymerized with six aromatic diamines to afford PAIs. PAI-1 (aBPFDI-4,4′-ODA) and PAI-2 (aBPFDI-3,4′-ODA) precipitated during the polymerization, indicating the insoluble natures of the polymers in the solvent. The residual reactions maintained homogeneous and silky polymer resins were obtained by precipitating the reaction solution into ethanol. The inherent viscosities of the PAIs are in the range of 0.86-1.03 dL/g (Table 1), revealing the high molecular weights of the polymers.



Scheme 1 Synthesis of PAIs

Flexible and tough PAI films were cast from their solutions in NMP except PAI-3 (aBPFDI-1,4,4-APB), which was not soluble in NMP at room temperature.

The solubility of the PAIs were evaluated by dissolving the resins in the tested solvents at room temperature with a solid content of 15% (wt%). The results in Table 2 indicate that the PAIs from aBPFDI and fluoro-containing diamines (PAI-4, 5, and 6) exhibit excellent solubility in the polar aprotic solvents, such as NMP, good solubility in cresol and cyclopentanone (CPA), and poor solubility in tetrahydrofuran (THF), chloroform and methanol. The good solubility could mainly be attributed to their loose molecular packing caused by the asymmetric molecular structure and bulky fluorine groups both in the diacid and diamine moieties. The PAI films exhibited good thermal stability with the glass transition temperatures of 250-280 °C and 10% weight loss temperatures higher than 460 °C in nitrogen (Table 1, Fig 1& Fig 2). The PAI films show acceptable transparency with the cutoff wavelengths of 330-380 nm and transmittances higher than 60% at 450 nm (Fig 3). In addition, the PAI films exhibit good tensile properties with the tensile strength of 89 MPa for PAI-4, 99 MPa for PAI-5, and 93 MPa for PAI-6. The dielectric constants of the films are around 3.0 due to the high fluorine loads of the polymers.

Thus, the fluorinated PAIs in the present study exhibit good combined properties and might find applications in advanced optical or microelectronic fabrications.

Table 1. Synthesis and characterization of PAIs

PAI	reaction	η_{inh} [a] (dL/g)	Film quality	λ_{cutoff} [d] (nm)	T_{450} [e] (%)	T_g [f] (℃)	$T_{10\%}$ [f] (℃)	R_{w700} [f] (%)	ε
PAI-1	gel	not measured							
PAI-2	gel	not measured							
PAI-3	homo.	-[c]	-[c]	-[c]	-[c]	not measured			
PAI-4	homo.	0.98	F & T[b)]	355	79	280	464	60	2.96
PAI-5	homo.	0.86	F & T	389	61	261	494	65	3.15
PAI-6	homo.	1.03	F & T	343	84	253	477	58	3.06

[a)] Measured at 30 °C with a 0.5 g/dL NMP solution; [b)] Flexible and tough; [c)] Not dissolved in NMP; [d)] Cutoff wavelength; [e)] Transmittance at 450nm; [f)] T_g: glass transition temperatures; $T_{10\%}$: temperatures at 10% weight loss; R_{w700}: residual weight ratio at 700℃ *in nitrogen.*

Table 2. Solubility of PAIs [a]

PAI	NMP	DMAc	*m*-Cresol	CPA	THF	$CHCl_3$	methanol
PAI-3	+	+	-	-	-	-	-
PAI-4	++	++	+	+	-	-	-
PAI-5	++	++	++	++	+	-	-
PAI-6	++	++	++	+	-	-	-

a) ++ wholly soluble; + partially soluble; - not soluble

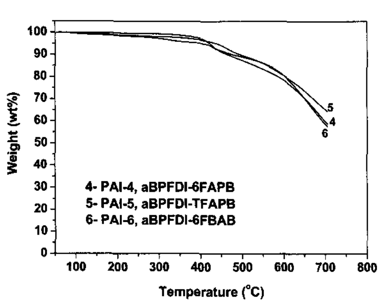


Fig 1. TGA curves

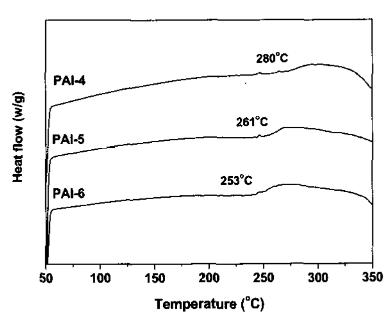


Fig 2. DSC curves

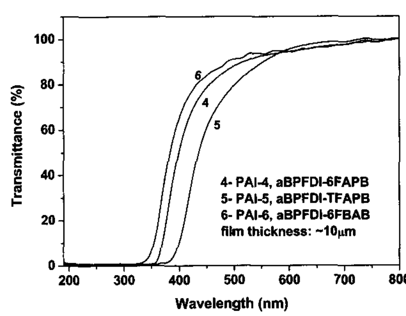


Fig 3. UV-Vis spectrum