PROGRESS IN NOVEL FLUORINATED AROMATIC POLYIMIDES
—— Synthesis, Characterization and Properties

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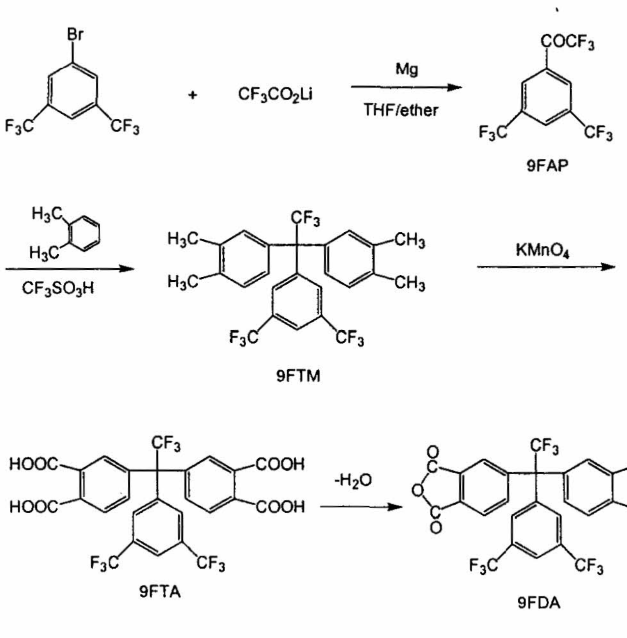
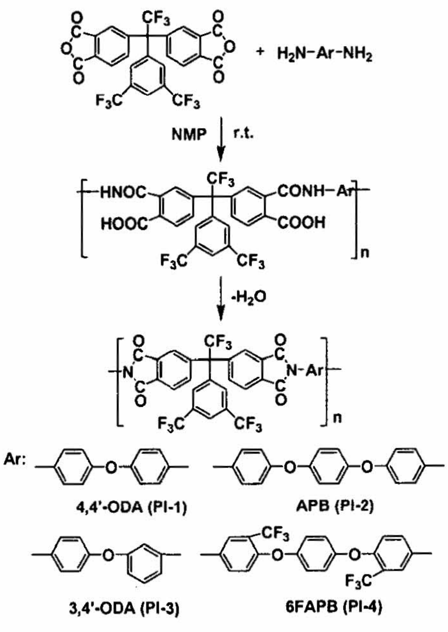
The recent progress in synthesis, characterization and properties of novel fluorinated aromatic polyimides in our laboratory were described. The novel fluorinated aromatic dianhydrides, such as 4,4'-{2,2,2-trifluoro-1-[3',5'-bis(trifluoromethyl)phenyl]ethylidene} diphthalic anhydride (9FDA) and 4,4'-[2,2,2-trifluoro-1-(3'-trifluoromethylphenyl)ethylidene] diphthalic anhydride (HFDA) or from the novel fluorinated aromatic diamines, such as 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) and 1,4-bis(4-amino-2-trifluoro methylbiphenoxy)benzene (6FBAB) were synthesized (Scheme1) [1-4]. The fluorinated aromatic polyimides were prepared via two different polymerization pathways, *i.e.* one-step polycondensation procedure at high temperature and two-step polycondensation route at ambient temperature, depending on the relative polycondensation reactivity between the fluorinated aromatic dianhydrides and the fluorinated aromatic diamines employed (Scheme 2). The effects of the chemical structures of the fluorinated aromatic polyimides on their combined properties, such as thermal stability, mechanical properties, electrical and dielectric properties, as well as the chemical and physical stability were investigated (Table 1-3).





Scheme 1. Synthesis of fluorinated aromatic dianhydrides. **Scheme 2.** Preparation of aromatic polyimides.

The molecular weight-controlled fluorinated aromatic polyimides were also prepared. The processability of the fluorinated aromatic polyimides, especially the solubility in organic solvents, the meltability and melt stability at elevated temperature, were not only strongly depended on the chemical structures and the polyimde backbones but also on the polymer molecular weights and the molecular weight distributions. High soluble and high meltable aromatic polyimides could be obtained by controlling the chemical structures of the polyimide backbone as well as the molecular weights. As high as 40-45 wt.% of dissolvability in NMP or DMAC could be obtained for some of fluorinated aromatic polyimides to form a storable polymer solution. High flowing and stable molten fluids at temperature of 260-280 °C could also be achieved for the molecular weight-controlled aromatic polyimides, which are suitable for infusing, injecting or resin transfer molding processing.

Table 1. Thermal properties of the fluorinated polyimides

Code	T_g [a] (°C)	T_d [b] (°C)	T_5 [c] (°C)	T_{10} [c] (°C)	Char yield [d] (%)	CTE [e] (ppm/°C)
PI-1	283.6	571.8	536.8	562.5	24.6	57.1
PI-2	259.5	582.0	546.4	578.2	41.9	58.3
PI-3	257.7	566.2	536.4	563.4	30.6	56.1
PI-4	245.8	570.4	546.2	573.5	48.8	59.8

[a]: Glass transition temperature determined by DSC; [b]: onset decomposition temperature; [c] 5% and 10% of weight loss temperature; [d]: residual weight retention at 800 °C; [e]: the in-plane coefficients of thermal expansion.

Table 2. Mechanical properties of the fluorinated polyimides

Code	Tensile Strength (MPa)	Elongation at Breakage (%)	Tensile Modulus (GPa)
PI-1	87.7	5.0	3.02
PI-2	87.8	6.8	2.56
PI-3	102.7	7.6	2.73
PI-4	99.5	7.8	2.79

Table 3. Dielectric properties of the fluorinated polyimides

Code	F [a] %	R_V [b] (Ω·cm)	R_S [c] (Ω)	ε (1MHz)	tanδ	Water Uptake (%)
PI-1	22.7	4.04×10^{15}	4.08×10^{17}	2.89	0.0014	0.35
PI-2	20.2	7.86×10^{15}	3.26×10^{15}	2.97	0.0022	0.18
PI-3	22.7	4.80×10^{16}	4.57×10^{17}	2.88	0.0013	0.40
PI-4	29.1	1.59×10^{17}	1.39×10^{17}	2.71	0.0028	0.14

[a] Fluorine content; [b] Volume resistance; [c] Surface resistance; [d] Dielectric constant.

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