FLUORINE-CONTAINING AROMATIC POLYBENZAZOLES: PREPARATION AND CHARACTERIZATION

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ABSTRACT

Three types of fluorine-containing aromatic polybenzazoles, polybenzimidazoles, polybenzoxazole and polybenzothiazoles, were synthesized by direct polycondensation of 4,4'-(hexafluoroisopropylidene)dibenzoic acid and tetrafluoroterephthalic acid with aromatic tetramines, bis(*o*-aminophenol) and diaminobenzenedithiol, respectively. The effect of introduction of fluorine atom on the synthesis and properties of these polymers was discussed in detail. The perfluoroisopropylidene unit-containing polymers were amorphous, and showed good solubility in various organic solvents, excellent mechanical properties and high thermal stability. The perfluoro-*p*-phenylene unit-containing polymer was highly crystalline, and exhibited lyotropic behavior in concentrated sulfuric acid.

INTRODUCTION

Aromatic polybenzazoles (PBZs) such as polybenzimidazoles (PBIs), polybenzoxazoles (PBOs) and polybenzothiazoles (PBTs) are among the most thermally and thermooxidatively stable polymers, and are also known for their nonflammability, outstanding chemical and environmental resistance and the third-order nonlinear optical susceptibility. The synthesis of such rigid chain PBZs has become of interest again, because many of them can be spun into highly oriented fibers of ultra-high strength and ultra-high modulus from their anisotropic dopes. This type of polymer, however, is insoluble in most organic solvents. In this study, with the hope of providing organic-soluble aromatic PBZs, the synthesis of fluorine-containing PBZs was tried.

RESULTS AND DISCUSSION

Fluorine-containing aromatic PBIs (**5aa**) and (**5ab**), PBO (**6aa**) and PBTs (**7aa**) and (**7ba**) were synthesized by direct polycondensation of fluorine-containing dicarboxylic acids (**1a**) and (**1b**) with aromatic tetramines (**2a**) and (**2b**), bis(*o*-aminophenol) (**3a**) and diaminobenzenedithiol (**4a**), respectively, using phosphorus pentoxide/methanesulfonic acid or polyphosphoric acid as both condensing agent and solvent.

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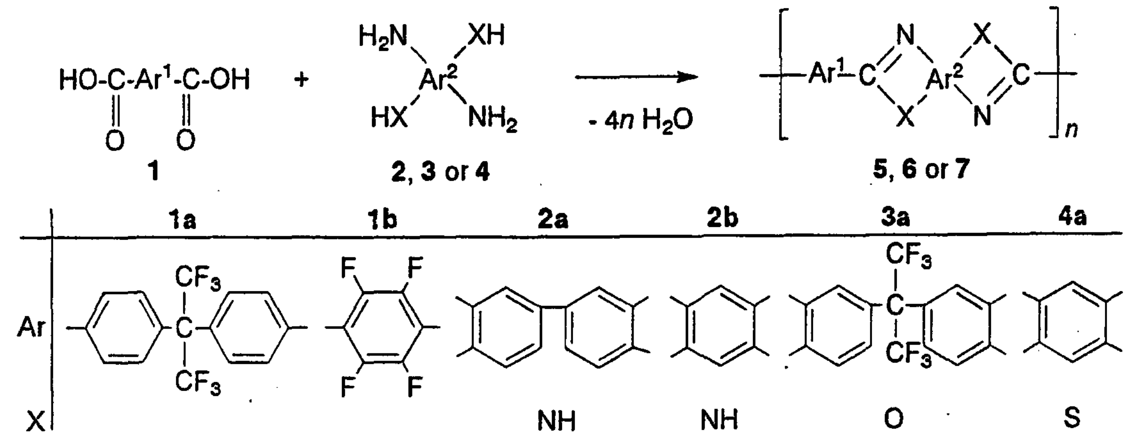

The respective maximum reduced viscosities attained were in the order 1.15, 0.59, 0.59, 1.60 and 0.61 dL/g.

The perfluoroisopropylidene (PFIP) unit-containing PBZs were amorphous and dissolved in polar aprotic solvents such as DMAc, HMPA and/or NMP and even in less polar *m*-cresol, *o*-chlorophenol, chloroform, pyridine and/or THF in addition to protic strong acids like concentrated sulfuric acid and methanesulfonic acid, whereas the perfluoro-*p*-phenylene (PFPP) unit-containing PBZ was highly crystalline and was insoluble in any organic solvents tried. Thus, the introduction of PFIP unit is effective for increasing solubility of aromatic PBZs in organic solvents. Optical anisotropy was observed for PFPP unit-containing PBT **7ba** in concentrated sulfuric acid. The surface, mechanical and thermal properties of these polymers are presented in Table I. The PFIP unit-containing PBZ films had tensile strength of 46-69 MPa, elongation at break of 4-6% and tensile moduli of 1.4-2.7 GPa, respectively. Their film properties are excellent as indicated by the high tensile strength and moderate pliability. The PFIP unit-containing PBZs were highly thermally and thermooxidatively stable and exhibited no weight loss up to around 480℃, with 10% weight loss being recorded at 506-527℃ in air.

Thus, these series of PFIP unit-containing PBZs are characterized by good solubility in organic solvents, excellent mechanical properties and high thermal stability, and, hence, are one of the very promising high-temperature film and plastic materials.

Table I Characterization of Fluorine-Containing Aromatic Polybenzazoles **5**, **6** and **7**

Polymer	θ_W [a] deg.	θ_I [b] deg.	Strength MPa	Elong. %	Modulus GPa	T_g [c] °C	T_{10} [d] °C	RW [e] %
1a + **2a** → **5aa**	72	33	46	6	1.4	330	520	96
1a + **2b** → **5ab**	69	44	— [f]	—	—	— [g]	506	92
1a + **3a** → **6aa**	77	38	62	5	1.7	295	515	97
1a + **4a** → **7aa**	76	42	69	4	2.7	327	527	96
1b + **4a** → **7ba**	— [h]	—	—	—	—	— [g]	484	75

[a] Contact angle to water at 25°C in air. [b] Contact angle to diiodomethane. [c] Glass transition temperature determined by DSC (10K/min). [d] 10% weight-loss temperature determined by TG in air (10K/min). [e] Residual weight at 500°C. [f] No tough film was obtained. [g] No T_g was detectable. [h] No homogeneous film was obtained.