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Synthesis and characterization of novel fluorinated polyimides derived from 1,3-bis(4-amino-2-trifluoromethylphenoxy)naphthalene and aromatic dianhydrides

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A new structurally asymmetric diamine monomer containing flexible ether linkages and bulky trifluoromethyl substituents, namely 1,3-bis(4-amino-2-trifluoromethylphenoxy)-naphthalene, was prepared from 1,3-dihydroxynaphthalene and 2-chloro-5-nitrobenzotrifluoride. New series of fluorinated polyimides were synthesized from the diamine with six commercially available aromatic tetracarboxylic dianhydrides using a conventional two-stage process with thermal or chemical imidization. The resulting polyimides were highly soluble in a variety of organic solvents and could afford transparent and tough films via solution casting. These polyimides exhibited moderately high glass-transition temperatures (by DSC) of 236–268 °C and softening temperatures (by thermomechanical analysis) of 231–250 °C, and they did not show significant decomposition before 500 °C under either nitrogen or air atmosphere. Also, they revealed low moisture absorptions (0.32–0.78%), low dielectric constants (2.81–3.24 at 10 kHz), and high optical transparency (ultraviolet–visible absorption cutoff wavelengths of 377–426 nm).

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1. Introduction

Aromatic polyimides are well known high-performance polymeric materials for their excellent thermal, mechanical and electrical properties [1–3]. Despite their outstanding properties, most of the conventional aromatic polyimides have high melting or glass-transition temperatures (T_g) and limited solubility in most organic solvents because of their rigid backbones and strong interchain interactions. These properties make them generally intractable or difficult to process, thus limiting their applicability. To overcome such a difficulty, many attempts have been made to improve the processability of polyimides while maintaining their excellent properties [4]. It has been generally recognized that aryl-ether linkage imparts properties such as better solubility, melt processing characteristics, and improved toughness in comparison with those polymers without an aryl-ether linkage [5–10]. However, the decrease in mechanical properties on heating is almost always a consequence of the reduced chain stiffness or T_gs. The introduction of bulky, rigid units in the polymer main chain or as pendent groups can impart an increase in T_gs by restricting the segmental mobility, while providing an enhanced solubility because of decreased packing density and crystallinity [11,12]. Thus, combining these two structural modifications minimized the trade-off between the processability and the useful/positive properties of aromatic polyimides [13–22]. Another attractive method is the incorporation of geometrically unsymmetrical or twisty units into the polymer backbone [23–32]. This method is quite effective to improve the solubility of polyimides without much deteriorating their inherent excellent

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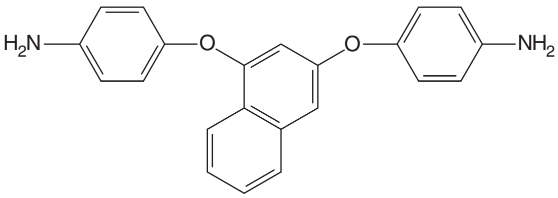
properties because close chain stacking and intermolecular interactions are restricted while the main-chain rigidity of the polyimide can also be maintained.

As reported in our previous publications [33,34], 1,3-bis(4-aminophenoxy)naphthalene (1,3-BAPON) was synthesized and used to prepare aromatic polyamides and polyimides containing 1,3-bis(phenoxy)naphthalene in the backbones. Because of the molecular asymmetry of the 1,3-BAPON component, the resulting polymers exhibited reduced chain-packing efficiency and intermolecular interactions such as hydrogen bonding. Therefore, several organosoluble polyamides with moderate T_gs and high thermal stability could be achieved by the incorporation of the 1,3-bis(phenoxy)naphthalene unit in the main chain. However, most of the polyimides based on 1,3-BAPON were insoluble in conventional organic solvents, possibly because of the rigid nature of the polymer backbones and strong intermolecular interactions. In view of the fact that polyimides derived from ether-bridged aromatic diamines with bulky trifluoromethyl (CF_3) groups are generally soluble and high temperature resistant polymer materials with low moisture uptake, low dielectric constant, and high optical transparency [35–50]. The present work reports the synthesis of a new unsymmetrical CF_3-substituted bis(ether amine), 1,3-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, and its derived fluorinated polyimides by reacting the diamine with various aromatic tetracarboxylic dianhydrides. The solubility, tensile properties, crystallinity, and thermal properties of all the obtained polymers, together with water absorption, optical transparency, color intensity, and dielectric constants of the polyimides, were investigated and compared with those of analogous counterparts prepared from non-fluorinated 1,3-BAPON.



1,3-BAPON

2. Experimental

2.1. Materials

1,3-Dihydroxynaphthalene (Tokyo Chemical Industry; TCI), potassium carbonate (K_2CO_3) (Fluka), 2-chloro-5-nitrobenzotrifluoride (Acros), *p*-chloronitrobenzene (Acros), 10% palladium on charcoal (Pd/C) (Fluka), and hydrazine monohydrate (Acros) were used as received. As reported previously [33,34], 1,3-BAPON (mp = 114–115 °C) was prepared by the aromatic nucleophilic substitution reaction of *p*-chloronitrobenzene with 1,3-dihydroxynaphthalene in the presence of K_2CO_3 and the subsequent reduction of the intermediate dinitro compound with hydrazine as the reducing agent and palladium as the catalyst. Pyromellitic dianhydride (PMDA; **3a**) (Aldrich) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA; **3c**) (Aldrich) were purified by recrystallization from acetic anhydride. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA; **3b**) (Oxychem), 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA; **3d**) (New Japan Chemical Co.), 4,4′-oxydiphthalic dianhydride (ODPA; **3e**) (Oxychem) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; **3f**) (Hoechst Celanese) were heated at 250 °C in vacuum for 3 h prior to use. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

2.2. Monomer synthesis

2.2.1. 1,3-Bis(2-trifluoromethyl-4-nitrophenoxy)naphthalene (*1*)

1,3-Dihydroxynaphthalene (8.0 g, 0.05 mol) and 2-chloro-5-nitrobenzotrifluoride (23.0 g, 0.10 mol) were dissolved in 80 mL of *N,N*-dimethylformamide (DMF) in a 300-mL round-bottomed flask. Then, potassium carbonate (14.0 g, 0.10 mol) was added, and the suspension mixture was heated at 100 °C for 12 h. The mixture was allowed to cool and then poured into 800 mL of water to give a yellow solid, which was collected, washed repeatedly with water, and dried. The crude product was recrystallized from methanol/water to give pale-yellow crystals (19.0 g, 71%); mp = 130–133 °C (onset to peak top temperature), by differential scanning calorimetry (DSC) at a scan rate of 2 °C/min. IR (KBr): 1531, 1349 ($–NO_2$ stretch), 1267 (C–O stretch), 1145 cm^{-1} (C–F stretch). ^1H NMR (500 MHz, DMSO-d_6; for peak assignments: see Fig. 1(a)): δ 8.57, 8.53 (d, J = 2.5 Hz, 2H, H_i, $H_{i'}$), 8.47, 8.42 (dd, J = 9.1, 2.5 Hz, 2H, H_h, $H_{h'}$), 8.12 (d, J = 6.7 Hz, 1H, H_e), 7.90 (d, J = 8.4 Hz, 1H, H_b), 7.87 (s, 1H, H_f), 7.71 (t, J = 7.2 Hz, 1H, H_d), 7.64 (t, J = 7.7 Hz, 1H, H_c), 7.48 (s, 1H, H_a), 7.42, 7.26 ppm (d, J = 9.1 Hz, 2H, H_g, $H_{g'}$). ^{13}C NMR (125 MHz, DMSO-d_6; for peak assignments: see Fig. 2(a)): δ 159.9 (C^{11}, $C^{11'}$), 151.3 (C^8), 150.9 (C^2), 142.1 (C^{14}), 142.0 ($C^{14'}$), 135.1 (C^{10}), 130.2 (C^{13}), 130.0 ($C^{13'}$), 128.4 (C^5), 128.2 (C^4), 127.3 (C^6), 123.9 (C^9), 123.4 (q, $^1J_{C-F}$ = 271 Hz, C^{17}), 123.3 (q, $^3J_{C-F}$ = 5 Hz, $C^{15} + C^{15'}$), 123.2 (q, $^1J_{C-F}$ = 271 Hz, $C^{17'}$), 120.8 (C^7), 119.2 (q, $^2J_{C-F}$ = 30 Hz, C^{16}), 119.0 (C^{12}), 118.9 (q, $^2J_{C-F}$ = 30 Hz, $C^{16'}$), 117.9 ($C^{12'}$), 115.5 (C^3), 111.3 ppm (C^1). Anal. Calcd for $C_{24}H_{12}F_6N_2O_6$ (538.36): C, 53.54%; H, 2.24%; N, 5.20%. Found: C, 53.51%; H, 2.15%; N, 4.81%. Crystal data: light-yellow crystal grown during slow crystallization in THF/methanol (2:1 v/v), 0.24 mm × 0.14 mm × 0.1 mm, orthorhombic $P2_12_12_1$ with a = 39.142(2), b = 8.2797(5), and c = 13.9935(10) Å, $\alpha = 90°$, $\beta = 92°$, $\gamma = 90°$, where D_c = 1.578 g/cm^3 for Z = 8 and V = 4531.3(5) $Å^3$.

2.2.2. 1,3-Bis(4-amino-2-trifluoromethylphenoxy)naphthalene (*2*)

A mixture of the purified dinitro compound **1** (16.0 g, 0.03 mol), 10% Pd/C (0.15 g), ethanol (100 mL), and hydrazine monohydrate (10 mL) was heated at reflux temperature for about 8 h. The resultant clear, darkened solution was filtered hot to remove Pd/C, and the filtrate was then distilled to remove the solvent. The crude product was purified by recrystallization from acetone/water to give pale-yellow crystals (11.2 g, 81%); mp = 109–110 °C by

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