Synthesis and Properties of Low-surface-energy Polyimides

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An aromatic diamine monomer, 1H,1H-perfluorooctyl 3,5diaminobenzoate (PFD), was synthesized in three steps, which was used to prepare the polyimides containing pendant perfluoroalkyl chains via the polymerization of PFD with commercial 4,4'-(hexafluoroisopropylidene)diphthalic anhydride. Various characterization techniques including thermogravimetric analysis, infrared spectroscopy, and X-ray photoelectron spectroscopy were used to characterize the new polyimides with perfluoroalkyl chains. The resulting polyimide film exhibits hydrophobicity with a contact angle of 95° for water, and the calculated surface free energy is 37.4 mN m⁻¹. Superhydrophobic surfaces were also demonstrated by coating the polyimide containing pendant perfluorooctyl chains on rough alumina substrate.

Polyimide (PI), due to its excellent mechanical, thermal, and dielectric properties, is one of the most widely used polymers in various applications that require robust organic materials including composites and precursors for high-performance aerospace materials and membranes for gas separation, as well as the microelectronics industry.¹ However, the relatively high dielectric constant of polyimide has limited its use as an insulating material, in which materials with dielectric constants as small as possible are preferred in order to achieve maximum possible device speed through smaller dimensions.² Furthermore, the moisture absorption up to about 3 wt % of the polvimide film can give rise to a further increase in its dielectric constant and decrease in its adhesion reliability to other substrates. On the other hand, fluoropolymers have very low moisture uptake property and are among the materials with the lowest dielectric constants, especially polymers containing long chains of perfluoroalkyl groups, which have been proved to be very low surface energy materials that can be used to fabricate superhydrophobic and superoleophobic surfaces with valuable potential in self-cleaning, antifreezing, anti-biofouling, anticreeping, etc.³ The combination of the complementary physicochemical properties of polyimide and fluoropolymer is, thus, of great interest in recent years. The plasma polymerization of perfluoroalkyl group-containing monomers has successfully prepared fluorinated polyimides.⁴ Despite the good hydrophobicity and low surface energy of the resulting polyimide films, the method needs a specific plasma polymerization machine with an expensive price. On the other hand, the adhesion of the plasma-deposited fluoropolymers with the substrates via physical bonding may be not very strong. However, rare polyimides with inherent perfluoroalkyl groups in the main chain were developed until now.⁵ The present work exhibits a new hydrophobic polyimide with pendant perfluoroalkyl chains by incorporating the pendant perfluoroalkyl group in the diamine monomer.



Scheme 1. Synthesis of diamine monomer with pendant perfluoroalkyl group. Reagents and conditions: a) SOCl₂, reflux; b) THF/Et₃N; c) ethanol/NH₂NH₂·H₂O, Pd/C.

Firstly, a new diamine monomer, 1H,1H-perfluorooctyl 3,5-diaminobenzoate (PFD), was synthesized via a three-step reaction, as shown in Scheme 1. 3,5-Dinitrobenzoinc acid was firstly transformed into benzoyl chloride by refluxing in SOCl₂ for 24 h, which then give the 1H,1H-perfluorooctyl 3,5-dinitrobenzoate by the condensation reaction with the 1H,1H-perfluorooctanol in anhydrous tetrahydrofuran (THF). Finally, the PFD was obtained by the Pd/C-catalyzed reduction of NO₂ to NH₂ in the presence of hydrazine hydrate. The structure of PFD was confirmed by NMR studies (82% total yield). The ¹H NMR (CDCl₃, 400 MHz, ppm) data were 6.75 (d, J = 2 Hz, 2H, H_{iv}), 6.16 (t, J = 2 Hz, 1H, H_i), 4.30 (q, J = 7.2 Hz, 2H, H_{vii}), 3.65 (s, 4H, H_{iii}). The ¹³C NMR (CDCl₃, 100 MHz, ppm) data were 166.9 (C_{vi}), 147.4 (C_{ii}), 132.4 (C_v), 106.9 (C_i), 105.5 (C_{iv}), 60.8 (C_{vii}).

The polyimide film was finally prepared via the polycondensation of PFD and commercial 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA)⁶ via the previous two-step method,⁷ as shown in Scheme 2. A representative polymerization procedure of polyimides via imidization method is as follows: 0.4443 g (1.0 mmol) of 6FDA was added into a stirring NMP (5 mL) solution of PFD (1.0 mmol, 0.2841 g) under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h, which formed a viscous solution of poly(amic acid) precursor. Then the poly(amic acid)s were poured into a glass substrate and solidified in an oven at each temperature condition (80, 150, 200, and 220 °C) for 1 h. The obtained polyimide films could be removed from the glass by immersing the glass substrate in hot water.

Figure 1 demonstrates the FT-IR spectra evolved from poly(amic acid) and polyimides based on PFD–6FDA. The conversion of imide ring from amic acid is shown according to the disappearance of the amic acid wide absorption peaks at 1650-1700 and 2500-3500 cm⁻¹, together with the appearance



Scheme 2. Synthesis of polyimide with pendant perfluoroalkyl group based on PFD–6FDA.



Figure 1. FT-IR spectra of poly(amic acid) (a) and polyimide (b) based on PFD–6FDA.

of characteristic imide absorption peaks at 1777 cm^{-1} (asymmetrical C=O stretch), 1717 cm^{-1} (symmetrical C=O stretch), 1372 cm^{-1} (C–N stretch), 1115 cm^{-1} , and 743 cm^{-1} (imide ring deformation). The results show that the polyimides have formed and that the conversion from poly(amic acid) to polyimide was basically completed by using thermal imidization method.

Investigation of the thermal properties of the resulting polyimide film shows that its T_g is 235 °C and that its thermal decomposition exhibits a two-step mechanism. As shown in Figure 2, the first decomposition temperature is 270 °C, and before the second decomposition temperature, the weight loss is 24%, which should be caused by the loss of partial pendent perfluoroalkyl groups because of the breakage of weak ester linkages under heating. However, its second decomposition temperature is 520 °C, and the residue at 800 °C is more than 40%, indicating that the resulting polyimides have good thermal stability. On the other hand, both the decomposition temperatures are higher than its T_g , implying the polyimides potential attraction for melt processing.



Figure 2. TGA trace of the polyimide film based on PFD-6FDA.



Figure 3. XPS full survey spectrum of polyimide based on PFD–6FDA (The inset is the high-resolution spectrum of the C1s region of polyimide).

Figure 3 displays the XPS full survey spectra (measured by a PHI-5702 multifunctional X-ray photoelectron spectrometer) of polyimides based on the PFD–6FDA film, which are mainly composed of C, O, and N as well as the presence of largeintensity peaks of the F1s peak at 689.0 eV, the C1s spectra of polyimide based on the PFD–6FDA film (inset of Figure) consist of five components centered at binding energies of 284.4, 285.2, 289.1, 291.5, and 293.8 eV, corresponding to C–C, C–O/C–N, CF₂–CH₂, CF₂–CF₂, and CF₃–CF₂ groups, respectively. This is in good agreement with previous reports.⁶ The surface chemistry composition exhibits a strong F signal with a content of 30.6%, which is higher than the calculated one (28.7%) because of the enrichment of low-surface-energy –CF₃ and –CF₂ groups in the outmost surface.⁸ The high F content in the outmost surface endows the surface with hydrophobicity.

The contact angle (CA) of the surface for water is 95° (Figure 4A), higher than that of the commercial polyimide film (55° for raw Kapton H[®]), indicating better hydrophobicity. The CA of the film for CH₂I₂ is 45° (Figure 4A), and according to the two-liquid geometric method in literature,⁵ the calculated surface free energy of the polyimide film is 37.4 mN m⁻¹. What's more, a superhydrophobic surface with a CA for water of 155° (advancing CA (ACA) = 159° and receding CA (RCA) = 156°) was obtained by directly coating the hydrophobic polyimides on a rough alumina substrate made in our



Figure 4. (A) The profile of water and CH_2I_2 on the polyimide film; (B) SEM image of surface morphology of the rough alumina (The inset is the profile of water droplet on the polyimide modified alumina).

laboratory (Figure 4B),⁸ with no need of traditional modification of rough polyimide film by using low-surface-energy materials like perfluoroalkyl silane.⁹

In conclusion, a new diamine monomer, 1H,1H-perfluorooctyl 3,5-diaminobenzoate was successfully synthesized and characterized in this article, which can be employed in polycondensation with various dianhydride monomers to gain hydrophobic polyimide films. The experimental result shows that the hydrophobic polyimides have been obtained via the condensation of the new diamine monomer (PFD) containing pendent perfluorooctyl group with commercial dianhydride monomer, and the obtained polyimides exhibit excellent thermal stability and fairly high T_g values. This work is financially supported by Key Project of National Nature Science Foundation of China (No. 21204095) and the National Natural Science Foundation of China (No. 51171202).

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