Preparation and Properties of Novel Fluorinated Polyimides Based on 2,2',6,6'-Tetrafluorobenzidine

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ABSTRACT: Fluorinated polyimides were prepared from 2,2',6,6'-tetrafluorobenzidine and four conventional dianhydride monomers by a solution polycondensation reaction followed by a chemical imidization. Polyimide based on 2,2',6,6'-tetrafluorobenzidine and hexafluoroisopropylidene bis(3,4-phthalic anhydride) (6FDA) is soluble in organic solvents such as NMP, DMA, DMF, THF, chloroform, and acetone while those based on 2,2',6,6'-tetrafluorobenzidine and pyromellitic dianhydride (PMDA), benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride (BTDA), diphenylether-3,3',4,4'-tetracarboxylic acid dianhydride (ETDA) are not. Polyimide from 2,2',6,6'-tetrafluorobenzidine and 6FDA possesses high optical transparency at 350–700 nm and has a in-plane refractive index of 1.558 at 632.8 nm. All polyimides exhibit glass transition temperatures above 350°C. They also possess very high thermal stability. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1605–1609, 1998

Key words: polyimide; fluorinated; 2,2',6,6'-tetrafluorobenzidine; preparation; property

INTRODUCTION

The introduction of fluorine and fluorinated groups into polyimide structure has been found to lead to lower dielectric constant,¹⁻⁹ lower moisture absorption,^{1-3,10} lower refractive index,^{1-3,6,9} higher solubility in organic solvents,^{1-3,11} and higher optical transparency.¹⁻³

Apart from hexafluoroisopropylidene bis(3,4phthalic anhydride) (6FDA), very few fluorinated dianhydrides are available because of the difficulties in syntheses. Fluorinated diamines are, however, much easier to obtain.⁶ Because the precursor of a polyimide, polyamic acid, is formed via nucleophilic attack by the diamine at a carbonyl carbon of the dianhydride, the rate of this reaction is dependent upon the electron-donating ability of the amine and the electron affinity of the dianhydride.⁶ Fluorinated aromatic diamines with fluorine or fluorinated substitution *ortho* to the amino groups would not lead to polyimides with large molecular weights by using a conventional polycondensation procedure because of the severe deactivation of these amino groups by the high electronegativity of fluorine.^{5,6} Fluorinated diamines with fluorine or fluorinated substitution *meta* to the amino groups, however, can result in polyimides with large molecular weight.⁶

In this article, the studies on the preparation and characterization of several novel fluorinated polyimides based on a m-fluorine-substituted benzidine, 2,2',6,6'-tetrafluorobenzidine, are presented.

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EXPERIMENTAL

Materials

2,2',6,6'-Tetrafluorobenzidine was synthesized in our lab.¹² PMDA (chemical reagent grade) was purchased from the Shanghai Chemical Reagent Company and used as received. BTDA was prepared from benzophenone-3,3',4,4'-tetracarboxylic acid (purchased from Beijing Tar Chemical Company, industrial product) by a dehydration reaction with an excessive amount of acetic anhydride at the refluxing temperature for 4 h. ETDA (industrial product) was purchased from the Shanghai Synthetic Resin Institute and dried at 190°C for 2 h before use. 6FDA was purchased from Hoester (Lab. Reagent) and recrystallized from acetic anhydride before use. N-methyl-2pyrrolidone (NMP) (analytical reagent grade) was purchased from the Shanghai Chemical Reagent Company. It was dried over molecular sieves and then distilled under a reduced pressure before use. Acetic anhydride (analytical reagent grade) and triethylamine (analytical reagent grade) were purchased from the Shanghai No. 1 Chemical Reagent Factory and Xin Da Chemical Factory, respectively, and used as received.

Preparation of Polyimides

Fluorinated polyimides were prepared by the polycondensation between 2,2',6,6'-tetrafluorobenzidine and pyromellitic dianhydride (PMDA), benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride (BTDA), diphenylether-3,3',4,4'-tetracarboxylic acid dianhydride (ETDA), and hexafluoroisopropylidene bis(3,4-phthalic anhydride) (6FDA) in NMP (solids content: 15 wt %) with efficient agitation at 25°C for 24 h followed by a chemical imidization with acetic anhydride and triethylamine [diamine/acetic anhydride/triethylamine = 4 : 36 : 9 (molar ratio)] at 25°C for 48 h. The resultant polyimides were precipitated in distilled water and dried at 90°C under vacuum (see Scheme 1).

Characterization of Polyimides

The IR spectra of polyimides were recorded on a PE 983 Infrared Spectrophotometer on their film form. The films were cast from their NMP solution and dried under vacuum at 90°C for 24 h.

The UV-visible spectra of polyimide films were recorded on a Shang Fen 7530 UV-Visible Spec-



trophotometer (manufactured by Shanghai Analytical Instruments Company). The films were cast on the quartz surface from their NMP solutions and dried under vacuum at 90°C for 24 h.

The solubility of polyimides was determined by observing the solubility of the solid polyimide samples in various solvents at room temperature.

The intrinsic viscosities of polyimides were measured with an Ubbelodhe Viscometer using NMP as the solvent at 30°C. The standard concentration was 1 g/dL.

The in-plane refractive indices and thickness of polyimides were measured using an optical waveguide method at 25°C with a wavelength of 632.8 nm.

The glass transition temperatures (T_g) of polyimides were obtained from their DSC spectra. The DSC spectra were recorded on a PE DSC7 under the protection of N₂. The scan rate was 20°C/min. All samples experienced two heating processes from 25 to 400°C, and the second one was recorded.

The thermal stability of polyimides was characterized by their TGA spectra. The TGA spectra were recorded on a PE TGA7 under the protection of N_2 . The scan rate was 20°C/min.

RESULTS AND DISCUSSION

Polyimide prepared from 2,2',6,6'-tetrafluorobenzidine and PMDA was named PI-pm. Those from 2,2',6,6'-tetrafluorobenzidine and BTDA, ETDA,



Figure 1 Infrared spectrum of PI-6f.

and 6FDA were named PI-bt, PI-et, and PI-6f, respectively.

Preparation of Polyimides

Because of the deactivation effect of the fluorine substitutions, the fluorinated diamines used in this study possesses much lower reactivity compared to the conventional nonfluorinated diamines. To obtain a high molecular weight, a much longer polycondensation time (24 h at 25°C) was used. (The polycondensation reaction for the preparation of conventional polyamic acids requires only a few hours.)

Infrared Spectrum

Infrared spectrum of PI-6f was shown in Figure 1. The absorption bands at 1790 cm^{-1} and 1732 cm^{-1} characteristic of C=O stretching in imide groups and that at 1383 cm^{-1} characteristic of C-N stretching in imide groups were clearly observed. The observation of these bands clearly indicates the existence of imide groups. In addition, the disap-

pearance of the absorption at ~ 3400 cm⁻¹ characteristic of —COOH and —NH— groups further support the success of the synthesis of polyimide. The absorption bands at 1285 cm⁻¹ and 1258 cm⁻¹ are characteristic of C—F stretching in hexafluoroisopropylidene groups.

Solubility

Gels were formed upon the chemical imidization processes of PI-pm, PI-bt, and PI-et. PI-6f, however, was soluble in NMP after the imidization. It possesses great solubility: it was soluble not only in strong polar solvents such as DMA, DMF, and DMSO, but also in conventional solvents such as THF, chloroform, and even acetone. It was not soluble in solvents such as toluene, benzene, ethanol, and cyclohexane. It should be pointed out that PI-6f was observed to be insoluble in *m*-cresol, which is the solvent for most of organosoluble polyimides, at room temperature. The higher solubility of PI-6f mainly comes from the existence of hexafluoroisopropylidene groups in the backbone, which leads to



Figure 2 UV-Vis spectrum of PI-6f film $(1.1 \ \mu m)$.

loose chain packing.¹³ The introduction of four fluorine atoms to the benzidine molecule does not result in sufficient solubility in the cases of

PI-pm, PI-bt, and PI-et because of the high rigidity of the benzidine structure.

Intrinsic Viscosity

The intrinsic viscosity of PI-6f using NMP as the solvent at 30° C was found to be 0.32 dL/g.

Optical Transparency

UV-Vis spectrum of a PI-6f film $(1.1 \ \mu m)$ was shown in Figure 2. It was observed that the sample possesses high optical transparency: the transmittance at 350–700 nm was above 90%. The cutoff wavelength was about 305 nm. Two small absorption bands were also observed at about 220 and 270 nm, respectively.

Refractive Indices

The in-plane refractive index of PI-6f measured at 632.8 nm was observed to be 1.558 at 25°C. This datum was much smaller than the conven-



Figure 3 DSC spectrum of PI-6f. N₂ protection; scan rate: 20°C/min.

tional unfluorinated aromatic polyimides because of the introduction of highly electronegative fluorine atoms.¹⁴

Glass Transition Temperature

The DSC spectrum of PI-6f was shown in Figure 3 and a T_g of 362.2°C was observed. Those of PI-bt and PI-et are found to be 353.2 and 359.7°C, respectively (see Table I). 6FDA, BTDA, and ETDA seem to pose similar rigidity to the polyimide backbone. T_g s obtained in this study are higher than polyimide prepared from 6FDA and 2,2′-ditrifluoromethyl benzidine, which was reported to have a T_g of 335°C.¹⁵ No obvious glass transition was observed from PI-pm in the temperature range of 50–400°C.

Thermal Stability

The TGA spectrum of PI-et was shown in Figure 4, from which an initial decomposition temperature (T_d) of 623.9°C was observed. T_d s of other polyimides were listed in Table I.

It was observed that the order of the thermal stability is: PI-pm \rangle PI-et \rangle PI-bt \rangle PI-6f. Polyimide prepared from PMDA possesses the highest thermal stability, and that prepared from 6FDA possesses the lowest thermal stability.

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Table IGlass Transition Temperatures (T_g) and Initial Thermal DecompositionTemperatures (T_d) of Polyimides

Sample	PI-pm	PI-bt	PI-et	PI-6f
$T_g \ (^{\circ}\mathrm{C})^{\mathrm{a}}$ $T_d \ (^{\circ}\mathrm{C})^{\mathrm{a}}$	/ 651.0	$353.2 \\ 602.0$	$359.7 \\ 623.9$	$362.2 \\ 541.8$

^a Scan rate: 20°C/min. N₂ protection.



Figure 4 TGA spectrum of PI-et. N_2 protection; scan rate: 20°C/min.

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