

Study on the Preparation and Properties of Copolyimides Based on Hexafluoroisopropylidene bis(3,4-phthalic anhydride) and 1,12-Di(4-aminophenoxy)dodecane

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Abstract: Copolyimides were prepared from hexafluoroisopropylidene bis(3,4-phthalic anhydride) (6FDA), 1,12-di(4-aminophenoxy)dodecane and 4,4'-diaminodiphenylether through a solution co-polycondensation reaction followed by a chemical imidization reaction. It was observed that copolyimides prepared with any diamine molar ratio studied (1,12-di(4-aminophenoxy)dodecane/4,4'-diaminodiphenylether = 7/3 ~ 1/9) were soluble in polar organic solvents such as NMP, DMA, DMF and *m*-cresol, THF and chloroform, while the corresponding homopolyimides were insoluble. WAXD results show a clear relationship between the crystallinity tendency and the solubility of polyimides. High crystallinity tendency leads to low organo-solubility. The glass transition temperature of a copolyimide was in good agreement with the Fox's Equation for random copolymers. The long flexible chains in the backbone of copolyimides are the least thermally stable part.

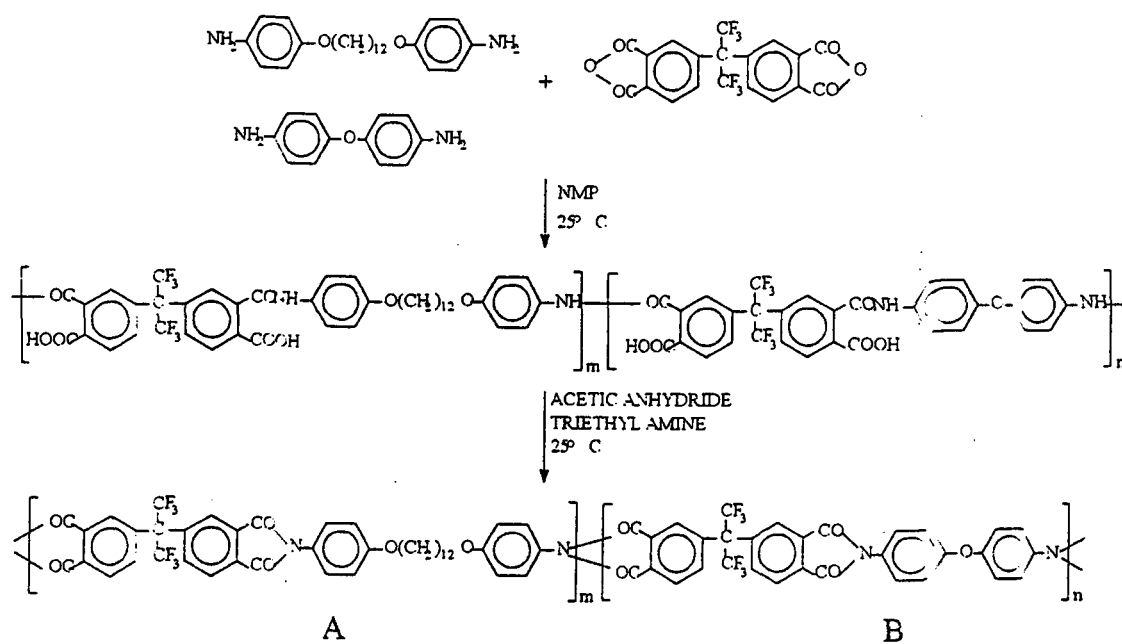
INTRODUCTION

Although the conventional Kapton type polyimide exhibits great thermal stability and excellent mechanical and electrical properties¹, the applications of such a polyimide are restricted because of its poor solubility in organic solvents and high glass-transition temperature that caused difficulty in fabrication. Intensive studies have been carried out to improve the processability of polyimides. One of the major target is to improve the solubility of polyimides in organic solvents. Several approaches such as the incorporation of flexible linkage in the main chain to reduce the packing force², the introduction of bulky pendant groups to the main chain to enhance the free volume³⁻⁴, replacing aromatic groups with alicyclic groups⁵⁻⁹ and the introduction of fluorinated groups¹⁰⁻¹³ have been taken. However, the success of all these approaches would largely rely on the design and synthesis of new polyimide monomers, which sometimes could be time consuming and costly. On the other hand, the solubility of polyimides may be effectively improved by the way of copolymerization. A copolyimide possesses much lower molecular regularity compared to the corresponding homopolyimides. This decrease in the regularity may lead to the decrease of intermolecular interaction, which in turn increases the solubility of the copolyimide. Furthermore, a copolyimide can be prepared from existing monomers and its properties may be adjusted by the variation of the ratio of the comonomers.

We studied polyimides based on α , ω -di(4-aminophenoxy)alkanes and hexafluoroisopropylidene bis(3,4-phthalic anhydride) (6FDA)¹⁴. It was observed that polyimides prepared from 6FDA and 1,4-di(4-aminophenoxy)butane, or 1,6-di(4-aminophenoxy)hexane, or 1,8-di(4-aminophenoxy)octane, or 1,10-di(4-aminophenoxy)-decane were soluble in organic solvents. That from 6FDA and 1,12-di(4-aminophenoxy)-dodecane was, however, insoluble. In this paper, we study the effect of copolymerization by introducing another conventional diamine, 4,4'-diaminodiphenylether, on the solubility and thermal properties of copolyimides. The crystallinity of these polyimides are also studied.

EXPERIMENTAL

Copolyimides were prepared by a polycondensation reaction using hexafluoroisopropylidene bis(3,4-phthalic anhydride) (6FDA) and two diamine monomers: 1,12-di(4-aminophenoxy)dodecane (DAD) and 4,4'-diaminodiphenylether (ODA) in N-methyl-2-pyrrolidone (NMP) (solid content: 15%) with efficient agitation at 25 °C for 4 hours followed by a chemical imidization with acetic anhydride and triethylamine (diamine/acetic anhydride/triethylamine = 4:36:9 (molar ratio)) at 25 °C for 16 hours¹⁴. The chemical imidization condition has been studied in our laboratory. The amounts of acetic anhydride and triethylamine used and the time are sufficient to achieve a maximum imidization degree¹⁴. The resultant polyimides were precipitated in distilled water and dried at 90 °C under vacuum. The polymerization and the structural diagram of copolyimides are shown in Scheme 1.



Scheme 1 Polymerization and Structural Diagram of Copolyimides

Note: The molecular structure in this scheme does not indicate either polyamic acid or polyimide is a block copolymer.

The infrared spectra of copolyimides were recorded on a Perkin Elmer Paragon 1000 Infrared Spectrophotometer. The intrinsic viscosities of copolyimides were measured using NMP as the solvent at 30 °C. The standard concentration was 1g/dl. The molecular weights of copolyimides were determined on a Perkin Elmer Series 200 Gel Permeation Chromatography (GPC) equipped with a refractive index detector and a PLgel 7.5mm ID column. The GPC measurements were carried out using 0.2 w/v% polyimide solutions in tetrahydrofuran (THF) at 25 °C with THF as the eluent. Polystyrene standards provided the molecular weight calibration. The solubility of copolyimides was determined by observing the solubility of the solid polyimide samples in various solvents. The wide-angle X-ray diffraction (WAXD) spectra of polyimides were recorded on a D-max 3A X-Ray Diffractometer. Powder samples were used for all polyimides. The scan rate was 1.0°/min. The glass transition temperatures (T_g) of polyimides were obtained from their differential scanning calorimetry (DSC) spectra. The DSC spectra were recorded on a PE DSC7 under the protection of N_2 . The scan rate was 20 °C/min. All samples experienced two heating processes from 25 to 300 °C and the second one was recorded. The thermal stability of

polyimides was characterized by their thermogravimetric analysis (TGA) spectra. The TGA spectra were recorded on a PE TGA7 under the protection of N_2 . The scan rate was $20\text{ }^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The copolyimide prepared from 6FDA and DAD/ODA was named PI-3/7 when the molar ratio of DAD and ODA was 3/7. Similarly, copolyimides were named PI-0/10, PI-1/9, PI-5/5, PI-7/3 and PI-10/0 when the molar ratios of DAD and ODA were 0/10, 1/9, 5/5, 7/3 and 10/0, respectively. Polyimide prepared from 6FDA and 1,10-di(4-aminophenoxy)decane was named F-10.

Infrared Spectra of Copolyimides

Fig. 1 is the infrared spectrum of PI-3/7. 1784cm^{-1} and 1727cm^{-1} are the characteristic absorption bands of C=O stretching of the imide groups. 1379cm^{-1} is the characteristic absorption band of C-N stretching of the imide groups¹. The appearance of these characteristic bands of an imide group and the disappearance of the absorption at about 3400cm^{-1} , which corresponds to the -COOH and -NH absorption in the precursor of the copolyimide (copolyamic acid) clearly indicate that copolyimides have been prepared and a maximum imidization degree has been achieved.

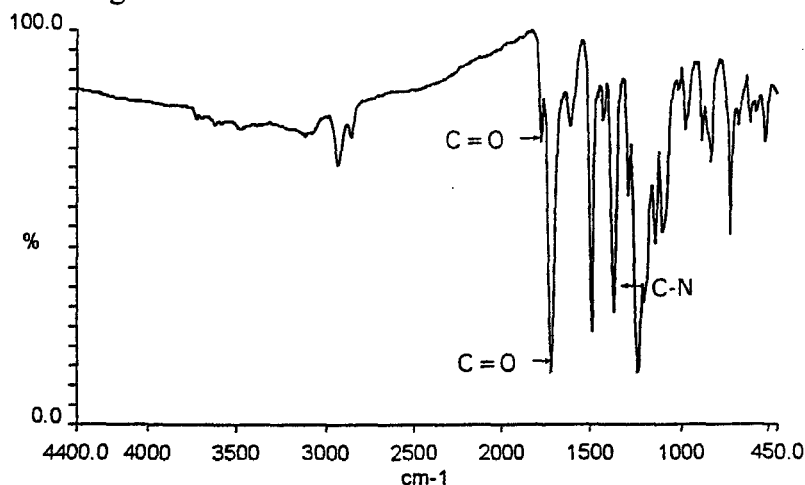


Fig. 1 IR Spectrum of PI-3/7

Intrinsic Viscosities and the Molecular Weights of Copolyimides

The intrinsic viscosities of PI-1/9, PI-3/7 and PI-5/5 measured at $30\text{ }^\circ\text{C}$ in NMP and the molecular weights measured with GPC are listed in Table 1. The intrinsic viscosity of a copolyimide is in the range of 0.43-0.57 dl/g, which corresponds to a number average molecular weight (M_n) range of 12000-21000 and a weight average molecular weight (M_w) range of 32000-54000 when polystyrene was used as the molecular weight calibration.

Solubility of Copolyimides

Solubility of copolyimides in various organic solvents is listed in Table 2.

It is observed that neither homopolyimide prepared from 6FDA and a "rigid" diamine monomer ODA or 6FDA and a "flexible" diamine monomer DAD can be dissolved in organic solvents. The copolymers prepared from 6FDA, DAD and ODA are, however, soluble in strong polar solvents such as N,N-dimethyl acetamide (DMA), N,N-dimethyl formamide (DMF), NMP, m-cresol, THF and weak polar solvent such as chloroform in the DAD/ODA molar ratio range studied. They can not be dissolved in solvents such as ethanol,

acetone and toluene. This result clearly indicates that to simply increase the flexibility of the molecular chain may not increase the solubility sufficiently: Although polyimide prepared from 6FDA and DAD possesses high molecular chain flexibility, it also exhibits very high structural regularity, which may lead to great intermolecular interaction and low solubility. Meanwhile, to reduce the regularity by the way of copolymerization could increase the solubility efficiently.

Table 1 Intrinsic Viscosities and Molecular Weights of Copolyimides

Sample	$[\eta]^a$ (dl/g)	M_n^b	M_w^b	M_w/M_n^b
PI-1/9	0.47	12161	32550	2.68
PI-3/7	0.57	21277	54002	2.54
PI-5/5	0.43	19563	41048	2.10
PI-7/3	/	13893	34765	2.50

a: measured at 30 °C using NMP as the solvent, standard concentration: 1g/dl.

b: measured on a GPC at 25 °C using THF as the solvent and the eluent. Polystyrene standards provided the molecular weight calibration.

Table 2. Solubility of Copolyimides in Various Organic Solvents (25 °C)

Samples	acetone	ethanol	toluene	chloroform	THF	DMA	DMF	NMP	<i>m</i> -cresol
PI-0/10	—	—	—	—	—	—	—	—	—
PI-1/9	—	—	—	+	+	+	+	+	+
PI-3/7	—	—	—	+	+	+	+	+	+
PI-5/5	—	—	—	+	+	+	+	+	+
PI-7/3	—	—	—	+	+	+	+	+	+
PI-10/0	—	—	—	—	—	—	—	—	—

+: soluble; —: insoluble.

Crystallinity of Polyimides and Copolyimides

WAXS spectra of F-10, PI-10/0 and PI-5/5 are shown in Fig.2. It is observed that no crystalline peak is visible for polyimide prepared from 6FDA and 1,10-di(4-aminophenoxy)decane (F-10) (see Scheme 1). As the length of the $-(CH_2)_m-$ chain in a polyimide increases from $m=10$ in F-10 to $m=12$ in PI-10/0, crystal is formed: WAXS spectrum of PI-10/0 exhibit clearly crystal peaks. This increase in the crystallinity tendency may result from the increase in the structural regularity as the length of the $-(CH_2)_m-$ chain is increased. This regularity and thus the crystallinity tendency could be effectively reduced using copolymerization: No obvious crystal peaks are visible in the WAXD spectrum of the copolyimide from 6FDA and DAD and ODA (PI-5/5).

The solubility test and WAXD results show a clear relationship between the solubility and the crystallinity tendency. The increase in the crystallinity tendency from PI-10 to PI-10/0 leads to a decrease in the solubility: PI-10 is organo-soluble while PI-10/0 is not; Similarly, the decrease in the crystallinity tendency from PI-10/0 to PI-5/5 leads to an increase in the solubility: PI-10/0 is not organo-soluble, while PI-5/5 is.

Glass Transition Temperatures of Copolyimides

Glass transition temperatures of copolyimides measured with DSC are listed in Table 3.

The relationship between T_g and the weight ratio of the copolyimide sequence B (see Scheme 1) of a copolyimide is shown in Fig. 3. The relationship is clearly in agreement with the Fox's Equation: $1/T_g = W_a/T_{ga} + W_b/T_{gb}$,

where T_{ga} and T_{gb} are the glass transition temperatures of the two homopolyimides, respectively; W_a and W_b are the weight ratios of sequences A and B, respectively; T_g is the glass transition temperature of the copolymer.

This result indicates that copolyimides studied are basically random copolymers.

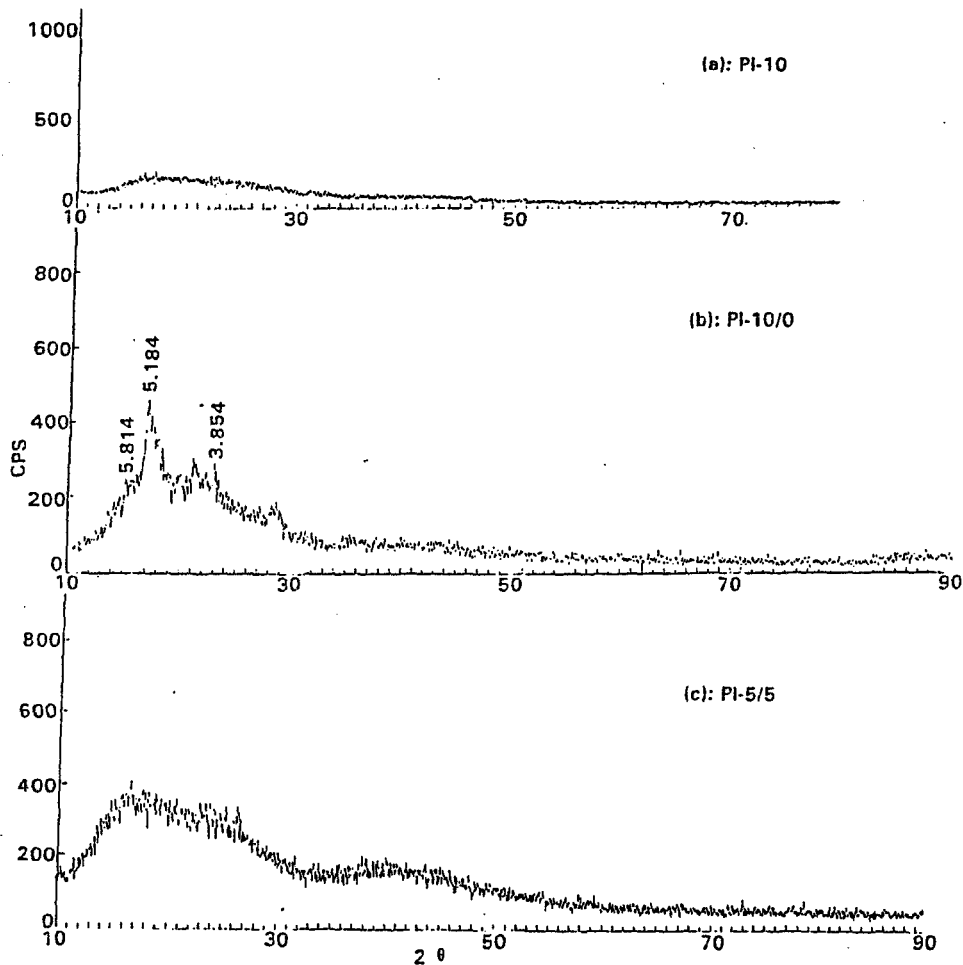


Fig. 2 WAXD Spectra of Polyimides PI-10 (a), PI-10/0 (b) and PI-5/5 (c)

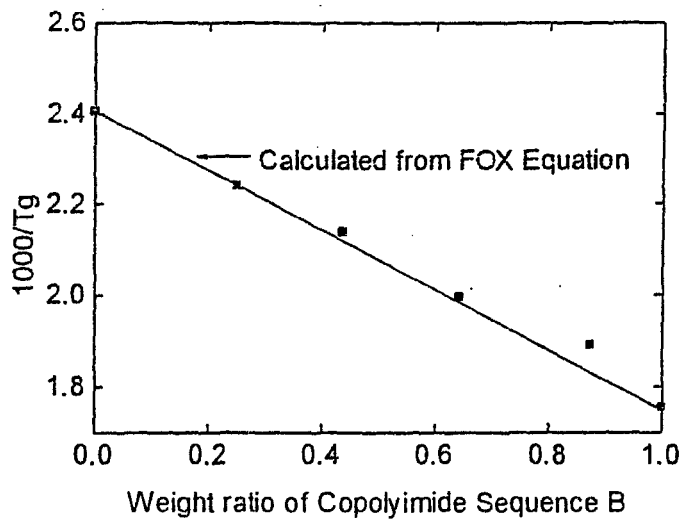


Fig. 3 Relationship between T_g and Weight Ratio of Copolyimide Sequence B

Table 3 Glass Transition Temperatures of Polyimides

Sample	PI-0/10	PI-1/9	PI-3/7	PI-5/5	PI-7/3	PI-10/0
T _g (°C) (tested data)	296.7	255.6	227.9	194.1	173.1	142.6
T _g ^a (°C) (calculated from Fox's Equation)	/	271.2	229.8	197.8	172.6	/

a: measured with DSC; N₂ protection; scan rate: 20 °C/min.

Thermal Stability of Copolymers

The initial thermal decomposition temperature (T_d) of polyimides obtained from their TGA spectra are listed in Table 4. It is observed that the homopolyimide prepared from 6FDA and ODA possesses a T_d of 550 °C. When the long flexible chain -O(CH₂)₁₂O- is introduced to the backbone of polyimide, T_d is decreased to about 480 °C. Therefore, the long flexible chain is the least thermally stable part of a polyimide.

Table 4 Initial Thermal Decomposition Temperature (T_d) of Polyimides

Sample	PI-0/10	PI-1/9	PI-3/7	PI-5/5	PI-7/3	PI-10/0
T _d ^a (°C)	549.8	473.2	471.4	460.2	444.9	480.0

a: N₂ protection , scan rate: 20 °C/min.

Acknowledgments: This study is funded by the “ Shu Guang Project ” of the Shanghai Educational Committee. The authors would like to express their thanks hereby.

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