Preparation and Properties of Novel Polyimides with Side Chains Containing Biphenyl Units

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ABSTRACT: Novel polyimides with side chains containing various methylene spacers and biphenyl end groups were prepared. They were characterized by the inherent viscosity, mechanical properties, and solubility and by Fourier transform infrared, [1]H-nuclear magnetic resonance, X-ray diffraction, differential scanning calorimetry, and thermogravimetric analysis. All the polyimides with biphenyl side groups could be formed into tough films. WAXD showed that all the films were apparently amorphous. By incorporating side chains, the solubility was greatly enhanced and all the polyimides with side chains showed good solubility in polar aprotic solvents, while the high moduli and strength of typical polyimides were maintained and even improved. However, the heat-resistant properties such as the thermal stability and glass transition temperature were generally decreased. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3291–3298, 2003

Key words: polyimides; synthesis; modification; strength

INTRODUCTION

Aromatic polyimides have long been known for their outstanding thermooxidative stability, mechanical strength, and resistance to environmental degradation and are widely used in electrical and electronic applications. However, most polyimides suffer from insolubility and infusibility, which make their processing difficult and expensive. Much effort, therefore, has been spent on synthesizing processable polyimides that reasonably maintain the desired properties. Extensive studies on the structure–property relationship of polyimides have indicated that the problems in processing conventional aromatic polyimides are due to the inherent molecular features of aromatic polyimides, such as the molecular chain stiffness, high polarity, and high intermolecular association force. Thus, the structural modifications to attain processable polyimides have been carried out by introducing alkyl groups[1–3] and bulky substitutes, such as pendent aryl or heterocyclic rings.[4–11]

In this study, a series of novel diamines containing various side chains with biphenyl groups was synthesized (see Fig. 1). One successful approach to improving the processability of polyimides is the synthesis of copolyimides. Based on this, three novel polyimides with various side chains containing biphenyl units were prepared by polycondensation of 3,5-diaminobenzoate and 4-aminophenyl ether (ODA) with aromatic dianhydride in N-methyl-2-pyrrolidone (see Fig. 2). As a reference, polyimide that does not have side groups was also prepared by polycondensation of *m*-phenylenediamine (*m*-PDA) and ODA with the same aromatic dianhydride. Systematic studies were carried out to investigate the effects of incorporating various side groups into polyimides on their physical properties. Some recent publications have suggested that polyimides with side chains containing mesogenic units generate high pretilt angles of liquid crystals by rubbing[12–15]; thus, this class of polyimides may potentially be important for technical applications as high-performance alignment-layer materials in a liquid crystal display.

EXPERIMENTAL

Materials

3,5-Dinitrobenzoic acid and 2-chloroethanol were obtained from the Shanghai Wulian Chemical Corp. (Shanghai, China), 4-hydroxybiphenyl was purchased from Fluka (Switzerland), and 4-dimethylaminopyridine, 6-chlorohexanol, and 5% palladium on activated carbon (from Acros Organics, New Jersey) were used as received. Reagent-grade 4,4′-oxydiphthalic anhydride (ODPA), from the Shanghai Institute of Synthetic Resins (Shanghai, China), was used after drying at 180°C under
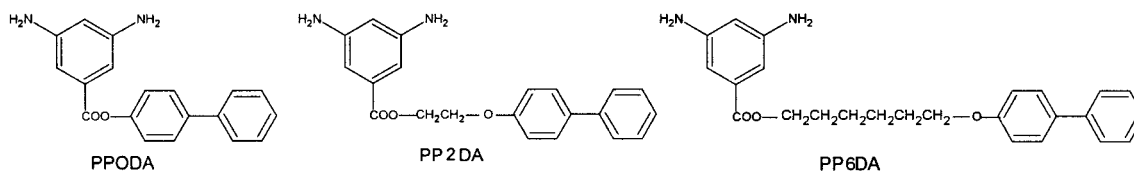
Figure 1 Diamines containing biphenyl side group.

a vacuum for 5 h. ODA and *m*PDA (from the Shanghai Institute of Synthetic Resins) were used as received. *N,N*-Dimethylformamide (DMF) and *N*-methyl-2-pyrrolidinone (NMP, Qunli Chemical Reagents Corp., Shanghai, China) were purified by vacuum-distillation over phosphorus pentoxide and stored over 4-Å molecular sieves. Tetrahydrofuran (THF), methylene chloride (MC), and triethylamine (TEA) from the Chengdu Kelong Chemical Reagents Corp. (Chengdu, China) were dried by 4-Å molecular sieves before use.

Measurements

Uncorrected melting temperatures were determined using an X4 microscopic melting-point apparatus using a ramping rate of 1°C/min. X-ray diffraction measurements were performed at room temperature using Ni-filtered CuKα radiation on a Rigaku D/MAX-Ra diffractometer consisting of a rotating anode X-ray generator operated at 40 kV × 80 mA. FTIR (KBr pellet) spectra were recorded on a Nicolet 560 Fourier transform spectrometer. Proton nuclear magnetic resonance (¹H-NMR) spectra were measured using a Bruker-ACE 200-MHz NMR spectrometer. DSC measurements were made using a TA Instruments DSC

2910 at a heating rate of 10°C/min and TGA thermograms were taken using a TA Instruments TGA2950 at a heating rate of 20°C/min under a nitrogen flow. Intrinsic viscosity [η] measurement of synthesized poly(amic acid)s was carried out in NMP at 25.0°C using an Ubbelohde suspended level capillary viscometer. Tensile properties were measured on an Instron Model 4505 universal tester with a crosshead speed of 5 mm/min. Measurements were performed at room temperature with film specimens 1.0 cm wide, 6.0 cm long, and about 0.03 mm thick. The reported data are average values of at least five replica tests.

Synthesis of monomers

4-biphenyl-3,5-diaminobenzoate (PP0DA) (Fig. 3)

Into a 100-mL round-bottomed flask equipped with a magnetic stirrer was placed 10.61 g (0.05 mol) of 3,5-dinitrobenzoic acid and approximately 6 mol equiv of thionyl chloride. The flask was equipped with a condenser and heated to reflux with an oil bath. After refluxing for 5 h, the excess thionyl chloride was removed by distillation under reduced pressure. Resi-
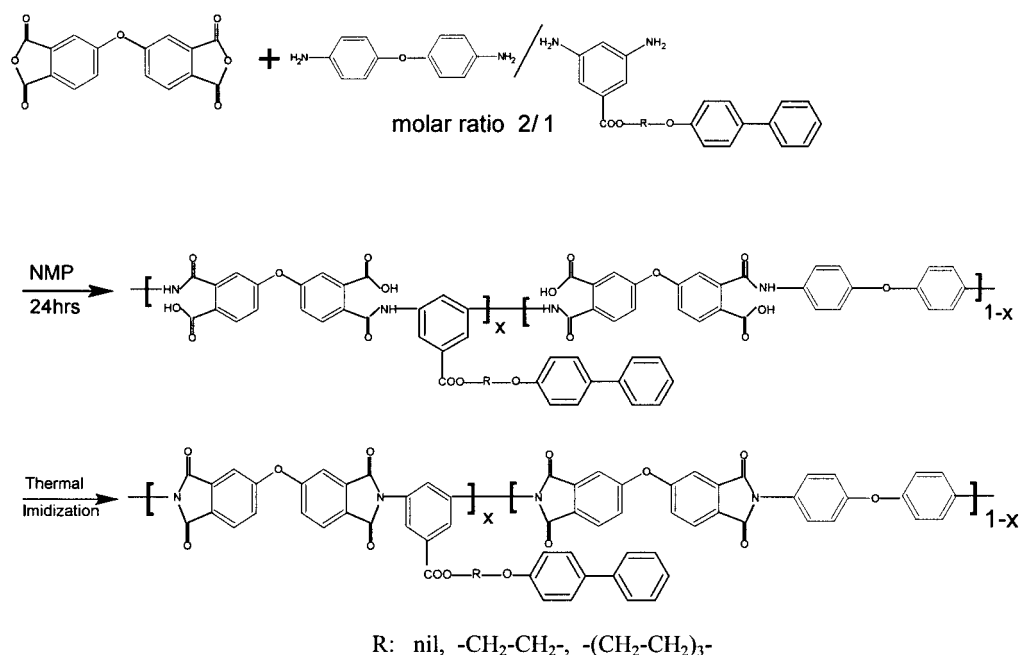

R: nil, -CH₂-CH₂-, -(CH₂-CH₂)₃-

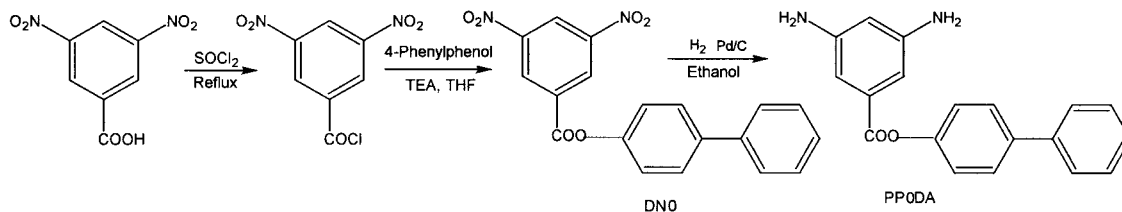**Figure 2** Preparation of polyimides with biphenyl side groups.

Figure 3 Synthetic route of diamine PP0DA.

due thionyl chloride was removed by adding 20 mL of n-hexane to the solution and with continuous distillation under a vacuum. The acid chloride product was isolated as a light yellow crystal.

A flask equipped with a magnetic stirrer was charged with a solution of 4-phenylphenol 8.5 g (0.05 mol) and triethylamine 5.6 g (0.055 mol) in 80 mL dry THF. The prepared acid chloride dissolved in 40 mL dry THF was added dropwise to the stirred solution at 0°C. The mixture was stirred at ambient temperature for 12 h and was subsequently poured into a large amount of water. The light yellow solid precipitate was filtered off, washed with dilute NaOH and then with water, and dried under a vacuum to yield 4-biphenyl-3,5-dinitrobenzoate. A purified sample was obtained by recrystallization from THF (mp 224–226°C; yield 92%).

FTIR (KBr), cm^{-1}: 1738 (C=O); 1554, 1345 (NO2); 1488 (aromatic) 1264, 1148 (C—O—C). ^{1}H-NMR (CDCl3), δ (ppm): 9.34–9.30 (m, 3H, aromatic *ortho* to NO2); 7.70–7.25 (m, 9H, aromatic of biphenyl).

A hydrogenation flask was charged with a mixture of 4-biphenyl-3,5-dinitrobenzoate (7.3 g, 0.02 mol), ethanol (150 mL), and a catalytic amount of 10% palladium on activated carbon. The hydrogen was introduced continually for 24 h at about 50°C. The catalyst

was then filtered off and the solution was rotary-evaporated to a yield light yellow diamine PP0DA. A purified sample was obtained by recrystallization from toluene/petroleum ether (mp 172–173; yield 83%).

FTIR (KBr), cm^{-1}: 3424, 3343 (N—H stretching); 1710 (C=O); 1488 (aromatic); 1203 (C—O—C). ^{1}H-NMR (CDCl3), δ (ppm): 7.64–7.34 (m, 9H, aromatic of biphenyl); 6.94 (s, 2H, aromatic *ortho* to C=O); 6.24 (s, 1H, aromatic between NH2).

2-(4-phenylphenoxy)ethyl-3,5-diaminobenzoate (PP2DA) (Fig. 4)

4-Phenylphenol, 0.1 mol, was dissolved in 150 mL hot ethanol, the mixture was stirred for 30 min, and 0.11 mol potassium hydroxide in 30 mL water was added and the mixture then stirred for another 30 min. 2-Chloroethanol, 0.11 mol, was then added and the mixture refluxed for 24 h. The solution was then diluted with an equal volume of water and ethanol was distilled off. The scalelike precipitate was filtered and washed with hot dilute potassium hydroxide and water. A purified sample of 2-(4-phenyphenoxy)ethanol with an mp of 120–121°C was obtained by recrystallization from methanol (18.2 g; yield 85%).
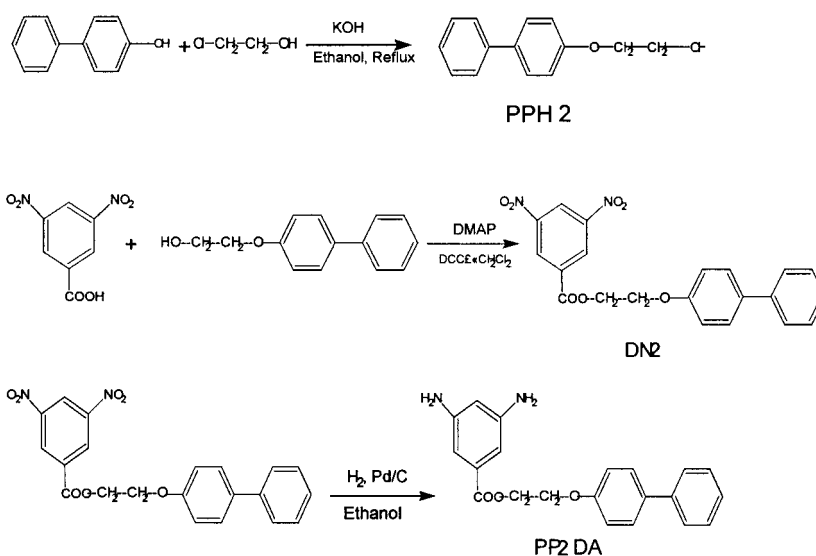

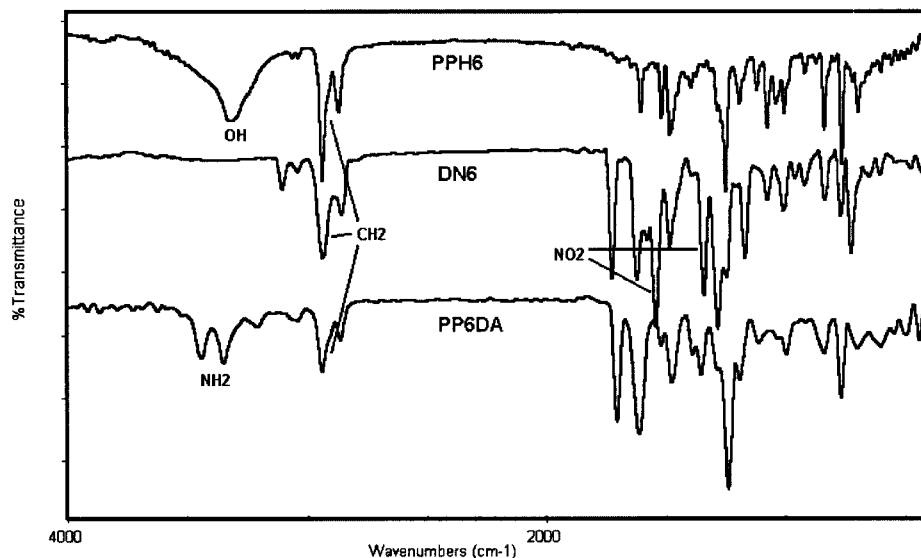**Figure 4** Synthetic route of diamine PP2DA.

Figure 5 FTIR of compounds PPH6, DN6, and PP6DA.

FTIR (KBr), cm^{-1}: 3500–3150 (OH); 2932, 2873 (CH2 stretching); 1255 (C—O—C). ^{1}H-NMR (CDCl3), δ (ppm): 7.56–6.87 (m, 9H, aromatic of biphenyl); 4.13 (t, 2H, ArCOO—CH2—); 3.99 (t, 2H, —CH2—OAr); 2.04 (s, 1H, OH).

3,5-Dinitrobenzoic acid, 0.02 mol (4.3 g), 2-(4-phenylphenoxy)ethanol, 0.02 mol (4.3 g), dicyclohexyl-carbodiimide, 0.021 mol, 4-dimethylaminopyridine, 0.0002 mol, and methylene chloride, 200 mL, were stirred at room temperature for 24 h. After the precipitate was removed by filtration, the filtrate was evaporated on a rotary evaporator to form a 5.9-g solid. Purified 2-(4-phenylphenoxy)ethyl-3,5-dini-trobenzoate was obtained by recrystallization from acetone as yellow crystal (mp 150–151°C, yield 81%).

FTIR (KBr), cm^{-1}: 2938, 2881 (CH2 stretching); 1727 (C=O); 1546, 1348 (NO2); 1488 (aromatic); 1287,1169 (C—O—C). ^{1}H-NMR (CDCl3), δ (ppm): 9.20–9.16 (m, 3H, aromatic *ortho* to NO2); 7.54–6.98 (m, 9H, aromatic of biphenyl); 4.84–4.80 (t, 2H, ArCOO—CH2—); 4.43–4.38 (t, 2H, —CH2—OAr).

The dinitro compound was hydrogenated in ethanol according to the procedure described for diamine PP0DA. The resulting diamine was recrystallized from toluene/petroleum ether as yellow crystals (mp 158–159°C, yield 80%).

FTIR (KBr), cm^{-1}: 3448, 3354 (N—H stretching); 2922, 2870 (CH2 stretching); 1707 (C=O); 1487 (aromatic); 1237 (C—O—C). ^{1}H-NMR (CDCl3), δ (ppm): 7.56–7.25 (m, 9H, aromatic of biphenyl); 7.03–6.99 (s, 2H, aromatic *ortho* to C=O); 6.77 (s, 1H, aromatic between NH2); 4.64–4.60 (t, 2H, ArCOO—CH2—); 4.35–4.30 (t, 2H, —CH2—OAr).

6-(4-phenylphenoxy)hexyl-3,5-diaminobenzoate (PP6DA)

6-(4-Phenylphenoxy)hexanol was obtained as a white solid according to the procedure described for 2-(4-phenylphenoxy)ethanol. It was recrystallized from ethanol (mp 104–105°C; yield 87%) (Figs. 5 and 6).

FTIR (KBr), cm^{-1}: 3550–3150 (OH); 2937, 2867 (CH2 stretching); 1252 (C—O—C). ^{1}H-NMR (CDCl3), δ (ppm): 7.56–6.94 (m, 9H, aromatic of biphenyl); 4.00 (t, 2H, ArCOO—CH2—); 3.66 (t, 2H, —CH2—OAr); 1.86–1.44 (m, 8H, the rest —CH2—).

The dinitro compound was obtained as a yellow solid in 70% yield according to the procedure described for 2-(4-phenylphenoxy)ethyl-3,5-dinitroben-zoate. It was recrystallized from acetone as yellow crystal (mp 103–105°C; yield 80%).

FTIR (KBr), cm^{-1}: 2931, 2852 (CH2 stretching); 1728 (C=O); 1545, 1344 (NO2); 1490 (aromatic); 1292,1170 (C—O—C). ^{1}H-NMR (CDCl3), δ (ppm): 9.18–9.13 (m, 3H, aromatic *ortho* to NO2); 7.54–6.91 (m, 9H, aromatic of biphenyl); 4.50–4.35 (t,2H, ArCOO—CH2—); 4.04–3.98 (t, 2H, —CH2—OAr); 1.92–1.55 (m, 8H, the rest —CH2—).

The dinitro compound was hydrogenated in ethanol according to the procedure described for diamine PP0DA. The resulting diamine was recrystallized from toluene/petroleum ether as yellow crystal (mp 128–129°C; yield 78%).

FTIR (KBr), cm^{-1}: 3438, 3348 (N—H stretching); 2939, 2864 (CH2 stretching); 1707 (C=O); 1487 (aromatic); 1238, (C—O—C). ^{1}H-NMR (CDCl3), δ (ppm): 7.56–7.25 (m, 9H, aromatic of biphenyl); 6.97–6.93 (s, 2H, aromatic *ortho* to C=O); 6.77 (s, 1H, aromatic between NH2); 4.31–4.24 (ArCOO—CH2—); 4.03–3.97
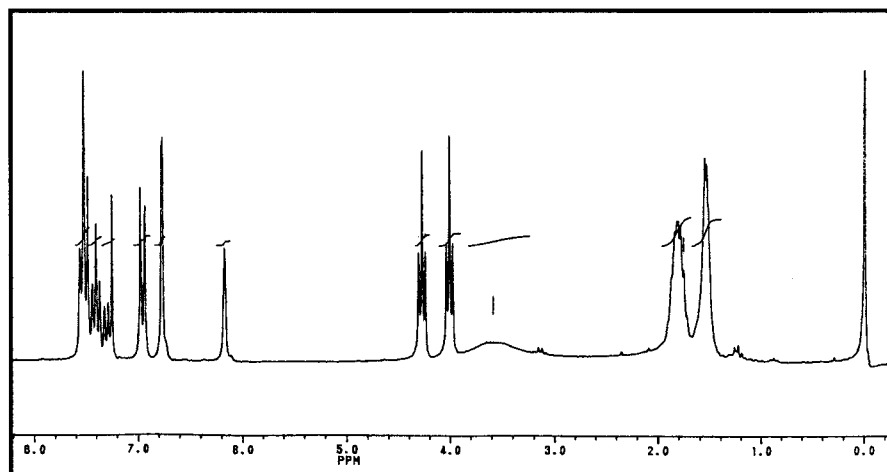
Figure 6 ^{1}H-NMR of diamine PP6DA.

(m, 2H, —CH2-OAr); 1.83–1.53 (m, 8H, the rest —CH2—).

Preparation of polyimide films

ODPA, 0.01 mol, was added to the solution of 0.001 mol diamines [ODA and *m*-phenylenediamine (or PP0DA, PP2DA, PP6DA) in a 2/1 mol ratio] in NMP, the reaction flask was then sealed tightly, and stirring was continued for 12 h at ambient temperature. The solid contents of the precursor solutions were 15–20 wt %. The precursor solutions were then spin-coated onto glass plates, followed by drying at 80°C under reduced pressure for 2 h. The self-standing films were thermally imidized in an oven with nitrogen gas by a typical three-step imidization process: 100°C/1 h, 200°C/1 h, and 300°C/1 h. The thickness of the resulting fully imidized films were 20–30μm. For measurements of the structures and properties, the polyimide films were cut into appropriate sizes.

RESULTS AND DISCUSSION

Synthesis of monomers

Diamines with directly linked pendent biphenyl groups or through flexible methylene spacers were prepared via three steps using 3,5-dinitrobenzoic acid as a starting material; the synthetic route is illustrated

in Figures 3 and 4. All the dinitro compounds provided good yields. The reduction of the dinitro compounds was performed by catalytic hydrogenation using palladium on active carbon and hydrogen gas. Hydrazine hydrate/ethanol is not preferable because the carbonyl group will be reduced, which had been confirmed by our experiments. The structures of the resulting dinitro and diamine compounds with various pendent groups were confirmed by melting points, FTIR, and ^{1}H-NMR spectroscopy. The results were in good agreement with the proposed structures.

Synthesis of polyimides

The polyimides were prepared by a conventional two-step method. First, the dianhydride reacted with diamines in NMP to form poly(amic acid), because the poly(amic acid)s are sensitive to hydrolysis by moisture. The resulting poly(amic acid) solutions were cast into films as soon as possible. The films were dried in a vacuum at 80°C for 2 h, then imidized by a typical three-step process. The chemical structure of the obtained polyimides were characterized by FTIR spectroscopy, and all the polyimides showed a similar pattern. IR spectra showed no trace of amine or acid peaks, indicating that the polyimides were fully imidized. This was also confirmed by the peaks at 1780 and 1710 cm^{-1} ascribed to the stretching of carbonyl

TABLE I
Basic Properties of Polyimides Prepared

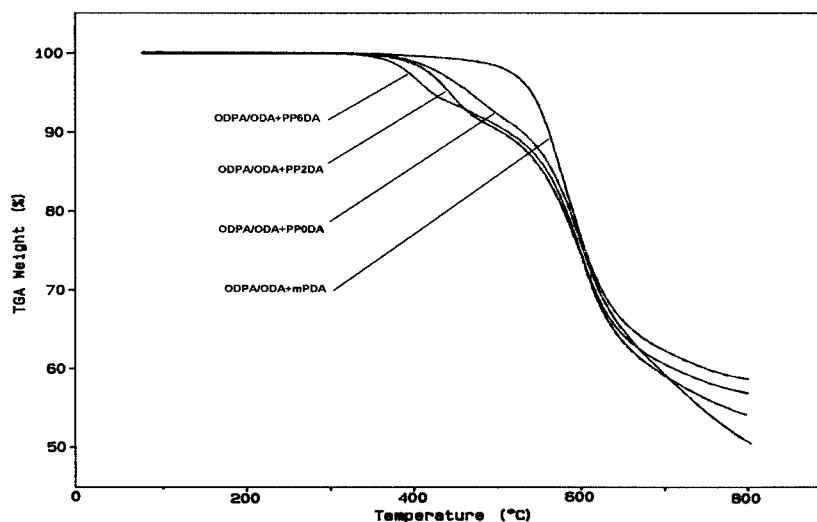| Sample codes	η_{inh} (dL/g)	T_g (°C)	T_d (°C)	T_{d5} (°C)	T_{d10} (°C)
ODPA/ODA + *m*-PDA	1.19	275	517	541	562
ODPA/ODA + PP0DA	0.91	231	390	466	529
ODPA/ODA + PP2DA	0.85	214	403	443	502
ODPA/ODA + PP6DA	0.86	210	377	421	510

Figure 7 Thermogravimetric diagrams of polyimides with various side chains.

groups and at 1380 cm^{-1} of C—N—C stretching. A hexylene spacer was confirmed by two strong C—H stretching peaks (2990–2910 and 2890–2800 cm^{-1}).

Properties of polyimides

The thermal stability of polyimides with side chains was investigated by thermogravimetry under a nitrogen atmosphere. The results are shown in Table I and Figure 7.

It can be concluded that the polyimides with side chains show a relatively lower stability than those without side chains. ODPA/ODA + mPDA PI was thermally stable to 517°C and then showed a large weight loss at about 600°C. The polyimides with side chains showed a two-step weight-loss behavior. Generally, in the heating run of polyimides with side chains, the weight decreases dramatically over the range of 400–500°C. The weight losses at this first step were almost equivalent to the weight of the side chains, which indicates that the side chains first degraded at about 400°C. This was followed by an large weight loss at about 600°C with an increasing temperature. For all the polyimides with or without side chains, the weight loss in the second step occurred over almost the same temperature ranges. As the four

kinds of polyimides have similar main-chain structures, this suggests that the second weight loss is due to the degradation of the polyimide main chains.

As described above, these polyimides have side chains consisting of a biphenyl end group and various flexible methylene spacers. From the TGA curves, we may see that the thermal stability according to a 5% weight loss with the temperature is in the decreasing order of ODPA/ODA + mPDA (T_{d5} 541°C) > ODPA/ODA + PP0DA (T_{d5} 466°C) > ODPA/ODA + PP2DA (T_{d5} 443°C) > ODPA/ODA + PP6DA (T_{d5} 421°C). This order is similar to the order of an increasing length of the flexible methlene spacer, which may indicate that the lower thermal stability is caused by the introduction of the longer flexible methylene linkage.

In addition, the glass transition temperatures (T_g) of polyimides were measured, and the results are shown in Table I. ODPA/ODA + mPDA without side chains exhibited a T_g of 275°C; however, all the polyimides with side chains show relatively low T_g's. The T_g was 231°C for ODPA/ODA + PP0DA, 214°C for ODPA/ODA + PP2DA, and 210°C for ODPA/ODA + PP6DA. This shows that the T_g was reduced by the introduction of side chains, and it was further decreased with the lengthening of the flexible methylene spacer.

TABLE II
Mechanical Properties of Polyimide Films

Sample codes	Strength at break (MPa)	Initial Moduli (GPa)	Elongation at Break (%)
ODPA/ODA + m-PDA	133	2.8	12
ODPA/ODA + PP0DA	143	2.9	13
ODPA/ODA + PP2DA	141	2.8	11
ODPA/ODA + PP6DA	143	3.6	8

TABLE III
Solubilities of the Polyimides in Organic Solvents

Sample codes	m-Cresol	NMP	DMAC	DMSO	Chloroform
ODPA/ODA + m-PDA	+	−	−	−	−
ODPA/ODA + PP0DA	++	++	++	+	+
ODPA/ODA + PP2DA	++	++	++	+	+
ODPA/ODA + PP6DA	++	++	++	+	+

++, Soluble; +, swellable; −, insoluble in hot solvent.

All the films were subjected to tensile testing, and the results are summarized in Table II. It was surprising that all the polyimides containing side chains showed high moduli and tensile strength. It is generally believed that the introduction of bulky side substitutes into polyimide main chains provides a molecular irregularity and separation of chains which is beneficial in terms of a free-volume increase and lowering of the cohesive energy density[16] and, hence, deteriorate their mechanical properties. However, in the present study, the tensile experiments revealed that all three polyimides with side chains showed higher tensile strength than that of the one without side chains. These results may indicate that the side biphenyl units in some way contributed to the improvements in the mechanical properties. According to our knowledge, even though some articles about the preparation and properties of polyimides with various rigid side chains have been published, reports on their mechanical properties are rare. Dowell suggested a supramolecular arrangement for rodlike liquid crystal polymers, such as aromatic polyamide and polybenzoxazole, carrying rigid side chains more or less perpendicular to the backbone would result an improvement in the mechanical properties.[17] The polyimides that we prepared contained rigid biphenyl side chains in the rodlike main chains, so we think Dowell's supramolecular arrangement of rodlike polymers carrying rigid side chains may be a reasonable explanation for the improvements of mechanical properties in our experiments. However, this explanation needs to be further investigated in detail for a better understanding.

One of the main objectives of this research work was the improvement of the solubility of polyimides through introducing bulky side chains. The solubility of polyimides with various side chains was tested quantitatively, and the results are summarized in Table III. It is obvious that all the polyimides with side chains were readily soluble in polar aprotic solvents such as m-cresol, NMP, and DMAC. They were also swollen in DMSO and chloroform. In contrast, the control polyimide without side chains was insoluble in any of these solvents except it did swell in m-cresol. This indicated that the introduction of side chains could considerably enhance the solubility of polyimides in common solvents.

Structures of polyimides

The structures of polyimides with various side chains were examined by X-ray diffraction, and the obtained diffraction patterns are illustrated in Figure 8. Similar diffraction patterns showing a broad peak centered around 20° (2θ) were observed for these polyimides, which is the amorphous halo. This may suggest that all of the polyimide films were amorphous.

CONCLUSIONS

A series of diamines containing pendent biphenyl-based groups were newly synthesized. Several novel polyimides with various side chains were synthesized from ODPA and these diamines. All the polyimides maintained high tensile moduli and exhibited higher tensile strengths than those without side chains. The polyimides with side chains were apparently amorphous and displayed a lower glass transition temperature, whereas the solubility in aprotic solvents was enhanced. With the introduction of side chains, the thermal stability of these polyimides decreased and displayed a two-step degradation behavior corresponding to the degradation of side chains and main chains, respectively. A detailed study to understand the structure–property relationship of the polyimides containing biphenyl units is underway, and the results will be published later.
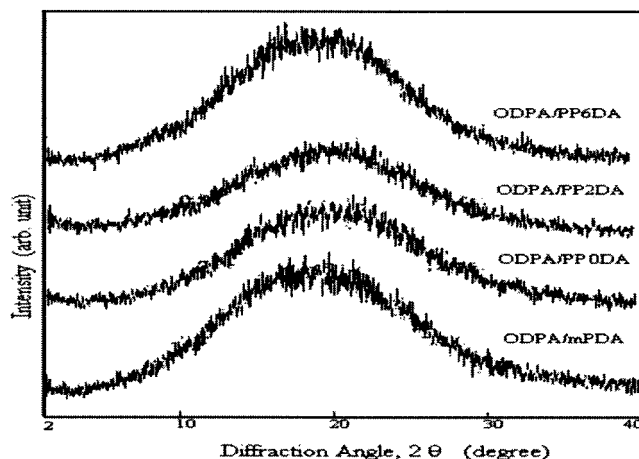

Figure 8 X-ray diffractograms of polyimide films.

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