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ORIGINAL CONTRIBUTION

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Preparation and characterization of organosoluble copolyimides based on a pair of commercial aromatic dianhydride and one aromatic diamine, 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene, series

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Abstract A series of copolyimides with high molecular weights, excellent mechanical properties, heat-resistant properties, and good solubilities in organic solvents were synthesized from six kinds of commercial dianhydrides and 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene. Monomers for synthesizing insoluble polyimides and monomers for synthesizing soluble polyimides were used to synthesize semialternating copolyimides with arbitrary solubilities. Fifteen kinds of soluble copolyimides were synthesized through chemical or thermal cyclodehydration. These copolyimides were found to be easily soluble as well as able to be processed by casting from solutions such as *N*-methyl-2-pyrrolidone, *N*,*N*-dimethylacetamide, dimethylformamide, dimethyl sulfoxide, *m*-cresol, and tetrahydrofuran. The easily dissolved characteristics of this series of copolyimides stemmed from the *tert*-butyl group, the ortho-linked aromatic unit, and the ether group within 4-*tert*-butylbenzene. Besides, when the dianhydride molecules used contained organosoluble groups and were mixed at varying molar ratios, the solubilities in organic solvents could be greatly enhanced. The copolyimides could improve the processability of polymers, while maintaining or increasing their excellent mechanical properties and heat-resistant properties.

Key words Copolyimides · 1,2-Bis- (4-aminophenoxy)-4-*tert*-butylbenzene · Organosoluble

Introduction

Aromatic polyimides are well known as polymer materials of high performance for their excellent thermal stabilities and balanced mechanical and electric properties [1–5]. Polyimides are mainly used in the aerospace and electronic industries in the forms of films and moldings. Other applications of these polymers, in addition to their being used for adhesives, gas-separation membranes, composite matrices, coatings, and foams, are rapidly increasing. However, aromatic polyimides are difficult to process because of high softening temperatures and limited solubilities in commercially available solvents; accordingly, studies to improve their solubilities or heat plasticities or both without decreasing their original excellent characteristics have been performed by numerous researchers. So far, many attempts have been made to improve the processabilities of aromatic polyimides [1–5]. The results reported include the incorporation of ether or other flexibilizing linkages into the main chain, which leads to lower glass-transition temperatures as well as significant improvements in the solubilities and other processing characteristics of the polymers without greatly sacrificing thermal stabilities. The introduction of a monosubstituted ortho-aromatic monomer into the polymer chain is expected to result in a decrease in the order along the chain but enhancement in solubility.

Therefore, some approaches to increase the solubility of polyimides are the incorporation of less symmetric, such as meta- or ortho-catenated, aromatic units in the main chains [6–10]. It has been demonstrated that the nucleophilic chlorodisplacement reaction between *p*-chloronitrobenzene with ortho-substituted aromatic diols, such as catechol and 2,3-dihydroxynaphthalene, could successfully proceed to form the ortho-linked dinitrocompounds, which could be readily reduced to the ortho-linked diamines used in polyamide and polyimide synthesis [10–12]. The lateral arrangement of ortho-linked aromatic moieties, particularly for the 2,3-naphthalenediyl unit, could interrupt interchain packing, reduce the glass-transition temperature, and increase the solubility. Although the polyimides obtained showed better solubility than that derived from para- or meta-linked aromatic monomers, the solubilities of pyromellitic dianhydride (PMDA), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) series polyimides were still poor in organic solvents. Recently, we found that the introduction of a *tert*-butyl group into the polyimide backbone is effective in enhancing the organosolubility [13, 14]. For example, in a comparison of polyimides synthesized from 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (1,4-BAP-*t*BB) with the corresponding polyimides without a *tert*-butyl group, the former [used dianhydride: 4,4′-oxydiphthalic anhydride (ODPA) or 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA)] were organosoluble owing to the presence of the *tert*-butyl group.

In the present work, we set out to prepare an ortho-linked bis(ether amine) containing a *tert*-butyl-substituted aromatic ring, 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene (1,2-BAP-*t*BB) [15], and used it for the preparation of polyimides by reacting it with various aromatic dianhydrides. The polyimides synthesized have better solubility than that based on diamine 1,4-BAP-*t*BB. The commercial dianhydrides, 4,4′-hexafluoroisopropylidenediphthalic anhydride (6FDA), DSDA, ODPA, and even BPDA, form soluble polyimides with diamine 1,2-BAP-*t*BB, but polyimides of the PMDA and BTDA series still are insoluble. Because few diamines with PMDA can prepare soluble polyimide [16], 1,2-BAP-*t*BB is relatively easy to form soluble polyimide among various diamines. In this research, 1,2-BAP-*t*BB and a pair of commercial aromatic dianhydrides were used to synthesize semialternating copolyimides, and the solubility of PMDA and BTDA series copolyimides were improved by copolymerization. A comparative study on the properties of the homopolyimide and copolyimide, specifically, their solubilities, mechanical properties, and thermal stabilities, is also presented.

Experimental

Materials

1,2-BAP-*t*BB (**I**) (m.p. 129–131 °C) was synthesized from 4-*tert*-butylcatechol and *p*-chloronitrobenzene in the presence of potassium carbonate and subsequent reduction with a 10% Pd-C catalyst and hydrazine hydrate in our previous study [15]. Aromatic dianhydrides: PMDA ($\mathbf{II_a}$ from TCI), BTDA ($\mathbf{II_b}$ from TCI), BPDA ($\mathbf{II_c}$ from Chriskev), ODPA ($\mathbf{II_d}$ from TCI), DSDA ($\mathbf{II_e}$ from New Japan Chemical Co.), and 6FDA ($\mathbf{II_f}$ from Hoechst) were recrystallized from acetic anhydride before use. *N*-Methyl-2-pyrrolidone (from Fluka), *N*,*N*-dimethylacetamide (DMAc from Fluka), and pyridine (Py from Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Synthesis of polyimides

Chemical cyclodehydration

Diamine **I** (0.348 g, 1 mmol) was dissolved in 6.86 ml dried DMAc in a 20-ml flask. After the diamine had dissolved completely, 0.155 g (0.5 mmol) ODPA $\mathbf{II_d}$ was added to it in one portion. After 30 min of stirring, 0.109 g (0.5 mmol) PMDA $\mathbf{II_a}$ was then added, and the mixture was stirred at room temperature for another 1 h. Then a 1.5-ml mixture of acetic anhydride (Ac_2O) and Py (volume ratio 2:1) was added to the poly(amic acid) (PAA) solution. The mixture was stirred at 80–100 °C for 1 h. The polymer solution was poured into methanol. The fibrous precipitate ($\mathbf{III_{a/d}}$) was collected by filtration, washed thoroughly with methanol, and dried at 100 °C. The inherent viscosity of the polymer in DMAc was 1.07 dl/g, measured at a concentration 0.5 g/dl at 30 °C. The polymer was further baked at 250 °C for 30 min to ensure cyclization.

Thermal cyclodehydration

The PAA solution, which was prepared by a similar method to that of chemical cyclodehydration, was spread on a glass plate, which was placed in an oven at 80 °C for 1 h to remove the solvent. The semidried PAA film was heated sequentially at 120 °C for 10 min, 150 °C for 10 min, 180 °C for 10 min, 210 °C for 10 min, and 250 °C for 30 min. By soaking in water, a flexible polyimide film was self-stripped from the glass surface.

Measurements

Elemental analyses were performed using a Perkin-Elmer model 2400 C,H,N analyzer. IR spectra were recorded using a Jasco FT/IR-7000 Fourier transform IR spectrometer with KBr disks or solution cast films. The inherent viscosities were measured with a Cannon–Fenske viscometer at 30 °C. Solubilities were determined at 1% (w/w) concentration. Differential scanning calorimeter traces were measured on TA Instruments DSC 2010 at a rate of 15 °C/min in flowing nitrogen (40 cm^3/min). Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen or air (100 cm^3/min) at a heating rate of 20 °C/min. An Instron model 1130 universal tester with a load cell of 5 kg was used to study the stress–strain behavior of the polymer films. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were taken at room temperature with film specimens (0.5-cm wide, 6-cm long, and about 0.5-mm thick), and an average of at least five individual determinations was used.

Results and discussion

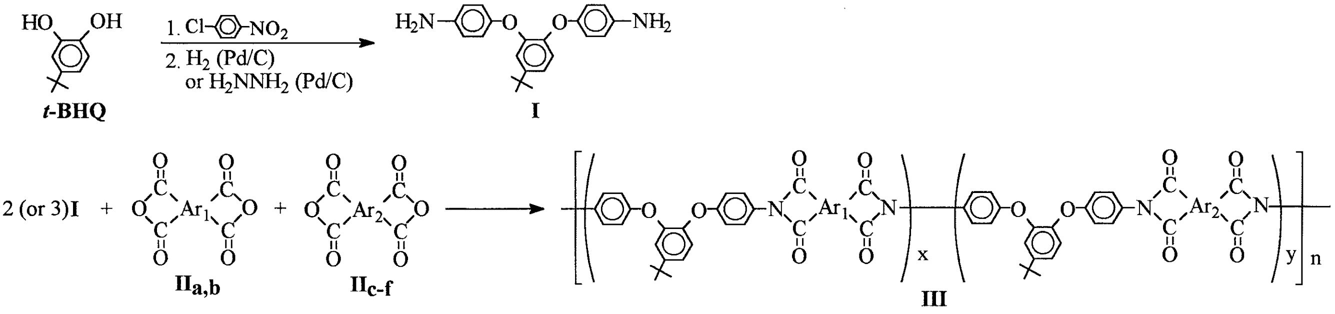
Polymer synthesis

In order to investigate the effect of modification of the *tert*-butyl group and the ortho-linked aromatic unit on the solubilities of polyimide, the synthesis of diamine (**I**) containing the *tert*-butyl group as a 4-*tert*-butylcatechol moiety was carried out, as shown in Scheme 1. In this reaction, regardless of whether *p*-chloronitrobenzene or *p*-fluoronitrobenzene was used as a solvent, high yields of dinitrocompounds were obtained. Besides, when reduced into **I**, **I** of high purity could be prepared, regardless of whether H_2NNH_2 or H_2 was used.

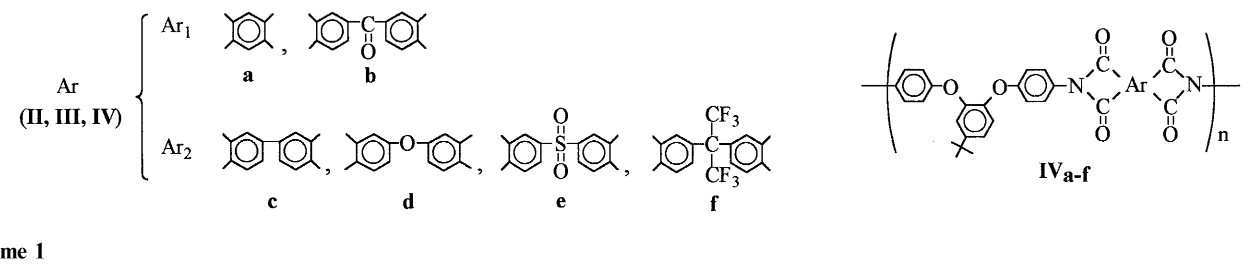
The preparation of common polyimides with diamine **I** has been reported in the literature [15], and we know the solubility of some polyimides obtained; however, more detailed investigation of the effect of this special diamine on the solubility of polyimide in organic solvents has yet to be performed. We designed a simple method for synthesizing soluble polyimide that enabled us to detect polyimide solubility. According to this method, equimolar amounts of diamines and dianhydrides were first used to prepare the PAA solution of 10–12% in DMAc and then suitable solutions of Ac_2O and Py were added. This solution was stirred at 80–100 °C for 1 h. At this time, if the solution still remained in the transparent and homogeneous phase, the formed polyimide would be soluble in organic solvents. If the solution showed gelation or produced precipitation, the polyimide formed would be slightly soluble or insoluble in organic solvents.

In this study, polyimides were synthesized from diamine **I** with six kinds of commercial dianhydrides $\mathbf{II}_{a-f}$ through the conventional chemical process as shown in Scheme 1. The synthesis conditions and the inherent viscosities of the polyimides produced are shown in Table 1. Diamine **I** formed insoluble precipitated polyimides ($\mathbf{IV}_{a,b}$) when **I** reacted with PMDA ($\mathbf{II}_a$) or BTDA ($\mathbf{II}_b$). Polyimides $\mathbf{IV}_{a,b}$ were insoluble in DMAc, and their viscosities measured in concentrated H_2SO_4 were 0.87 and 0.78 dl/g, respectively. When diamine **I** reacted with the remaining dianhydrides $\mathbf{II}_{c-f}$ (i.e., BPDA, ODPA, DSDA, and 6FDA), homogeneous, transparent polyimide solutions were formed. After these polymer solutions were poured into methanol, white filament-like products ($\mathbf{IV}_{c-f}$) were collected. Polyimides $\mathbf{IV}_{c-f}$ were soluble in DMAc, and the inherent viscosities were in the range 0.41–0.81 dl/g.

The solubility of polyimides depends upon the molecular structures of the dianhydrides or diamines used. When both or either of these monomers tended to form easily soluble polyimide in organic solvents, the copolyimides synthesized were easily soluble in solvents. 6FDA has recently been known as a dianhydride monomer, which forms most easily the organic-solvent-soluble polyimide. The solubility of dianhydrides $\mathbf{II}_{c-e}$



Co-PI	$III_{a/c}$	$III_{a/d}$	$III_{a/e}$	$III_{a/f}$	$III_{a/2c}$	$III_{a/2d}$	$III_{a/2e}$	$III_{a/2f}$	$III_{a/c/d}$	$III_{a/c/e}$	$III_{a/c/f}$	$III_{b/c}$	$III_{b/d}$	$III_{b/e}$	$III_{b/f}$
Ar_1/Ar_2	a/c	a/d	a/e	a/f	a/2c	a/2d	a/2e	a/2f	a/(c/d)	a/(c/e)	a/(c/f)	b/c	b/d	b/e	b/f
x/y	1/1	1/1	1/1	1/1	1/2	1/2	1/2	1/2	1/(1/1)	1/(1/1)	1/(1/1)	1/1	1/1	1/1	1/1



Scheme 1

Table 1 Synthesis of polyimides

Polymer	Reactants			Products
	I (mmol)	**IIa,b** (mmol)	**IIc–f** (mmol)	Polyimides η_{inh} (dl/g)^a
$\mathbf{III}_{a/c}$	(2)	$\mathbf{II}_a(1)$	$\mathbf{II}_c(1)$	0.82
$\mathbf{III}_{a/d}$	(2)	$\mathbf{II}_a(1)$	$\mathbf{II}_d(1)$	1.07
$\mathbf{III}_{a/e}$	(2)	$\mathbf{II}_a(1)$	$\mathbf{II}_e(1)$	0.80
$\mathbf{III}_{a/f}$	(2)	$\mathbf{II}_a(1)$	$\mathbf{II}_f(1)$	0.78
$\mathbf{III}_{a/2c}$	(3)	$\mathbf{II}_a(1)$	$\mathbf{II}_c(2)$	0.84
$\mathbf{III}_{a/2d}$	(3)	$\mathbf{II}_a(1)$	$\mathbf{II}_d(2)$	1.02
$\mathbf{III}_{a/2e}$	(3)	$\mathbf{II}_a(1)$	$\mathbf{II}_e(2)$	0.87
$\mathbf{III}_{a/2f}$	(3)	$\mathbf{II}_a(1)$	$\mathbf{II}_f(2)$	0.82
$\mathbf{III}_{a/c/d}$	(3)	$\mathbf{II}_a(1)$	$\mathbf{II}_c/\mathbf{II}_d(1/1)$	0.86
$\mathbf{III}_{a/c/e}$	(3)	$\mathbf{II}_a(1)$	$\mathbf{II}_c/\mathbf{II}_e(1/1)$	1.22
$\mathbf{III}_{a/c/f}$	(3)	$\mathbf{II}_a(1)$	$\mathbf{II}_c/\mathbf{II}_f(1/1)$	0.97
$\mathbf{III}_{b/c}$	(2)	$\mathbf{II}_b(1)$	$\mathbf{II}_c(1)$	0.84
$\mathbf{III}_{b/d}$	(2)	$\mathbf{II}_b(1)$	$\mathbf{II}_d(1)$	1.32
$\mathbf{III}_{b/e}$	(2)	$\mathbf{II}_b(1)$	$\mathbf{II}_e(1)$	1.34
$\mathbf{III}_{b/f}$	(2)	$\mathbf{II}_b(1)$	$\mathbf{II}_f(1)$	1.66
$\mathbf{IV}_a$	(1)	$\mathbf{II}_a(1)$		0.87^b
$\mathbf{IV}_b$	(1)	$\mathbf{II}_b(1)$		0.78^b
$\mathbf{IV}_c$	(1)		$\mathbf{II}_c(1)$	0.81
$\mathbf{IV}_d$	(1)		$\mathbf{II}_d(1)$	0.58
$\mathbf{IV}_e$	(1)		$\mathbf{II}_e(1)$	0.81
$\mathbf{IV}_f$	(1)		$\mathbf{II}_f(1)$	0.41

[a] Measured at a concentration of 0.5 g/dl in *N*,*N*-dimethylacetamide at 30 °C. Data of the corresponding **IV** polymers are reported in Ref. [15]

[b] Measured at a concentration of 0.5 g/dl in concentrated H_2SO_4 at 30 °C

depends upon the characteristics of the diamines used, but most of the PMDA-polyimides or the BTDA-polyimides are insoluble or slightly soluble in organic solvents.

In fact, it was most convenient and economical to use the commercial dianhydride to prepare polyimide; among the polyimides formed from **I** and six kinds of commercial dianhydrides, four are organic-solvent soluble and two are insoluble. In this research, we investigated the possibilities of preparing soluble copolyimides by carrying out the copolymerization of dianhydrides of both soluble and insoluble polyimides with **I**. The diamine dissolved completely in solvents, and one kind of dianhydride was then added to react in the first step. After 30 min of stirring, an intermediate product with a terminal group of amine was formed, and another kind of dianhydride was added to synthesize semialternating PAA in the second step. Then, condensing agent (Ac_2O/Py) was added with stirring at 80–100 °C to obtain semialternating copolyimides (**III**), as shown in Scheme 1. The order of the addition of the two kinds of dianhydrides depends upon the amount of dianhydride used, and a lower amount of dianhydride is added in the second step. The inherent viscosities and the reaction conditions of the copolyimides produced are shown in Table 1. The copolyimides formed from those mixed by PMDA and equivalent moles of $\mathbf{II}_{c\text{–}f}$ were all soluble, the chemical imidization reactions were carried out homogeneously, and the inherent viscosities ranged from 0.78 to 1.07 dl/g. When BTDA was used to replace PMDA, soluble copolyimides could be produced under the previously cited matching of diamines and dianhydrides, and the inherent viscosities were higher (0.84–1.66 dl/g). Besides, rigid PMDA and BPDA with $\mathbf{II}_{d\text{–}f}$ could also prepare organosoluble copolyimides $\mathbf{III}_{a/c/d\text{–}a/c/f}$. For this reason, **I** was used as the specific diamine, which could mix with various groups of dianhydrides to prepare PMDA- or BTDA-containing copolyimides of any solubility; therefore, **I** could be said to be an important monomer for preparing easily soluble polyimides.

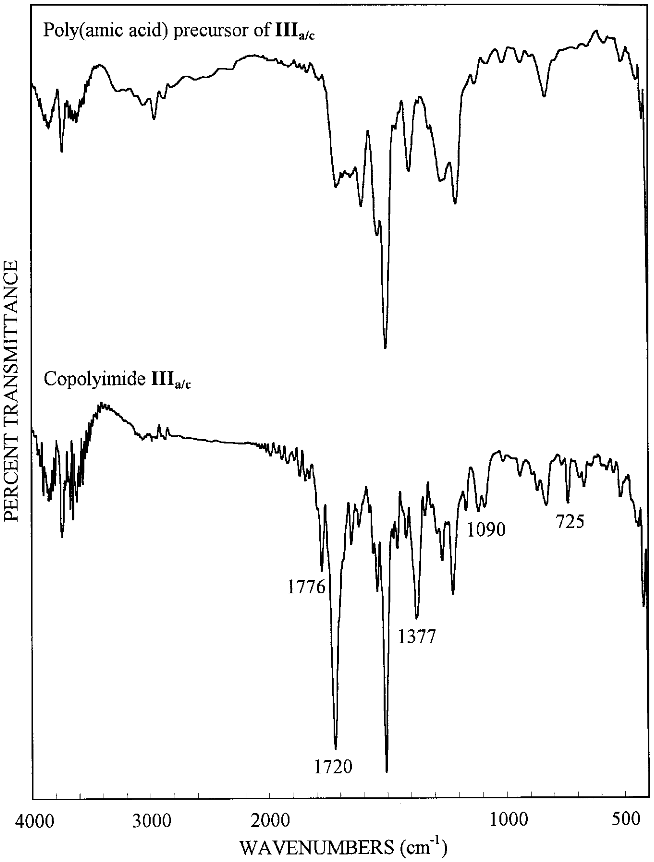


Fig. 1 IR spectra of copolyimide $\mathbf{III}_{a/c}$ and its poly(amic acid) precursor

IR spectroscopy allows monitoring of the imide ring formation during thermal curing or chemical treatment. Typical IR spectra are shown in Fig. 1. As the PAA was converted into the polyimide, the characteristic absorption bands of the imide ring were observed near 1780, 1720 (asymmetrical and symmetrical C=O stretching vibration), 1390 (C–N stretching vibration), 1100, and 720 cm^{-1} (imide ring deformation) and those of amide and carboxyl groups in the regions of 3000–3500 and 1500–1720 cm^{-1} disappeared, indicating a virtually complete conversion of the PAA precursor into polyimide. The elemental analysis values of these copolyimides are shown in Table 2. They agree roughly with the theoretical values.

Properties of Polymers

The qualitative solubilities of these polyimides are shown in Table 3. Except for H_2SO_4, polyimides $\mathbf{IV_{a,b}}$, synthesized from **I** and $\mathbf{II_{a,b}}$, were insoluble in all the organic solvents tested. When the dianhydrides adopted were $\mathbf{II_{c\text{–}f}}$, the polyimides synthesized ($\mathbf{IV_{c\text{–}f}}$) could be dissolved in most solvents, even in tetrahydrofuran. When the polyimides were formed from the dianhydrides ($\mathbf{II_{a,b}}$) that caused low solubility of polyimides, these dianhydrides were matched and mixed with the other dianhydrides ($\mathbf{II_{c\text{–}f}}$) that led to easily soluble polyimide forming the semialternating copolyimides. These copolyimides could be modified into easily soluble polymers, such as $\mathbf{III_{a/c\text{–}a/f}}$ and $\mathbf{III_{b/c\text{–}b/f}}$. $\mathbf{III_{a/c/d\text{–}a/c/f}}$ containing a large proportion of rigid dianhydride ($\mathbf{II_a}$ and $\mathbf{II_c}$) were also soluble, so using diamine **I** with copolymerization is indeed an effective method to improve the solubility of polyimides.

The solubilities listed in Table 3 are qualitative. Incidentally, the solubilities of the polyimides formed through chemical cyclodehydration were almost identical to those of the polyimides formed through thermal cyclodehydration, although the films obtained through thermal cyclodehydration might have a different physical state (e.g. chain packing was denser) and the dissolving rates were slower than those obtained through chemical cyclodehydration (heating could be applied to promote the solubilization). Especially, the solubilities of $\mathbf{III_{b/c\text{–}b/f}}$ containing BTDA exhibited a great difference between the two different cyclization methods. $\mathbf{III_{b/c\text{–}b/f}}$ synthesized by chemical imidization were soluble in all the solvents tested, but the solubilities became poor for thermal imidized ones. This may be attributable to the formation of some intermolecular links of the C=O group of BTDA during the thermal imidization [17], and this phenomenon will be the subject of a future publication.

Opposite to the brittleness of PMDA-based film $\mathbf{IV_a}$ and the poor solubility of film $\mathbf{IV_b}$, flexible and

Table 2 Elemental analysis of copolyimides

Polymer	Formula (Molecular weight)		Elemental analysis (%)		
			C	H	N
$\mathbf{III_{a/c}}$	$(C_{70}H_{48}N_4O_{12})_n$	Calc.	73.94	4.25	4.93
	$1137.17)_n$	Found	73.42	4.22	4.60
$\mathbf{III_{a/d}}$	$(C_{70}H_{48}N_4O_{13})_n$	Calc.	72.91	4.20	4.86
	$(1153.17)_n$	Found	72.57	4.07	4.55
$\mathbf{III_{a/e}}$	$(C_{70}H_{48}N_4O_{14}S)_n$	Calc.	69.99	4.03	4.66
	$(1201.23)_n$	Found	69.35	3.91	4.35
$\mathbf{III_{a/f}}$	$(C_{73}H_{48}N_4O_{12}F_6)_n$	Calc.	68.12	3.76	4.35
	$(1287.19)_n$	Found	67.54	3.62	3.93
$\mathbf{III_{a/2c}}$	$(C_{108}H_{74}N_6O_{18})_n$	Calc.	74.39	4.28	4.82
	$(1743.80)_n$	Found	73.75	4.10	4.52
$\mathbf{III_{a/2d}}$	$(C_{108}H_{74}N_6O_{20})_n$	Calc.	73.05	4.20	4.73
	$(1775.80)_n$	Found	72.51	4.19	4.61
$\mathbf{III_{a/2e}}$	$(C_{108}H_{74}N_6O_{22}S_2)_n$	Calc.	69.30	3.98	4.49
	$(1871.92)_n$	Found	68.52	3.98	4.23
$\mathbf{III_{a/2f}}$	$(C_{114}H_{74}N_6O_{18}F_{12})_n$	Calc.	66.99	3.65	4.11
	$(2043.85)_n$	Found	66.60	3.58	3.93
$\mathbf{III_{a/c/d}}$	$(C_{108}H_{74}N_6O_{19})_n$	Calc.	73.71	4.24	4.78
	$(1759.80)_n$	Found	73.14	4.22	4.64
$\mathbf{III_{a/c/e}}$	$(C_{108}H_{74}N_6O_{20}S)_n$	Calc.	71.75	4.13	4.65
	$(1807.86)_n$	Found	71.25	4.15	4.43
$\mathbf{III_{a/c/f}}$	$(C_{111}H_{74}N_6O_{18}F_6)_n$	Calc.	70.40	3.94	4.44
	$(1893.83)_n$	Found	69.90	3.95	4.22
$\mathbf{III_{b/c}}$	$(C_{77}H_{52}N_4O_{13})_n$	Calc.	74.51	4.22	4.51
	$(1241.28)_n$	Found	73.89	4.26	4.31
$\mathbf{III_{b/d}}$	$(C_{77}H_{52}N_4O_{14})_n$	Calc.	73.56	4.17	4.46
	$(1257.28)_n$	Found	72.94	4.20	4.36
$\mathbf{III_{b/e}}$	$(C_{77}H_{52}N_4O_{15}S)_n$	Calc.	70.85	4.02	4.29
	$(1305.34)_n$	Found	70.35	4.01	4.12
$\mathbf{III_{b/f}}$	$(C_{80}H_{52}N_4O_{13}F_6)_n$	Calc.	69.06	3.77	4.03
	$(1391.30)_n$	Found	68.81	3.78	3.84

Table 3 Solubility of polyimides in various solvents: *N*-methyl-2-pyrrolidone (*NMP*), *N*,*N*-dimethylacetamide (*DMAc*), *N*,*N*-dimethylformamide (*DMF*), dimethyl sulfoxide (*DMSO*), *m*-cresol, tetrahydrofuran (*THF*), and H_2SO_4. Measured at a concentration of about 1 wt%. + indicates soluble and – indicates insoluble. The thermally imidized polyimides showed the same solubility behavior as those obtained by chemical imidization, unless otherwise indicated in *parentheses*. Data of polymers **IV** are reported in Ref. [15]

Polymer	Solvent						
	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	H_2SO_4
$\mathbf{III_{a/c}}$	+	+	+	+	+	+	+
$\mathbf{III_{a/d}}$	+	+	+	+	+	+	+
$\mathbf{III_{a/e}}$	+	+	+	+	+	+	+
$\mathbf{III_{a/f}}$	+	+	+	+	+	+	+
$\mathbf{III_{a/c/d}}$	+	+	+	+	+(–)	+	+
$\mathbf{III_{a/c/e}}$	+	+	+	+	+	+	+
$\mathbf{III_{a/c/f}}$	+	+	+	+	+	+	+
$\mathbf{III_{b/c}}$	+(–)	+(–)	+(–)	+(–)	+(–)	+(–)	+
$\mathbf{III_{b/d}}$	+(–)	+(–)	+(–)	+(–)	+(–)	+(–)	+
$\mathbf{III_{b/e}}$	+	+(–)	+(–)	+(–)	+(–)	+(–)	+
$\mathbf{III_{b/f}}$	+	+(–)	+(–)	+(–)	+(–)	+(–)	+
$\mathbf{IV_a}$	–	–	–	–	–	–	–
$\mathbf{IV_b}$	–	–	–	–	–	–	–
$\mathbf{IV_c}$	+	+	+	+	+	+	+
$\mathbf{IV_d}$	+	+	+	+	+	+	+
$\mathbf{IV_e}$	+	+	+	+	+	+	+
$\mathbf{IV_f}$	+	+	+	+	+	+	+

Table 4 Mechanical properties of polyimide films. The films were obtained by a thermal cyclodehydration method

Polymer	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
$\mathbf{IV_a}$			
$\mathbf{III_{a/c}}$	92	7	1.98
$\mathbf{III_{a/d}}$	106	8	2.00
$\mathbf{III_{a/e}}$	88	5	2.05
$\mathbf{III_{a/f}}$	85	4	2.07
$\mathbf{III_{a/2c}}$	99	10	2.03
$\mathbf{III_{a/2d}}$	108	9	2.10
$\mathbf{III_{a/2e}}$	98	6	2.16
$\mathbf{III_{a/2f}}$	93	5	2.14
$\mathbf{III_{a/c/d}}$	110	9	2.05
$\mathbf{III_{a/c/e}}$	93	9	2.16
$\mathbf{III_{a/c/f}}$	94	7	2.15
$\mathbf{IV_b}$	103	9	2.06
$\mathbf{III_{b/c}}$	99	8	1.92
$\mathbf{III_{b/d}}$	106	10	2.10
$\mathbf{III_{b/e}}$	105	9	2.14
$\mathbf{III_{b/f}}$	95	7	1.94

transparent films of organosoluble copolyimides could be prepared from **I** and a pair of commercial aromatic dianhydride by the previously mentioned copolymerization. The mechanical properties of the copolyimides are summarized in Table 4. The mechanical properties of PMDA-based copolyimide films were modified and were changed arbitrarily depending upon the molecular weight and the components of the polymers. Copolyimide **III** films had tensile strengths in the range of 85–110 MPa, elongations at break of 4–10%, and initial moduli of 1.92–2.16 GPa. In a comparison of $\mathbf{III_{a/c\text{–}a/f}}$ with $\mathbf{III_{b/c\text{–}b/f}}$, the latter showed larger tensile strengths and elongations at break than the former. This observation may be attributed to the fact that PMDA was more rigid and that the molecular weight (inherent viscosity) of $\mathbf{III_{a/c\text{–}a/f}}$ was lower, so their mechanical properties were affected. When comparing $\mathbf{III_{a/c/d\text{–}a/c/f}}$ with $\mathbf{III_{a/c\text{–}a/f}}$, the former exhibited better mechanical properties, so using rigid $\mathbf{II_c}$ for copolymerization was useful to improve the mechanical properties of polyimides. For confirming the effect of dianhydride $\mathbf{II_a}$ on the properties of polyimide films, $\mathbf{III_{a/2c\text{–}a/2f}}$ were synthesized with a lower $\mathbf{II_a}$ proportion of the dianhydride component. The mechanical properties were improved with a decreasing proportion of $\mathbf{II_a}$, confirming the previously cited description.

The thermal properties of all the copolyimides obtained from thermal cyclodehydration were evaluated through TGA and differential scanning calorimetry (DSC), and the results are summarized in Table 5. DSC measurements were conducted with a heating rate of 20 °C/min in nitrogen. Quenching the samples from an elevated temperature (400 °C) to room temperature in air gave predominantly amorphous samples, so the glass-transition temperatures (T_gs) of almost all the copolyimides could be easily observed in the second heating traces of DSC. The components of copolyimides **III** combined two of polyimides $\mathbf{IV_{a\text{–}f}}$. It was found that not all the T_gs of the copolyimides were intermediate between the T_gs of their corresponding polyimides, and even some copolyimides had higher T_gs than both their corresponding polyimides. For $\mathbf{III_{a/c\text{–}a/f}}$, their high T_gs were caused by rigid PMDA, but $\mathbf{III_{a/d}}$ containing a flexible ether group in ODPA showed a lower T_g than the rest of the copolyimides. By decreasing the proportion of PMDA in the copolyimides, the copolyimides $\mathbf{III_{a/2c\text{–}a/2f}}$ formed showed slightly lower T_gs than copolyimides $\mathbf{III_{a/c\text{–}a/f}}$. $\mathbf{III_{a/c/d\text{–}a/c/f}}$ containing three kinds of dianhydrides also exhibited high T_g values,

Table 5 Thermal properties of polyimides. The data of polymers **IV** are reported in Ref. [15]

Polymer	Differential scanning calorimetry T_g (°C)[a]	Thermogravimetric analysis			
		Decomposition temperature (°C)[b]		Abnormal range (°C)[c]	Char yield (%)[d]
		In air	In nitrogen		
$\mathbf{III}_{\mathbf{a/c}}$	272	531	535	540–600	53
$\mathbf{III}_{\mathbf{a/d}}$	256	526	529	535–610	48
$\mathbf{III}_{\mathbf{a/e}}$	274	511	501	480–620	42
$\mathbf{III}_{\mathbf{a/f}}$	265	528	533	540–580	53
$\mathbf{III}_{\mathbf{a/2c}}$	261	533	537	560–575	51
$\mathbf{III}_{\mathbf{a/2d}}$	247	531	531	530–620	50
$\mathbf{III}_{\mathbf{a/2e}}$	269	503	490	450–620	40
$\mathbf{III}_{\mathbf{a/2f}}$	262	530	534	540–560	54
$\mathbf{III}_{\mathbf{a/c/d}}$	254	532	535	545–615	50
$\mathbf{III}_{\mathbf{a/c/e}}$	266	523	514	480–630	44
$\mathbf{III}_{\mathbf{a/c/f}}$	264	533	535	540–590	54
$\mathbf{III}_{\mathbf{b/c}}$	248	533	535	540–610	54
$\mathbf{III}_{\mathbf{b/d}}$	232	530	533	535–610	50
$\mathbf{III}_{\mathbf{b/e}}$	250	516	507	490–630	45
$\mathbf{III}_{\mathbf{b/f}}$	245	530	532	540–580	55
$\mathbf{IV}_{\mathbf{a}}$	260(-)[e]	530	533	–	48
$\mathbf{IV}_{\mathbf{b}}$	239(244)	535	526	–	51
$\mathbf{IV}_{\mathbf{c}}$	251(258)	551	533	–	48
$\mathbf{IV}_{\mathbf{d}}$	229(228)	528	530	–	54
$\mathbf{IV}_{\mathbf{e}}$	256(259)	513	506	–	41
$\mathbf{IV}_{\mathbf{f}}$	242(263)	541	543	–	55

[a] From the second heating traces of differential scanning calorimetry measurements conducted with a heating rate of 15 °C/min in nitrogen

[b] Temperatures at which 10% weight loss was recorded by thermogravimetric analysis at a heating rate of 20 °C/min

[c] In this range, the decomposition rate is lower in air than in nitrogen

[d] Char yield when heated to 800 °C in nitrogen

[e] The value in parentheses is T_g of polymer **IV** that was synthesized in this study

which were even higher than their corresponding polyimides. The reason some copolyimides had higher T_g values than their corresponding polyimides might be caused by different sources and grades of dianhydrides between those reported in Ref. [15] and those in this study. We also synthesized polyimides $\mathbf{IV}_{\mathbf{a\text{–}f}}$ using the same dianhydrides of this study, and their T_g values are shown in Table 5. No T_g value was observed for polyimide $\mathbf{IV}_{\mathbf{a}}$ prepared in this study; however, there was an endothermic peak at 405 °C in its DSC heating trace. Therefore, higher T_g values for copolyimides **III** were reasonable when comparing then with polyimides **IV** of Ref. [15]. In a comparison of $\mathbf{III}_{\mathbf{b/c\text{–}b/f}}$ prepared from C=O group-containing BTDA with $\mathbf{III}_{\mathbf{a/c\text{–}a/f}}$, the former showed lower T_g values than the latter. From the data, the T_gs of copolyimides **III** were in the range 232–274 °C, indicating that the T_gs did not decrease significantly as a result of the ortho-linked phenylene and the *tert*-butyl group. This result is good for those polymers to be applied in more applications.

The thermal stability of the copolyimides was determined through TGA conducted at a heating rate of 20 °C/min. The temperatures of 10% weight loss (T_{10}) both in nitrogen and in the atmosphere were determined from original thermograms and are also tabulated in Table 5. The T_{10}s of these copolyimides stayed in the range 490–537 °C in nitrogen and 503–533 °C in air. All copolyimides showed a similar pattern of decomposition with no significant weight loss below 450 °C in both air and nitrogen and with more than 40 wt % residue remaining when heated to 800 °C in nitrogen. Typical TGA curves of copolyimides are illustrated in Fig. 2. It was interesting to note that the decomposition rate is lower in air than in nitrogen over a certain temperature range. This may be attributable to the oxidation of aliphatic segments in the polymer chain, which forms carbonyl (C=O) and hydroxyl (O–H) groups and then causes a weight gain [18–20]. We also found a similar phenomenon in previous work, when diamines contained cardo [21], isopropylene [22], phenylethane [23], or *tert*-butyl [24] groups. In this work, diamine **I** had a pendant *tert*-butyl group along the molecular moiety, so CH_3 oxidation may have occurred. However, the abnormal range changed with the dianhydrides used. BPDA- or ODPA-based copolyimides showed decomposition curves as shown in Fig. 2A. When 6FDA was

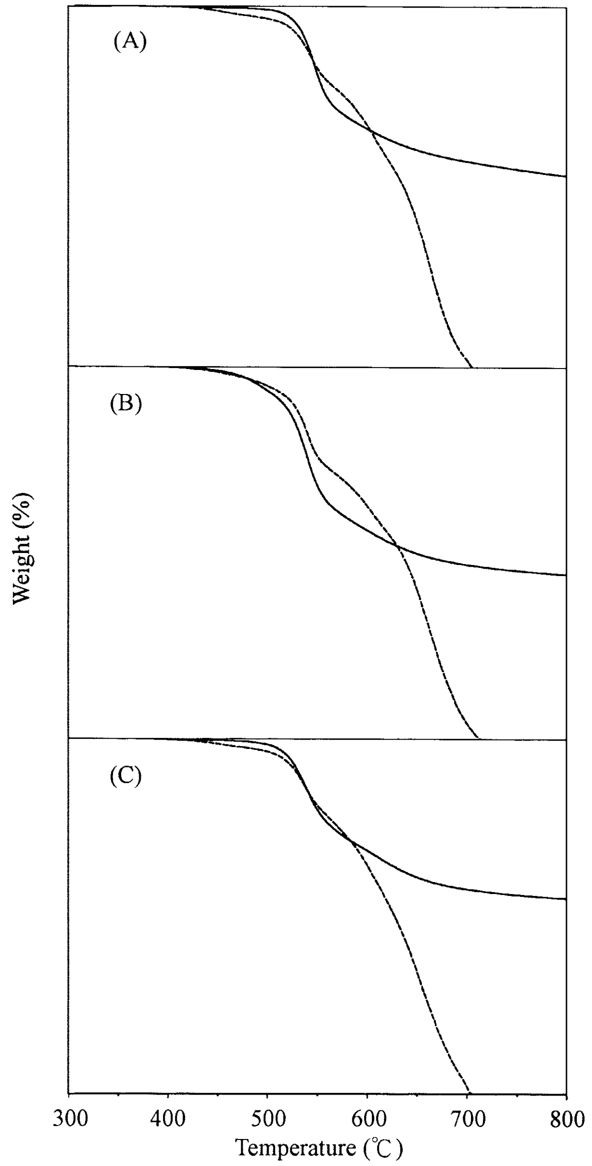


Fig. 2 Thermogravimetric analysis curves for **A** typical copolyimides, **B** diphenylsulfonetetracarboxylic dianhydride containing copolyimides, and **C** hexafluoroisopropylidenediphthalic anhydride containing copolyimides at a heating rate of 20 °C/min in nitrogen (*solid line*) and air (*dashed line*)

used as a dianhydride monomer, the abnormal range became significantly small, as shown in Fig. 2C. This may be due to the fluorine atoms of 6FDA having the function of a halogen, which can inhibit the occurrence of free radicals during oxidation, so a weight gain does not easily occur during thermal degradation in air. In contrast, copolyimides bearing a sulfonyl group in dianhydride DSDA (**III**$_{\mathbf{a/e}}$, **III**$_{\mathbf{a/2e}}$, **III**$_{\mathbf{a/c/e}}$, and **III**$_{\mathbf{b/e}}$) exhibited lower T_{10} values and larger abnormal ranges than the other polymers, as shown in Fig. 2B. This may be attributed to the weak bonding of the C–S bond and easy degradation during the heating process, which was also confirmed by the lower char yields. According to the data, the range of T_{10}s of series **III** copolyimides was similar to that of series **IV** polyimides, meaning that the copolyimides maintain excellent thermal properties as polyimides do.

Conclusion

The introduction of the ortho-linked aromatic moiety and the side-chain *tert*-butyl group into the aromatic polyimides could improve the organosolubilities. By using 1,2-BAP-*t*BB (**I**) prepared from 4-*tert*-butylcatechol, organosoluble copolyimides **III** were obtained. The copolyimides prepared from **I** with commercial dianhydrides had excellent solubilities in organic solvents. Although the solubilities of the polyimides synthesized from **I** with PMDA and BTDA were poor, the copolyimides based on these mixed dianhydrides of insoluble polyimide and soluble polyimide (used BPDA, ODPA, DSDA, and 6FDA) could produce arbitrarily soluble polymers. These copolyimides were characterized by good film-forming ability, a wide temperature range between T_g and the decomposition temperature, and good thermal stability together with good mechanical properties.

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