Synthesis of Aromatic Poly(amide-imide) Copolymers Containing *para-meta* Benzoic Structure

HUEI-HSIUNG WANG, GIN-CHI LIN

Graduate School of Textile Engineering, Feng Chia University, Taichung 40724, Taiwan, Republic of China

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ABSTRACT: Thermostable poly(amide-imide)s containing *para-meta* benzoic structure were synthesized by reacting a *para-meta* benzoic polyamide prepolymer with various diisocyanate-terminated polyimide prepolymers. The polyamide prepolymers were prepared by first reacting *m*-phenylene diamine and isophthaloyl dichloride to form a poly(*m*-phenylphthalamide) prepolymer, then the terephthaloyl dichloride was subsequently added to form a *para-meta* benzoic polyamide prepolymer. The polyimide prepolymers were also prepared by using 4,4'-diphenylmethane disocyanate to react with pyromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, or 3,3',4,4'-sulfonyldiphthalic anhydride using the direct one-pot method to improve their solubility, but without sacrificing thermal and physical properties. From the experimental results, the inherent viscosity of the copolymers was 0.72-1.15 dL/g and they were readily soluble in a wide range of organic hot solvents such as N-methyl-2pyrrolidone, dimethylimidazole, N,N-dimethylacetamide, dimethyl sulfoxide, and N,Ndimethylformamide; however, some of the copolymers were not soluble in pyridine. The solubility was related to their chemical structure. Those copolymers with sulfonyl and high amide content displayed good solubility. All the poly(amide-imide)s had a glass transition temperature of 260-324°C, but the melting point did not vary much. The 10% weight loss temperatures were in a range of 463–580°C in nitrogen and 450–555°C in an air atmosphere. The tensile strength, elongation at break, and initial modulus of the copolymer films ranged from 59 to 102 MPa, 3.1 to 5.1%, and 1.52 to 3.59 GPa, respectively. These copolymers, except those of high imide content (e.g., P-6, B-4, B-6 and D-6), which showed an amorphous structure, mostly display a crystalline morphology. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2671–2679, 1999

Key words: copoly(amide-imide); polyamideimide; *para-meta* containing; thermostable polymer

INTRODUCTION

Aromatic polyimide is known as one of the best materials for use in high-temperature applications.^{1–3} Its imperviousness to heat is due to its aromatic and heterocyclic structure. Polyimides can resist 500°C for a few minutes or 300°C for several months. The rigid structure in the polyimide chain imparts good properties, such as thermooxidative stability,⁴⁻⁶ but makes the material hard to process because of its poor solubility.⁷⁻¹⁰ In our previous studies^{11,12} we employed the diacid-terminated poly[*m*-phenylene isophthalamide (PmIA)] prepolymer (fully benzoic metastructure) to modify the polyimides. It improved the solubility, mechanical properties, and processing characteristics of the copolymers. This article addresses the use of diacid-terminated *para-meta* benzoic polyamide prepolymer instead

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Scheme 1 Synthesis of aromatic polyimide.

of a diacid-terminated PmIA prepolymer to modify the polyimide, and the effect of *para-meta* benzoic structure on the properties of copoly-(amide-imide)s is investigated.

EXPERIMENTAL

Materials

Three commercially obtained kinds of dianhydrides [pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and 3,3',4,4'-sulfonyl diphthalic anhydride (DSDA)] were dried under a vacuum at -40° C for 4 h. 4,4-Diphenylmethane diisocyanate (MDI) was used without previous purification. m-Phenylenediamine (MPA), isophthaloyl dichloride (IPC), and terephthaloyl chloride (TPC) were supplied to synthesize para-meta benzoic polyamide prepolymer, were of high purity when received from the manufacturers, and were used without previous purification. Solvents such as N-methyl-2-pyrrolidone (NMP), N,Ndimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and 1,3dimethyl-2-imidazolidone (DMI) were purified by vacuum distillation on calcium hydride. Tri-



Scheme 2 Synthesis of diamine-terminated PmIA prepolymers.



Scheme 3 Synthesis of diamine-terminated *para-meta* benzoic structure.

ethamine, which was used as a catalyst, was used without further purification.

Synthesis of Aromatic Polyimide

Equimolar MDI and dianhydride were dissolved in solvent NMP with a solid content of 15%, poured into the 250-mL reaction flask, and heated at 60°C for 1.5 h. The triethylamine catalyst at 0.03 g/L was then added and the temperature was raised to 80°C. The viscosity gradually increased and the bubbles of gas (carbon dioxide) evolved. The viscosity was adjusted by adding the solvent. The reaction was completed after 1 h. A golden viscous solution of polyimide was obtained. The reaction Scheme 1 is shown as follows:

Synthesis of Diamine-Terminated *para-meta* Benzoic Polyamide Prepolymer

A low molecular weight of diamine-terminated *para-meta* benzoic polyamide prepolymer was prepared by the low-temperature polymerization method.^{11,12} The MPA was first dissolved in NMP and cooled to -5 to -15° C; the IPC (molar ratio of $\frac{1}{2}$ or $\frac{3}{2}$) was then added with vigorous stirring over a period of 2 h. The diamine-terminated PmIA prepolymers were obtained. The polymer solution was poured into water, washed with methanol, and vacuum dried at 80°C for 8 h. Reaction Scheme 2 follows.

In order to obtain a polyamide prepolymer with a *para-meta* benzoic structure, the diamine-terminated meta-containing PmIA prepolymer was first dissolved in NMP and the temperature cooled to -5 to -15° C; the TPC (molar ratio of $\frac{1}{2}$) was then added with vigorous stirring over a period of 1.5 h, and the temperature was raised to room temperature for another hour. A pale golden viscous solution was obtained. Reaction Scheme 3 shows this process.



Polymer :

P:MDI - PMDA - Amide = 1 - 1 - 0P - 1: MDI - PMDA - Amide = 2 - 1 - 1P - 2: MDI - PMDA - Amide = 3 - 2 - 1P - 3: MDI - PMDA - Amide(a) = 3 - 2 - 1P - 4: MDI - PMDA - Amide(a) = 4 - 3 - 1P - 5: MDI - PMDA - Amide(a) = 4 - 3 - 1P - 6: MDI - PMDA - Amide(a) = 4 - 3 - 1B:MDI - PMDA - Amide = 5 - 4 - 1B:MDI - BTDA - Amide = 1 - 1 - 0B - 1: MDI - BTDA - Amide = 3 - 2 - 1

B-4: MDI-BTDA-Amide=4-3-1 **B-5**: MDI-BTDA-Amide(a)=4-3-1 **B-6**: MDI-BTDA-Amide=5-4-1 **D**: MDI-DSDA-Amide=2-1-0 **D-1**: MDI-DSDA-Amide=2-1-1 **D-2**: MDI-DSDA-Amide=3-2-1 **D-3**: MDI-DSDA-Amide(a)=3-2-1 **D-4**: MDI-DSDA-Amide(a)=4-3-1 **D-5**: MDI-DSDA-Amide(a)=4-3-1**D-6**: MDI-DSDA-Amide=5-4-1

Scheme 4 Synthesis of copoly(amide-imide) with para-meta benzoic structure.

Synthesis of Copoly(amide-imide) with *para-meta* Benzoic Structure

B-3: MDI-BTDA - Amide(a) = 3-2-1

The copoly(amide-imide) with *para-meta* benzoic structure was synthesized by first preparing diisocyanate-terminated polyimide prepolymer by an excess of MDI. The diamine-terminated polyamide prepolymer with *para-meta* benzoic structure was then added to a reaction flask that contained the diisocyanate polyimide prepolymer at 60°C for 0.5 h; then the temperature was gradually raised to 80°C and left to react for another hour. A pale golden viscous solution was obtained. This reaction is shown in Scheme 4.

Measurements

IR spectra of polyimides and copoly(amide-imide)s were obtained (Hitachi model 260-50 Type) over a range of 250-4000 cm⁻¹. The samples were in the

	Elemental Analysis (%)				
	С	Н	Ν		
Calcd Found	$67.29 \\ 66.91$	$4.05 \\ 4.33$	8.72 9.09		

Table IElemental Analysis ofPrepolymer (2:1:2)

form of a film of about 10 μ m thickness. Elemental analysis (C, H, N) was performed using a Perkin–Elmer 2400 analyzer. Inherent viscosity was per-

Table II Inherent Viscosity of Polymers

Code	Polymer	$\eta_{\rm inh}$ (dL/g)	Imide Content (%)	Amide Content
	1 019 11101	(unig)	(,0)	(,0)
Р	PMDA-MDI(1-1)	0.92	100	0
P-1	PMDA-MDI- amide(1-2-1)	0.82	46.1	53.9
P-2	PMDA-MDI- amide(2-3-1)	1.03	59.2	40.8
P-3	PMDA-MDI- amide(a)(2-3-1)	0.78	51.4	48.6
P-4	PMDA-MDI- amide(3-4-1)	1.11	67.2	32.8
P-5	PMDA-MDI- amide(a)(3-4-1)	0.80	59.9	40.1
P-6	PMDA-MDI- amide(4-5-1)	0.96	72.5	27.5
В	BTAD-MDI(1-1)	1.08	100	0
B-1	BTDA-MDI- amide(1-2-1)	0.99	50.5	49.5
B-2	BTDA-MDI- amide(2-3-1)	1.15	64.0	36.0
B-3	BTDA-MDI- amide(a)(2-3-1)	0.73	56.4	43.6
B-4	BTDA-MDI- amide(3-4-1)	1.03	71.7	28.3
B-5	BTDA-MDI- amide(a)(3-4-1)	0.80	64.9	35.1
B-6	BTDA-MDI- amide(4-5-1)	0.84	76.7	23.3
D	DSDA-MDI(1-1)	0.94	100	0
D-1	DSDA-MDI- amide(1-2-1)	0.77	51.8	48.2
D-2	DSDA-MDI- amide(2-3-1)	0.98	65.4	34.6
D-3	DSDA-MDI- amide(a)(2-3-1)	0.73	57.9	42.1
D-4	DSDA-MDI- amide(3-4-1)	0.94	73.0	27.0
D-5	DSDA-MDI- amide(a)(3-4-1)	0.94	66.3	33.7
D-6	DSDA-MDI- amide(4-5-1)	0.72	77.9	22.1



Figure 1 The IR spectrum of diamine-terminated para-meta containing prepolymer.

formed by a Connon type apparatus in a constant temperature water bath at 25°C with NMP as the solvent of. The inherent viscosity value (η_{inh}) was calculated as: $\eta_{inh} = (\ln(t/t_0))/C$, where t_0 is the



Figure 2 The IR spectra of P series poly(amideimide)s.

	Solvent ^b								
Code	Conc Sulfuric Acid	NMP	DMF	DMAc	DMAc + 5%LiCl	DMSO	Ру	Me	DMI
Р	++	++	_	_	+-	+-	_	_	_
P-1	++	++	+-	+-	+	+-	_	_	+-
P-2	++	++	+-	+-	+	+-	_	_	+-
P-3	++	++	+-	+-	+	+	+-	—	+
P-4	++	++	+-	—	+-	+-	_	_	+-
P-5	++	++	+-	+-	+	+-	—	—	+
P-6	++	+	_	—	+-	+-	_	_	+-
В	++	++	—	+-	+-	+-	_	_	+-
B-1	++	++	+-	+-	+	+	_	_	+
B-2	++	++	+-	+	++	+	+-	_	+
B-3	++	++	+-	+	++	++	+-	-	+
B-4	++	++	+-	+	+	+	—	_	+-
B-5	++	++	+-	+	++	+	+	_	+
B-6	++	++	+-	+-	+	+	—	_	+
D	++	++	+-	+-	+	+-	_	_	+-
D-1	++	++	+	+	+	+	_	_	+
D-2	++	++	+-	+	+	+	_	_	+-
D-3	++	++	+	+	++	++	+-	_	+
D-4	++	++	+-	+-	+	+	_	_	+-
D-5	++	++	+-	+	++	+	+-	_	+
D-6	++	++	+-	+-	+	+-	_	_	+-

Table IIISolubility of Polymers

^a Solubility of polymer: (++) soluble in room temperature, (+) soluble at 80°C, (+-) partially soluble at 80°C, and (-) completely insoluble at 80°C.

^bNMP, *N*-methyl-2-pyrrolidone; Py, pyridine; DMF, *N*,*N*-dimethylformamide; Me, methanol; DMAc, *N*,*N*-dimethylacetamide; DMI, 1,3-dimethyl-2-imidazolidone; and DMSO, dimethyl sulfoxide.

flowing time of the pure solvent, t is the flowing time of the polymer solution; and C, is the polymer concentration (g/dL).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a Du Pont 9900 differential scanning calorimeter and a Seiko SSC-5000 type thermogravimetric analyzer at a heating rate of 20°C/min under a nitrogen atmosphere to obtain the glass transition temperature (T_{σ}) and the weight loss, respectively.

Wide-angle X-ray photographs were taken with Ni-filtered Cu K α radiation using a Rigaku D' max-II type X-ray diffractometer. All stress– strain data were obtained on an Instron 1122 type testing instrument at an extension rate of 10 mm/ min with the specimen of 50 mm length, 10 mm width, and 0.5 mm thickness.

RESULTS AND DISCUSSION

Syntheses of Diamine-Terminated *para-meta* Benzoic Polyamide Prepolymer

Diamine-terminated polyamide prepolymer with *para-meta* benzoic structure was prepared from

MPA, IPC, and TPC. The results of the elemental analysis (Table I) show that the found values are in good agreement with calculated values. The IR spectrum of diamine-terminated *para-meta* benzoic polyamide prepolymer (Fig. 1) exhibits the —NH stretching vibrations of the amide group at 3300 cm⁻¹ and the characteristic *para* and *meta* benzoic absorption's at 700 and 800 cm⁻¹, respectively. These support the formation of diamineterminated *para-meta* benzoic polyamide prepolymer.

Synthesis of Polyimide and Copoly(amide-imide) with *para-meta* Benzoic Structure

MDI and three kinds of aromatic dianhydrides (PMDA, BTDA, and DSDA) were used to prepare three polyimides. Eighteen copolymers were synthesized from four different molar ratios of MDI, three kinds of dianhydride (PMDA, BTDA, and DSDA), and two diamine-terminated prepolymers. The inherent viscosities of the polyimide and copoly(amide-imide) are listed in Table II. It was found that the inherent viscosity of the poly-



Figure 3 X-ray patterns of P series poly(amideimide)s.

mers was higher than 0.72. Some copolymers had values of more than 1.00. In the table the content of the amide and imide groups in the copolymer is also calculated. These polymers can be cast into transparent, tough, and flexible films. Figure 2 shown the typical IR spectra of P series copolymers; the characteristic absorption at 1720, 1780, 1360, and 720 cm^{-1} indicates the existence of an imide group. The absorption peaks of 700 and 800 cm⁻¹ demonstrate the presence of *para* and *meta* benzoic structure, respectively; and the characteristic absorption at $3300-3400 \text{ cm}^{-1}$ represents the ----NH stretching vibrations of the amide group. From these facts it could be concluded that the para-meta benzoic polyamide was introduced into the main chain of the polyimide.

Solubility Properties of Polymers

Table III displays the solubility of all polymers. As indicated, the polyimide from the monomer BTDA is only soluble in NMP at room temperature. Nevertheless, the copolymer of polyimides from BTDA such as B-2 or B-3 are soluble in DMAc + 5% LiCl, NMP, and sulfuric solvents. In

general, the copolymers are readily soluble in a wide range of organic hot solvents such as NMP, DMI, DMAc + 5% LiCl, DMSO, and DMF; but some of copolymers are not soluble in pyridine. Their solubility is related to their chemical structure. Those copolymers with sulfonyl and high amide content display good solubility. Thus, the solubility of the copolymer from PMDA is inferior to that of BTDA, but the DSDA copolymer with the sulfonyl structure shows the best solubility. From that it is manifested that the addition of *para-meta* benzoic polyamide in the polyimide chain does increase its solubility.

Wide-Angle X-ray Diffraction (WAXD) of Polymers

The WAXD patterns of the copolymer P, B, and D series were measured by the Rigaku diffractomer and are shown in Figures 3–5. From the WAX scattering diffraction patterns it is found that the copoly(amide-imide)s have three diffractions at $2\theta = 16^{\circ}$, 26° , and 28° , although the polyimides do not show any scattering peaks.^{11,12} This evidently



Figure 4 X-ray patterns of B series poly(amideimide)s.



Figure 5 X-ray patterns of D series poly(amideimide)s.

indicates that a new crystal structure of copoly-(amide-imide) formed. Because the diffraction peaks of these copolymers are more pronounced as the content of *para-meta* benzoic polyamide increases, the peak is believed to be the scattering of the amide chain in the copolymer. Thus, these copolymers, except those of high imide content (e.g., P-6, B-4, B-6, and D-6), which show an amorphous morphology, are mostly partially crystalline in structure.

Thermal Properties of Polymers

The thermal properties of all polymers were evaluated by DSC and TGA. Their thermal behavior data is listed in Table IV. With the presence of benzoic and heterocyclic ring structures of polyimide or a benzoic ring and an amide group of *para-meta* benzoic polyamide, these polymers have excellent thermooxidative stability and also show a high glass transition temperature (T_g) . The T_g values of the polyimides P, B, and D range from 309 to 348°C. Among P, B, and D, polyimide

D has the lowest T_g due to its sulfonyl structure. The T_g values of the copolymers are 260–324°C and decreased with an increasing amount of *para-meta* benzoic polyamide. The explanation is that the incorporation of *para-meta* benzoic polyamide into the polyimide backbones can increase the flexibility of the copolymer chain and hence decrease the T_g values of the copolymers. The relationship between the T_g and imide content is shown in Figure 6.

Table IV also summarizes the thermogravimetric data of all polymers. As indicated, all polymers possess good thermal stability and thermooxidation stability with no significant weight loss up to a temperature of approximately 360°C in nitrogen and in an air atmosphere. Moreover, polyimide P has the best thermal stability and 10% weight loss properties at 577 and 590°C, respectively. The decomposition temperatures at 10% weight loss of these copolymers are 450–555°C in air and 463–580°C in a nitrogen atmosphere. With the increase of polyamide content, the 10% weight loss temperature is lowered. This suggests

Table IV Thermal Properties of Polymers

			Degradation Temperature ^a (°C)	
Code	T_g (°C)	$T_m \; (^{\rm o}{\rm C})$	Air	Nitrogen
Р	348	_	575	590
P-1	283	372	463	488
P-2	302	375	520	540
P-3	290	377	472	485
P-4	309	378	544	555
P-5	295	380	507	530
P-6	324	_	555	580
В	309	_	568	581
B-1	262	372	460	471
B-2	275	366	500	531
B-3	266	370	470	492
B-4	290	_	532	552
B-5	272	369	500	518
B-6	302	_	545	559
D	317	_	554	568
D-1	260	364	450	463
D-2	276	370	485	502
D-3	266	366	460	482
D-4	293	368	530	543
D-5	277	371	491	501
D-6	308	—	540	553

 $^{\rm a}$ A 10% weight loss temperature at a heating rate of 20°C/ min with TGA measurement.



Figure 6 The relation between T_g values and imide content.

that the amide linkage does contribute less thermooxidative stability than that of the imide.

Mechanical Properties

The mechanical properties of the polymers is shown in Table V and Figures 7–9. It is shown that the tensile strength, the breaking elongation,

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Table V	Mechanical	Properties	01 1	Polymers
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Polymer Code	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
Р	62.8	5.08	1.66
- P-1	100.0	4.19	2.74
P-2	74.5	3.11	2.91
P-3	81.7	3.68	2.38
P-4	68.5	4.18	2.20
P-5	72.6	3.20	2.80
P-6	66.5	4.91	1.91
В	65.3	5.49	1.13
B-1	102.0	3.10	3.59
B-2	78.6	4.15	2.16
B-3	84.2	3.56	2.77
B-4	66.0	5.22	1.58
B-5	73.7	3.99	2.61
B-6	66.4	5.05	1.43
D	55.5	6.12	0.96
D-1	94.0	3.85	2.74
D-2	71.3	4.95	1.75
D-3	78.2	3.97	2.36
D-4	64.3	4.99	1.52
D-5	68.7	4.23	1.95
D-6	59.2	5.10	1.53



Figure 7 The stress-strain relationship of P series poly(amide-imide)s.

and the initial modulus of the polymer are 59-102 MPa, 3.1-5.1%, and 1.52-3.59 GPa, respectively. Most of the polymers have high strength and modulus but medium elongation. This indicates that the polymer is a medium tough material. From Table IV it is found that the tensile strength of the copolymers is higher than that of polyimides and increases with polyamide content. Thus, the use of *para-meta* benzoic polyamide to modify the polyimide does intensify the tensile strength of the copolymers. It is believed that the introduction of the para-meta structure of polyamide to the polyimide can increase the solubility of the copolymers and consequently increase their molecular weight. In addition, the hydrogen bonding of the amide group in the polyamide can



Figure 8 The stress–strain relationship of B series poly(amide-imide)s.



Figure 9 The stress–strain relationship of D series poly(amide-imide)s.

promote the intermolecular force in the copolymers and therefore increase their tensile strength. Thus, copolymers P-6, B-6, and C-6 are found to be less reinforced due to their low polyamide content.

Surprisingly, it is found in Table V that the breaking elongation of the copolymers is decreased and the initial modulus of the copolymers is increased with the increase of polyamide content. This suggests that the introduction of *parameta* benzoic polyamide into polyimide by copolymerization can increase the stiffness of the copolymer chain due to the *para-meta* structure of the polyamide part. Besides, the presence of a crystalline structure in the copolymers may also contribute some degree of their modulus.

CONCLUSIONS

In this experiment we used a one-step method to synthesize three polyimides and 18 *para-meta*

benzoic poly(amide-imide) copolymers. The copoly(amide-imide)s showed an increase in their molecular weight and an improvement in their solubility. The inherent viscosity of these polymers was found to be 0.72–1.15 dL/g, and they can be cast into a transparent and flexible film. The tensile strength of copolymer films are better than those of polyimides. Moreover, the modulus of the copolymer is higher than that of polyimide because of more stiffness in their para-meta structure in the polyamide part. From the thermal analysis, the glass transition temperature of the copolymer is less than that of pure polyimides. The amide linkage is therefore considered to be less thermostable than that of imide. The Xray diffraction patterns show that the copolymers are partially crystalline in structure.

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