Synthesis and Properties of New Poly(amide-imide)s Based on 2,5-Bis(trimellitimido)chlorobenzene

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ABSTRACT: A series of new aromatic poly(amide-imide)s were synthesized by the triphenyl phosphite-activated polycondensation of the diimide-diacid, 2,5-bis(trimellitimido)chlorobenzene (**I**) with various aromatic diamines in a medium consisting of N-methyl-2-pyrrolidone (NMP), pyridine, and calcium chloride. The poly(amide-imide)s had inherent viscosities of 0.76–1.42 dL g^{-1}. The diimide-diacid monomer (**I**) was prepared from 2-chloro-p-phenylenediamine with trimellitic anhydride. Most of the resulting polymers showed an amorphous nature and were readily soluble in a variety of organic solvents, including NMP and N,N-dimethylacetamide. Transparent, flexible, and tough films of these polymers could be cast from N,N-dimethylacetamide or NMP solutions. Their cast films had tensile strengths ranging from 74 to 95 MPa, elongations at break from 7 to 11%, and initial moduli from 1.38 to 3.25 GPa. The glass transition temperatures of these polymers were in the range of 233°–260°C, and the 10% weight loss temperatures were above 450°C in nitrogen. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1691–1701, 1999

Key words: poly(amide-imide); 2,5-bis(trimellitimido)chlorobenzene; phosphorylation

INTRODUCTION

Wholly aromatic poly(amide-imide)s (PAIs) are an important class of materials having excellent resistant to high temperatures, and favorable balance of other physical and chemical properties.[1,2] However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms due to their high melting or glass transition temperatures and limited solubility in organic solvents. Conventionally, trimellitic anhydride (TMA)-based PAIs could be prepared in several ways, such as two-

step polycondensation from the acid chloride of TMA with aromatic diamines involving polyaddition and subsequent cyclodehydration,[3] low-temperature solution polycondensation of TMA-derived imide ring-preformed diacid chlorides and aromatic diamines,[4–7] and polycondensation of TMA or TMA-derived imide ring-containing dicarboxylic acids with diisocyanates.[8–10] Other synthetic routes of PAIs included the polymerization of N,N'-bis(trimethylsilyl)-substituted aromatic diamines with 4-chloroformylphthalic anhydride,[11] the palladium-catalyzed carbonylation and coupling of aromatic diamines and diimide-containing diiodides,[12] as well as the simultaneous catalytic amidation and imidization of TMA-derived o-ester acids.[13] Recently, we have successfully applied phosphorylation reaction[14] to

the synthesis of high-molecular weight PAIs by the direct polycondensation of imide-containing dicarboxylic acids with aromatic diamines using triphenyl phosphite (TPP) and pyridine (Py) as condensing agents.[15–25] The direct polycondensation route avoids using moisture-sensitive acid chlorides or isocyanates and provides significant advantages in manufacturing operations, compared with conventional methods.

Recently, in a continuation of these studies, we are interested in the potential usefulness of substituent-containing *p*-phenylene structure as simultaneously bulky and symmetrical unit in the polymer main chain. However, only a limited number of poly(ester-imide)s derived from diimide-diacid, 2,5-bis(trimellitimido)chlorobenzene, and bisphenols had been reported earlier[26] and have not been investigated in detail. The present article describes the synthesis of a series of novel poly(amide-imide)s from 2,5-bis(trimellitimido)-chlorobenzene and various aromatic diamines. The solubility, tensile properties, crystallinity, and thermal properties of the obtained polymers will also be investigated.

To obtain more insight into the effect of the introduction of bulky group on properties of poly-(amide-imide)s, 1,4-bis(trimellitimido)benzene was also synthesized in present study, and the diimide-diacid was used to prepare poly(amide-imide)s to make a comparison of the solubility behavior with the previously described corresponding poly(amide-imide)s derived from 2,5-bis(trimellitimido)chlorobenzene.

EXPERIMENTAL

Materials

2-Chloro-*p*-phenylenediamine dihydrochloride (from Acros Organics, Pittsburgh, PA), TMA (from Wako Pure Chemical Co., Osaka, Japan), and TPP (from TCI, Tokyo, Japan) were used without further purification. Commercially obtained anhydrous calcium chloride was dried under vacuum at 150°C for 6 h. *N*-methyl-2-pyrrolidone (NMP) and Py were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieve. *p*-Phenylenediamine (**IIa**; from Wako) and *m*-phenylenediamine (**IIb**; from TCI) were distilled under vacuum before use. All other diamines, such as 2,4-diaminotoluene (**IIc**; from TCI), 4,4′-oxydianiline (**IId**; from TCI), 3,4′-oxydianiline (**IIe**; from Teijin Ltd., Tokyo, Japan), 4,4′-thiodianiline (**IIf**;

Scheme 1 Synthesis of poly(amide-imide)s.

from TCI), 4,4′-methylenedianiline (**IIg**; from TCI), 1,4-bis(4-aminophenoxy)benzene (**IIh**; from TCI), and diamines [including 1,3-bis(4-aminophenoxy)-benzene (**IIi**), 2,2′-[4-(4-aminophenoxy)phenyl]propane (**IIj**), and 2,2′-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**IIk**)] were obtained from Chriskev Corp. and used without further purification.

Monomer Synthesis

2,5-Bis(trimellitimido)chlorobenzene (I)

A mixture of 6.46 g (30 mmol) of 2-chloro-*p*-phenylenediamine dihydrochloride and 11.55 g (60 mmol) of TMA was dissolved in 80 mL of dry NMP at 60°C and stirred for 1 h. About 30 mL of toluene was then added, and the mixture was heated with reflux for 3 h until ~ 1.1 mL of water was distilled off azeotropically under a Dean-Stark trap. Heating was continued to distill off the residue toluene. After cooling, the white precipitate of diimide-diacid (**I**) was isolated by filtration and washed with methanol. The product obtained was dried under vacuum affording 13.8 g (94% yield) of white powders; m.p.: 430°–431°C. ANAL. Calcd

Figure 1 Infrared spectra of diimide-diacid (**I**) and poly(amide-imide) (**IIIe**).

for $C_{24}H_{11}N_2O_8Cl$: C, 58.72%; H, 2.24%; N, 5.71%. Found: C, 58.70%; H, 2.58%; N, 5.62%.

1,4-Bis(trimellitimido)benzene was synthesized analogously.

Polymerization

A typical example (**III_b**) of polycondensation follows: a mixture of 0.214 g (1.23 mmol) of diamine

Table I Preparation of Poly(amide-imide)s from Diimide-diacids and Various Aromatics Diamines

Polymer	Amount Monomer (mmol)	Amount of Reagents Used				
		NMP (mL)	CaCl₂ (g)	Py (mL)	TPP (mL)	η_{inh}[a] (dL g⁻¹)
III-a	1.0	6.0	0.5	1.2	0.6	0.64[b]
III-b	1.2	5.0	0.3	1.2	0.7	1.42
III-c	1.5	5.0	0.4	1.2	0.9	0.81[c]
III-d	1.0	4.5 + 3.0	0.3	1.0	0.6	1.32[c]
III-e	1.3	6.0 + 2.0	0.3	1.2	0.8	1.09
III-f	1.0	4.5 + 4.0	0.3	1.0	0.6	1.39
III-g	1.0	4.5	0.3	1.0	0.6	0.84
III-h	1.0	4.0	0.4	1.0	0.6	0.90[c]
III-i	1.0	4.0	0.4	1.0	0.6	0.76
III-j	1.0	4.5 + 3.5	0.3	1.0	0.6	1.09
III-k	1.0	4.5 + 3.0	0.3	1.0	0.6	1.13

[a] Measured at a concentration of 0.5 g dL⁻¹ in DMAc at 30°C.
[b] Measured at a concentration of 0.5 g dL⁻¹ in conc. H₂SO₄.
[c] Measured at a concentration of 0.5 g dL⁻¹ in DMAc + 5% LiCl at 30°C.

IIb, 0.603 g (1.23 mmol) of diimide-diacid **I**, 0.31 g of calcium chloride, 5 mL of NMP, 1.2 mL of pyridine, and 0.7 mL of TPP was heated at 100°C for 3 h. The obtained polymer solution was trickled into 300 mL of methanol. The stringy polymer was washed thoroughly with methanol and hot water, collected by filtration, and dried at 100°C under vacuum. The yield was quantitative. The inherent viscosity of the polymer was 1.42 dL g⁻¹, measured at a concentration of 0.5 g dL⁻¹ in *N,N*-dimethylacetamide (DMAc) at 30°C.

Other poly(amide-imide)s (**III**$_{a,c-k}$, **IV**) were synthesized analogously.

Characterization

Infrared spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. Elemental analyses were run in a Perkin-Elmer model 240 CHN analyzer (Perkin-Elmer, Norwalk, CT). Inherent viscosities of all polymers were determined at 0.5 g dL⁻¹ concentration using a Cannon-Fenske viscometer. Thermogravimetric analysis (TGA) was conducted with a Rigaku thermal analysis station TAS-100. Measurements were performed with 10 ± 2 mg samples heated in flowing nitrogen (50 cm³ min⁻¹) at a heating rate of 20°C min⁻¹. Differential scanning calorimetry (DSC) analyses were performed on a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller in flowing nitrogen

(30 cm³ min⁻¹) at a heating rate of 20°C min⁻¹. Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa, using nickel-filtered CuK$_\alpha$ radiation (40 kV, 15 mA), and the scanning rate was 4° min⁻¹. Measurements were performed with film specimens of ∼ 0.1 mm in thickness. An Instron Universal Tester Model 1130, with a load cell of 5 kg, was used to study the stress-strain behavior of the samples at a drawing speed of 5 cm min⁻¹. Measurements were performed at room temperature (∼ 20°C) with film specimens (0.5 cm wide, 6 cm long, and ∼ 0.1 mm thick) and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Synthesis

2,5-Bis(trimellitimido)chlorobenzene (**I**), the novel poly(amide-imide)s-forming diimide-diacid with preformed imide rings, was synthesized *via* the two-stage procedure that included ring-opening addition of 2-chloro-*p*-phenylenediamine dihydrochloride with two equivalent amounts of TMA, followed by cyclodehydration to the imidodicarboxylic acid by toluene-water azeotropic distillation (Scheme 1). The Fourier transform-infrared spectrum (KBr) of dicarboxylic acid (**I**) showed absorption bands at 3438 ∼ 3182 cm⁻¹ (acid —OH), 1781 cm⁻¹ (imide, symmetric C=O

Table II   Elemental Analysis of Poly(amine-imine)s

Polymers	Formula (Molecular Weight)		Elemental Analysis[a] (%)			Moisture Intake (%)[b]
			C	H	N	
III-a	$(C_{30}H_{16}N_4O_6Cl)n$	Calcd	63.90	2.86	9.94	1.28
	$(563.93)n$	Found	63.08	3.33	9.44	
		Corrected	63.88	3.28	9.59	
III-b	$(C_{30}H_{16}N_4O_6Cl)n$	Calcd	63.90	2.86	9.94	3.36
	$(563.93)n$	Found	61.75	3.14	9.28	
		Corrected	63.82	3.03	9.59	
III-c	$(C_{31}H_{18}N_4O_6Cl)n$	Calcd	64.42	3.14	9.69	2.00
	$(577.96)n$	Found	63.13	3.29	9.50	
		Corrected	64.39	3.19	9.69	
III-d	$(C_{36}H_{20}N_4O_7Cl)n$	Calcd	65.91	3.07	8.54	2.56
	$(656.03)n$	Found	64.22	3.27	8.07	
		Corrected	65.86	3.19	8.28	
III-e	$(C_{36}H_{20}N_4O_7Cl)n$	Calcd	65.91	3.07	8.54	2.09
	$(656.03)n$	Found	64.53	3.33	8.07	
		Corrected	65.88	3.26	8.24	
III-f	$(C_{36}H_{20}N_4O_6SCl)n$	Calcd	64.34	3.00	8.34	2.41
	$(672.09)n$	Found	62.79	3.21	7.78	
		Corrected	64.30	3.13	7.97	
III-g	$(C_{37}H_{22}N_4O_6Cl)n$	Calcd	67.95	3.39	8.57	1.86
	$(654.06)n$	Found	66.68	3.53	7.94	
		Corrected	67.92	3.46	8.09	
III-h	$(C_{42}H_{24}N_4O_8Cl)n$	Calcd	67.43	3.23	7.49	1.04
	$(748.13)n$	Found	66.73	3.47	7.21	
		Corrected	67.42	3.43	7.29	
III-i	$(C_{42}H_{24}N_4O_8Cl)n$	Calcd	67.43	3.40	7.31	0.55
	$(748.13)n$	Found	67.06	3.42	7.27	
		Corrected	67.42	3.40	7.31	
III-j	$(C_{51}H_{34}N_4O_8Cl)n$	Calcd	70.71	3.96	6.47	2.16
	$(866.31)n$	Found	69.18	3.97	6.15	
		Corrected	70.67	3.88	6.28	
III-k	$(C_{51}H_{28}N_4O_8F_6Cl)n$	Calcd	62.88	2.90	5.75	1.14
	$(974.25)n$	Found	62.12	3.06	5.59	
		Corrected	62.83	3.03	5.65	

[a] For C and N: corrected value = found value $\times$ (100% + moisture intake %). For H: corrected value = found value $\times$ (100% − moisture intake %).

[b] Moisture intake (%) = $(W - W_0)/W_0 \times 100\%$. W = weight of polymer sample after standing at room temperature. W_0 = weight of polymer sample after dried in a vacuum at 100°C for 10 h.

stretching), 1721 cm^{-1} (acid C=O stretching and asymmetric imide C=O stretching) (Fig. 1).

A series of new poly(amide-imide)s (**III$_{a-k}$**) containing the 2-chloro-p-phenylene unit were prepared from diimide-diacid **I** and various aromatic diamines **II$_{a-k}$** by the direct polycondensation reaction using TPP and Py as condensing agents (Scheme 1). The reaction condition and results of the polycondensation are summarized in Table I. These polymers were obtained in almost quantitative yield with inherent viscosities of 0.64–1.42 dL

g^{-1}. Solubility of the polymer solution and the state of stirring affected the inherent viscosity of the resulting poly(amide-imide)s significantly. Generally, the molecular weight of the polymers obtained from the phosphorylation reaction is highly dependent on the reactant concentration. Higher molecular weights of these polymers could be obtained by using a higher initial reactant concentration and adding a proper amount of supplemental NMP into the viscous reaction medium before the formation of swollen gel. Most of the molecular weights of these

Table III Solubility[a] of Poly(amide-imide)s

Polymer	DMAc	DMAc + 5% LiCl	NMP	DMF	DMSO[b]	Py	Conc. H$_2$SO$_4$
III-a	−	±	±	−	−	−	+
III-b	+	+	+	+	+	±	+
III-c	+	+	+	+	+	±	+
III-d	+	+	+	±	±	−	+
III-e	+	+	+	+	+	±	+
III-f	+	+	+	+	+	±	+
III-g	+	+	+	±	+	±	+
III-h	±	+	+	±	±	−	+
III-i	+	+	+	+	±	−	+
III-j	+	+	+	+	+	+	+
III-k	+	+	+	+	+	+	+

[a] Solubility: (+) soluble at room temperature; (−) insoluble; (±) partially soluble.
[b] DMSO, dimethylsulfoxide.

polymers are sufficiently high to permit casting tough and flexible films.

Formation of poly(amide-imide)s was confirmed by elemental analysis and infrared spectroscopy. Elemental analysis values of these polymers are listed in Table II. In all cases, however, the found values of carbon were lower than the calculated values for the proposed structures. These may be attributed to the hygroscopic characteristics of the amide group. The moisture intake for poly(amide-imide)s **III$_{a-k}$** was in the range of 0.55–3.36% at room temperature and normal pressure in our laboratory. Corrected values were in good agreement with the calculated ones after deducting the amount of moisture intake. The infrared spectra (Fig. 1) of the polymers exhibited characteristic absorptions for the imide ring at 1783 cm^{-1} and 1729 cm^{-1}, peculiar to the symmetrical and asymmetrical carbonyl stretching vibration. Bands of amide groups appeared at

Table IV Solubility[a] of Poly(amide-imide)s

Polymer	DMAc	DMAc + 5% LiCl	NMP	DMF	DMSO[b]	Py	Conc. H$_2$SO$_4$
IV-a	−	±	−	−	−	−	+
IV-b	−	+	−	−	−	−	+
IV-c	−	+	−	−	−	−	+
IV-d	−	+	−	−	−	−	+
IV-e	−	+	−	−	−	−	+
IV-f	−	+	−	−	−	−	+
IV-g	−	+	−	−	−	−	+
IV-h	−	±	−	−	−	−	+
IV-i	−	−	−	−	−	−	+
IV-j	−	−	−	−	−	−	+
IV-k	−	+	−	−	−	−	+
IV-l	−	+	−	−	−	−	+

[a] Solubility: (+) soluble at room temperature; (−) insoluble; (±) partially soluble.
[b] DMSO, dimethylsulfoxide.

Figure 2 Wide-angle X-ray diffractograms of some poly(amide-imide)s.

3618 cm^{-1}, 3370 cm^{-1} (N—H), and 1671 cm^{-1} (C=O).

Properties of Polymers

Table III shows the qualitative solubility of the PAIs in various solvents. Most polymers were

soluble in aprotic polar solvents, such as DMAc, NMP, and N,N-dimethylformamide (DMF). Polymer **IIIa**, with rigid and symmetrical p-phenylene, had somewhat limited solubility. This may be due to the semicrystalline nature of these polymers, as evidenced by X-ray diffrac-

Table V Tensile Properties of Poly(amide-imide) Films

Polymer	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
III-b	103	95	10	3.25
III-c	—[b]	79	7	3.15
III-e	—	74	11	1.98
III-f	—	83	8	2.17
III-i	—	83	7	2.54
III-j[a]	—	82	8	1.38
III-k	—	92	10	1.74

[a] The polymer (**IIIj**) film is too thick ($\sim$ 0.015 mm).
[b] —, no yielding was observed.

tograms discussed herein. All of the polymers are insoluble in common organic solvents, such as tetrahydrofuran, chloroform, acetone, and benzene. The solubility behavior of the new poly(amide-imide)s derived from the diimide-diacid (**I**) with aromatic diamines were compared with those of the corresponding poly-(amide-imide)s derived diimide-diacid without chloro substituent, 1,4-bis(trimellitimido)ben-

zene summarized in Table IV. Thus, the solubility of poly(amide-imide)s was found to be greatly improved by the introduction of a bulky chloro substituent into the phenylene unit along the polymer backbone.

Crystallinity of the prepared poly(amide-imide)s was measured by wide-angle X-ray diffraction studies. Figure 2 revealed that polymer **IIIa** had a fair degree of crystallinity, whereas all of the other polymers showed completely amorphous pattern. Thus, the amorphous nature of these polymers was reflected in their excellent solubility, which is in agreement with the general rule that the solubility decrease with increasing crystallinity. The semicrystalline behavior of the previously described polymer was speculated to be caused by the introduction of the rigid-rod and symmetrical *p*-phenylene structure (**IIa**).

Transparent, flexible, and yellowish films could be cast from the DMAc or NMP solutions of most PAIs, and were subjected to the tensile test. Tensile properties of some typical PAIs are summarized in Table V. These films had a tensile strength of 74–95 MPa, an elongation to

Figure 3 TGA curves for poly(amide-imide) (**IIIf**) with a heating rate of 20°C min^{-1}: (---) in air; (—) in nitrogen.

Table VI   Thermal Behavior of Poly(amide-imide)s

Polymer	DSC[a] T_g (°C)	Decomposition Temperature (°C)[b] In Air	In Nitrogen	Wt % Residue at 800°C in Nitrogen
III-a	—[c]	421	452	56
III-b	260	470	492	53
III-c	253	450	465	54
III-d	—[c]	475	485	59
III-e	244	465	487	52
III-f	—	477	493	51
III-g	—	448	454	59
III-h	—	460	470	59
III-i	233	450	456	60
III-j	240	440	470	59
III-k	242	460	488	58

[a] From DSC measurements conducted with a heating rate of 20°C min^{-1} in nitrogen.
[b] Temperature at 10% weight loss was recorded by TGA at a heating rate of 20°C min^{-1} in nitrogen.
[c] —, no T_g was observed in DSC traces.

break of 7–10%, and an initial modulus of 1.98–3.25 GPa.

Thermal stability of the poly(amide-imide)s was studied by TGA. Typical TGA curves in both air (dashed line) and nitrogen (solid line) atmospheres of representative poly(amide-imide) (**IIIf**) are shown in Figure 3. Temperatures of 10% weight loss in nitrogen and air atmosphere were determined from original thermograms and tabulated in Table VI. In general, all of the polymers exhibited good thermal stability with no significant weight loss up to temperatures of ~ 400°C in nitrogen, and their 10% weight loss temperatures were recorded in the range of 455°–495°C in nitrogen and 420°–475°C in air, respectively. The amount of carbonized residue (char yield) of poly(amide-imide)s in nitrogen atmosphere was in the range of 51–60% weight, even at 800°C, showing high intrinsic fire-retardant characteristics.

Table VI also summarizes the thermal transition data of the poly(amide-imide)s. Quenching from the elevated temperatures to room temperature in air yields more amorphous samples so that in most cases the glass transition temperatures (T_gs) could be easily measured in the second heating traces of DSC. The T_gs of the poly(amide-imide)s were in the range of 233°–260°C. Figure 4 shows typical DSC curves of polymer **IIIj**. A broad melting (T_m) endotherm peak of polymer **IIIj** could be observed on its first DSC trace. Although the as-precipitated polymer melted, they failed to crystallize under the condition of the DSC measurement and exhibited clear T_gs in second heating runs, as shown in Figure 4. No cold crystallization was observed above T_g. Thus, it appears that the initial crystallinity results from the presence of solvent and the way the material was precipitated.

CONCLUSIONS

A series of new high molecular weight aromatic poly(amide-imide)s based on the diimide-diacid, 2,5-bis(trimellitimido)chlorobenzene, were successfully prepared by direct polycondensation with various aromatic diamines using TPP and Py as condensing agents. Typical poly(amide-imide)s were noncrystalline. Introduction of a bulky and symmetrical 2-chloro-p-phenylene unit into the polymer backbone lead to signifi

Figure 4 DSC curves of poly(amide-imide) (**IIIj**) with a heating rate of 20°C min^{-1}:
(- - -) first heating; (—) second heating.

cantly improved solubility of the polymer in various organic solvents. Most of these polymers exhibited a desired combination of properties requiring high-performance materials that include excellent mechanical properties, high thermal stability, excellent solubility in organic solvents, and moderately high T_gs.

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