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Polyisoimides: Synthesis and Evaluation as Efficient Precursors for Polyimides

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ABSTRACT: Polyisoimides have been evaluated as potential precursors for polyimides since they are expected to be tractable and isomerized to polyimides without producing water. Detailed studies on isoimides were carried out first with model compounds. Compared to *N*-phenyl- and *N*-benzylphthalisoimides, *N*-(benzyloxy)phthalisoimide proved to be superior in terms of ease of synthesis, hydrolytic stability, and quantitative isomerization to the imide. Polymerizations of *p*- and *m*-xylylenebis(oxyamine)s with tetracarboxylic dianhydrides such as pyromellitic dianhydride, benzophenonetetracarboxylic dianhydride, and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride proceeded efficiently in *N*-methyl-2-pyrrolidone, and the resulting poly(amic acid)s had inherent viscosities up to 0.61 dL/g. The poly(amic acid)s were then converted into polyisoimides by chemical dehydration. Under appropriate conditions with *N,N'*-dicyclohexylcarbodiimide, isoimide formation was preferred to imide formation, and the isoimide contents of the polymers were about 90%. The polyisoimides obtained exhibited high solubility and low glass transition temperatures unlike the corresponding polyimides. Furthermore, on heating or treating with a base catalyst, the polyisoimides were isomerized to polyimides quantitatively, indicating the high potential of the polyisoimides as precursors for polyimides.

Introduction

Aromatic polyimides are indispensable in various high-technology areas because of their outstanding performance even under severe conditions. Since they are insoluble, soluble precursors, poly(amic acid)s, have to be utilized for fabrication followed by cyclization to polyimides. There are, however, some problems associated with this process. For example, poly(amic acid)s are unstable, and, moreover, dehydration cyclization tends to cause the formation of voids or pinholes and also poor dimensional stability owing to the liberation of water. If, therefore, polyimides can be synthesized without producing water, the procedure may have various advantages over the conventional methods.

Our recent attention has been focused on the synthesis of polyisoimides as potential precursors for polyimides, since they are expected to be isomerized to polyimides without forming water to enable void-free fabrication. Furthermore, they would show high solubility and low glass transition temperatures owing to the bent molecular structures.

Polymers containing isoimide rings were first claimed in a patent,[1] where poly(amic acid) films obtained from 4,4'-diaminodiphenyl ether and pyromellitic dianhydride (PMDA) were converted into copoly(imide isoimide) films with trifluoroacetic anhydride. Recently polyisoimides were prepared by treating poly(amic acid)s based on PMDA with *N,N'*-dicyclohexylcarbodiimide (DCC), and they were soluble in aprotic polar solvents when the diamine components had solubilizing bulky pendant groups.[2] In the cyclization of the poly(amic acid) derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 1,5-diaminonaphthalene with acetic anhydride, isoimide formation was about 5 times slower than imide formation, and, moreover, the isoimide units underwent conversion into the more stable imide units.[3] An acetylene-terminated amic acid oligomer[4] known by the trade name Thermid[5] gave a derivative containing some isoimide rings in addition to imide rings on treatment with trifluoroacetic anhydride.[6] Cyclization of amic acids to isoimides is generally achieved with special dehydrating agents such as trifluoroacetic anhydride[7] and DCC,[8] and, furthermore, isoimide rings are rather susceptible to hydrolysis as well as to other nucleophilic attacks.[2,9] The synthetic obstacle and inherent instability of isoimide structures have hence made difficult quantitative studies on polyisoimides.

We have already reported some preliminary results of basic isoimide work,[10] and here we describe the detailed studies on the structural influence on the properties of model isoimides, facile synthesis of polyisoimides, efficient isomerization of the polyisoimides to polyimides, and characteristic properties of the polyisoimides in comparison with those of the polyimides.

Experimental Section

General Procedures. Solvents were purified in the usual manners and stored over molecular sieves (3 Å). Phthalic anhydride was sublimed. PMDA was recrystallized from acetic anhydride and then sublimed at 220 °C in vacuum. Benzophenonetetracarboxylic dianhydride (BTDA) was recrystallized from acetic anhydride and then from dioxane. 6FDA and DCC were of reagent grade (Tokyo Kasei Kogyo Co.) and used without further purification. IR and UV spectra were recorded on a JEOL JIR-3510 or Jasco IR-700 and Jasco Ubest-30 spectrometers, respectively. NMR spectra were taken with a JEOL JNM-GX270, with tetramethylsilane being used as the internal reference. Thermal properties were elucidated with a Seiko SSC-5200 with TG/DTA and DSC units. X-ray diffraction diagrams were obtained by the powder method using nickel-filtered Cu Kα radiation with a Rigaku RAD-IA diffractometer.

***N*-(Benzyloxy)phthalisoimide.** (Benzyloxy)amine[11] (1.23 g, 0.01 mol) was dissolved in 5 mL of dioxane, and a solution of 1.49 g (0.01 mol) of phthalic anhydride in 10 mL of dioxane was added dropwise over a period of 10 min under nitrogen.

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After stirring at room temperature for 24 h, the solvent was removed under reduced pressure. The residual solid was recrystallized from ethanol/petroleum ether to give 2.10 g (77%) of *N*-(benzyloxy)phthalamic acid as colorless needles: mp 140–142 °C; IR (KBr) ν 3500–2400 (OH), 3178 (NH), 1711, 1637 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 4.93 (s, 2, CH$_2$), 7.31–7.85 (m, 10, aromatic H and NH), 11.42 (s, 1, OH). Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.46, H, 5.13; N, 5.21.

To a solution of 0.271 g (1 mmol) of *N*-(benzyloxy)phthalamic acid in 1.5 mL of pyridine was added 1.0 mL of acetic anhydride. The mixture was stirred at room temperature for 24 h under nitrogen and poured into 30 mL of ice water. The precipitate was collected by filtration, washed thoroughly with water, and dried to give 0.200 g (79%) of a white powdery material. It was composed of 87% of the isoimide and 13% of the imide, as determined by ^{1}H NMR spectroscopy in CDCl$_3$ with benzyl methylene peaks at 5.27 and 5.21 ppm for the isoimide and imide. Recrystallization from ethanol gave 0.162 g (64%) of pure *N*-(benzyloxy)phthalisoimide as colorless needles: mp 130–131 °C; IR (KBr) ν 1806, 1655 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 5.27 (s, 2, CH$_2$), 7.33–7.94 (m, 9, aromatic H). Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.18; H, 4.33; N, 5.62.

***N*-Benzylphthalisoimide.** *N*-Benzylphthalamic acid was prepared from equimolar amounts of benzylamine and phthalic anhydride and recrystallized from ethanol/petroleum ether to give colorless needles: yield 89%; mp 149–151 °C (lit.[12] mp 152 °C).

To a solution of 2.00 g (8 mmol) of *N*-benzylphthalamic acid in 24 mL of dioxane was added 1.60 g (8 mmol) of DCC, and the solution was stirred at room temperature under nitrogen for 4 h. Precipitated *N,N'*-dicyclohexylurea was removed by filtration, and the filtrate was poured into 300 mL of water. The precipitate was collected by filtration and dried. It was recrystallized from tetrahydrofuran (THF)/hexane to give 1.30 g (68%) of *N*-benzylphthalisoimide as colorless needles: mp 79–81 °C (lit.[12] mp 81–81.5 °C).

***N*-Phenylphthalisoimide.** Starting from aniline and phthalic anhydride, *N*-phenylphthalamic acid was prepared in a similar manner and recrystallized from ethanol/petroleum ether to give colorless needles: yield 83%; mp 169–171 °C (lit.[13] mp 170 °C).

Cyclization of *N*-phenylphthalamic acid was carried out with DCC under the same conditions described above. Recrystallization from THF/petroleum ether gave slightly yellow powdery crystals: yield 67%; mp 115–117 °C (lit.[13] mp 115–117 °C).

Stability and Isomerization of Isoimides. A solution of 50 mg of *N*-(benzyloxy)phthalisoimide in 5 mL of *N,N*-dimethylacetamide (DMAc)/water (90/10 by volume) was stirred at room temperature for 24 h and poured into 50 mL of water. The precipitate was filtered, washed with water, and dried to give 46.5 mg (93% recovery) of a white solid. The ^{1}H NMR spectrum showed that the product contained 89% of the isoimide and 11% of the imide.

N-Benzylphthalisoimide was dissolved in dimethyl-d_6 sulfoxide (DMSO-d_6), and the time course was followed by NMR spectroscopy. The isoimide and imide were determined with benzyl methylene peaks at 4.86 and 4.78 ppm, respectively.

In the case of *N*-phenylphthalisoimide, products were isolated in water, and the product compositions were determined with a calibration curve based on the absorbances at λ_{max} 325 and 292 nm for the isoimide and imide in UV spectra in acetonitrile.

***p*-Xylylenebis(oxyamine).** To a solution of 8.60 g (0.02 mol) of *p*-xylylenebis(oxyphthalimide),[14] prepared from *p*-xylylene dichloride and 2 equiv of *N*-hydroxyphthalimide in the presence of triethylamine, in 60 mL of dioxane was added 2.20 g (0.04 mol) of hydrazine hydrate. After refluxing for 3 h, the precipitated phthalhydrazide was filtered. The filtrate was evaporated under reduced pressure, and the residual syrup was dissolved in 40 mL of 2 mol/L aqueous sodium hydroxide. The solution was extracted with eight 50-mL portions of chloroform. The extract was dried with magnesium sulfate and concentrated under reduced pressure. The residue was recrystallized from dichloromethane/petroleum ether to give 2.39 g (71%) of colorless plates: mp 56–58 °C; IR (KBr) ν 3312, 3248, 1600 cm^{-1} (NH); ^{1}H NMR (CDCl$_3$) δ 4.69 (s, 4, CH$_2$), 5.40 (s, 4, NH$_2$), 7.36 (s, 4 aromatic H). Anal. Calcd for $C_8H_{12}N_2O_2$: C, 56.82; H, 7.15; N, 16.57. Found: C, 56.79; H, 7.25; N, 16.27.

***m*-Xylylenebis(oxyamine).** *m*-Xylylenebis(oxyphthalimide)[14] was treated with hydrazine hydrate in a similar manner. The crude diamine was distilled to give a colorless liquid: yield 38%; bp 134–136 °C (1 mmHg); IR (neat) ν 3312, 3230, 1588 cm^{-1} (NH); ^{1}H NMR (CDCl$_3$) δ 4.69 (s, 4, CH$_2$), 5.34 (s, 4, NH$_2$), 7.30–7.36 (m, 4, aromatic H).

To a solution of 1.26 g (7.5 mmol) of *m*-xylylenebis(oxyamine) in 50 mL of dioxane was added 7.0 mL (8.4 mmol) of concentrated hydrochloric acid. The mixture was stirred at room temperature for 1 h, and the precipitate was collected by filtration. It was recrystallized from water/ethanol to give 1.30 g (72%) of *m*-xylylenebis(oxyamine) dihydrochloride as colorless needles: mp 265 °C (dec) (lit.[14] mp 235–237 °C (dec)).

Poly(amic acid) and Polyimide. *m*-Xylylenebis(oxyamine) dihydrochloride (0.241 g, 1 mmol) in 3 mL of *N*-methyl-2-pyrrolidone (NMP) was treated with 0.202 g (2 mmol) of triethylamine, and to the slurry was added 0.444 g (1 mmol) of 6FDA at 0 °C. The mixture was stirred under nitrogen at 0 °C for 2 h and then at room temperature for 22 h. The resulting viscous mixture was poured into 300 mL of acetone, and the precipitate was collected by filtration. It was washed thoroughly with chloroform to remove triethylamine hydrochloride and dried to give 0.349 g (57%) of the poly(amic acid) as a white fibrous material. Inherent viscosity was 0.28 dL/g as determined in DMAc at a concentration of 0.25 g/dL at 25 °C: IR (KBr) ν 3500–2500 (OH and NH), 1723, 1656 cm^{-1} (C=O).

On heating at 200 °C for 30 min in vacuum, the poly(amic acid) was converted into the corresponding polyimide quantitatively. Inherent viscosity of the resulting slightly off-white polyimide was 0.26 dL/g in DMAc at a concentration of 0.25 g/dL at 25 °C: IR (KBr) ν 1791, 1739 cm^{-1} (C=O).

Polymerizations of *p*-xylylenebis(oxyamine) with dianhydrides were conducted similarly except in the absence of triethylamine.

Polyisoimide. To a solution of 50 mg of the poly(amic acid) derived from *m*-xylylenebis(oxyamine) and 6FDA in 1 mL of NMP was added 3.5 mL of toluene to give a slightly cloudy mixture. DCC (0.5 g) was added, and the mixture was stirred at 0 °C for 24 h. The product was isolated by pouring the mixture into 50 mL of ethanol, washed with ethanol thoroughly to remove *N,N'*-dicyclohexylurea, and dried in vacuum to give 25 mg (53%) of a white powdery material. Inherent viscosity was 0.26 dL/g in DMAc at a concentration of 0.25 g/dL at 25 °C: IR (KBr) ν 1807 cm^{-1} (C=O).

The isoimide to imide ratio of the resulting polymer was 89:11 as determined by a calibration curve which was obtained on the basis of absorbance ratios of the bands at 1806 and 1730 cm^{-1} in the IR spectra of the mixtures of model *N*-(benzyloxy)phthalisoimide and the imide.

Conversion of Polyisoimide into Polyimide. The polyisoimide synthesized from *m*-xylylenebis(oxyamine) and 6FDA (50 mg) was dispersed in 5 mL of dichloromethane, and 5 μL of triethylamine (0.1% by volume) was added. After stirring the mixture at room temperature for 24 h, the solvent and catalyst were evaporated in vacuum and washed with ethanol to give 46 mg (92%) of a slightly off-white powdery material. Inherent viscosity was 0.16 dL/g in DMAc at a concentration of 0.25 g/dL at 25 °C: IR (KBr) ν 1791, 1739 cm^{-1} (C=O). The IR spectrum indicated that the isoimide to imide ratio of the product was 100:0.

With the other polyisoimides, the isomerization extents and isolation yields were also 100% and 92–99%, respectively, under these conditions.

Results and Discussion

Model Studies. As candidates for appropriate amine components, oxyamines appear to be suitable due to their characteristic properties. (Benzyloxy)amine, for

Scheme 1

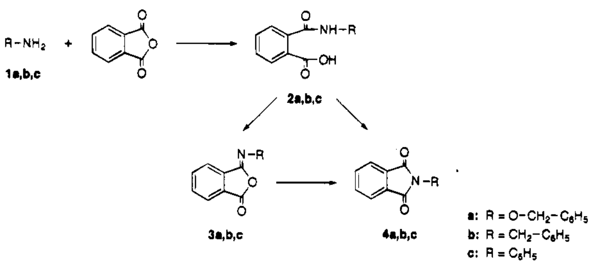


Table 1. Dehydration Cyclization of Model Amic Acids 2[a]

amic acid	cyclization agent	solvent	yield, %	products ratio isoimide 3	imide 4
2a	Ac_2O	DMAc	76	56	44
2a	Ac_2O	DMSO	86	63	37
2a	Ac_2O	pyridine	80	87	13
2a	Ac_2O	dioxane	82	96	4
2a	Ac_2O	toluene	64	100	0
2a	DCC	DMAc	94	81	19
2a	DCC	toluene[b]	75	78	22
2a	$SOCl_2$	toluene	59	80	20
2b	Ac_2O	pyridine	72	0	100
2c	Ac_2O	pyridine	93	0	100

[a] Reactions were carried out at room temperature for 24 h, and the products were isolated in water. [b] The solvent was removed under reduced pressure after reaction.

example, behaves as a difunctional amine to allow facile diacylation, and we reported the formation of a high molecular weight open-chain polyimide[11] and polybiurets.[15] This indicates that the *N*-attached oxygen atom plays an important role in the reactivity of the oxyamines and derivatives as a result of the reduced basicity and the possible delocalization of the p electrons. (Benzyloxy)amine would hence serve as a model for the formation and stability of the isoimide structure.

(Benzyloxy)amine (**1a**) was converted into the phthalamic acid (**2a**) (Scheme 1). For elucidation of the structural influences, benzylamine (**1b**) and aniline (**1c**) were also treated similarly to prepare two other phthalamic acids (**2b** and **2c**). The resulting phthalamic acids were then treated with dehydration agents to examine cyclization behavior under various conditions. As summarized in Table 1, cyclization of **2a** gave the corresponding isoimide **3a** preferentially with small amounts of imide **4a** even with acetic anhydride, and in some cases only the isoimide was obtained. As a solvent, nonpolar solvents such as benzene and toluene were appropriate. With DCC and thionyl chloride, similar results were obtained. **2b** and **2c**, however, gave only the imides **4b** and **4c** with acetic anhydride under the same conditions, indicating that they are much inferior to **2a** in terms of isoimide formation. The isoimides **3b** and **3c** from these two amines were, however, prepared with trifluoroacetic anhydride or DCC. Thermal cyclization of **2a**–**c** resulted in the quantitative formation of **4a**–**c**.

On heating, the isoimides were isomerized to the corresponding imides. The thermal isomerization of **3a** was very clean without any side reactions, and only **4a** was formed quantitatively above the melting temperature. However, the products obtained from **3b** and **3c** showed some additional absorption bands in the IR spectra, suggesting some side reactions.

Stability and isomerization behavior of the resulting model isoimides were then examined in solution at room temperature. As evident in Table 2, **3a** was quite stable even in polar solvents and recovered quantitatively. Water catalyzed the isomerization reaction of **3a** to **4a** in DMAc instead of causing hydrolysis. Considerable hydrolytic stability of **3a** was confirmed by ^1H NMR spectroscopy in DMSO-d_6 containing 10% D_2O; the hydrolysis extent was only 1% in 24 h. With acetic acid, the isomerization was complete in 24 h. Triethylamine was much more effective as a catalyst, and complete isomerization was accomplished in 5 h. Catalytic isomerization behavior was followed in detail in DMSO-d_6 in the presence of a catalytic amount of triethylamine by ^1H NMR spectroscopy, and the transformation of **3a** into **4a** proved to be quite clean and quantitative without any appreciable side reactions. In a DMAc/H_2O/triethylamine medium, the isomerization was remarkably facile and reached completion in 0.5 h.

Stability of **3b** was particularly poor, and hydrolysis took place instead of isomerization in aqueous DMSO to give amic acid **2b** exclusively in 7 h. It decomposed gradually even at room temperature in a desiccator. **3c** was also very susceptible to hydrolysis, and only a small amount was recovered. Catalytic isomerization of both of these isoimides was slow and not effective.

Isoimide **3a** is therefore superior to **3b** and **3c** in terms of ease of synthesis, hydrolytic stability, and conversion into the corresponding imide **4**. Consequently, the benzyloxy structure is quite appropriate for isoimide formation and also for the favorable characteristics of the derived isoimides.

Synthesis of Poly(amic acid)s. (Benzyloxy)amine has proved to be superior to the other amines, and thus bis(oxyamine)s **5p** and **5m** were prepared starting from *p*- and *m*-xylylene dichlorides according to Scheme 2.

Table 2. Stability and Isomerization of Model Isoimides 3[a]

isoimide	solvent	catalyst[b]	time, h	yield, %	products ratio isoimide 3	imide 4
3a	DMAc		24	91	100	0
3a	DMSO		24	93	100	0
3a	pyridine		24	95	100	0
3a	DMAc/H_2O (90/10)		24	93	89	11
3a	DMAc/H_2O (80/20)		24	76	69	31
3a	DMAc	AcOH	24	95	0	100
3a	DMAc	Et_3N	5	88	0	100
3a	DMSO-d_6	Et_3N	24	*c*	0	100
3a	DMAc/H_2O (80/20)	Et_3N	0.5	86	0	100
3b	DMSO-d_6/D_2O (90/10)		7	*c*	0	0[d]
3b	DMSO-d_6	Et_3N	48	*c*	16	84
3c	DMAc/H_2O (90/10)		24	3	19	81
3c	DMAc	Et_3N	24	10	47	53

[a] Reactions were carried out at room temperature, and the products were isolated in water. [b] 0.1% of the solvent. [c] In NMR tubes [d] Only amic acid **2b** was formed quantitatively.

Scheme 2

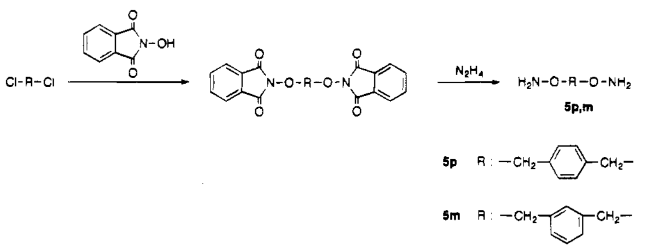
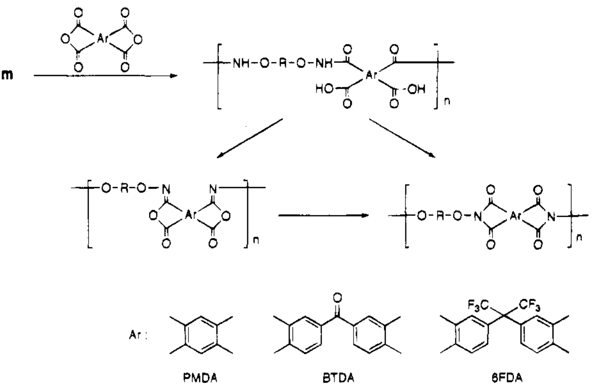


Table 3. Synthesis of Poly(amic acid)s

dianhydride	diamine	solvent	temp[a]	yield, %	η_{inh},[b] dL/g
PMDA	**5p**	DMSO	rt	93	0.29
PMDA	**5p**	DMAc	rt	94	0.38
PMDA	**5p**	NMP	rt	88	0.47
PMDA	**5p**	NMP	0 °C, rt	97	0.61
PMDA	**5m**	NMP	0 °C, rt	48	0.13
PMDA	**5m**	NMP	0 °C, rt	91	0.55[c]
BTDA	**5p**	NMP	0 °C, rt	91	0.50
BTDA	**5m**	NMP	0 °C, rt	83	0.46[c]
6FDA	**5p**	NMP	0 °C, rt	69	0.38
6FDA	**5m**	NMP	0 °C, rt	57	0.28[c]

[a] Room temperature for 24 h, or 0 °C for 2 h and then at room temperature for 22 h. [b] In DMAc, c = 0.25 g/dL, 25 °C. [c] **5m** dihydrochloride was used.

Scheme 3



In order to seek optimum polymerization conditions, *p*-xylylenebis(oxyamine) **5p** was subjected to the reaction with PMDA at room temperature. As shown in Table 3, NMP turned out to be suitable as a solvent. Moreover, better results were obtained when the reaction temperature was lowered to 0 °C for the initial 2 h, and the inherent viscosity was up to 0.61 dL/g. Other polymerizations were thus conducted under these conditions (Scheme 3).

Table 3 includes the results of polymerizations of **5p** and **5m** with three kinds of dianhydrides, PMDA, BTDA, and 6FDA. **5m** is a liquid, and the dihydrochloride gave rise to poly(amic acid)s with higher viscosities than the free diamine. The resulting poly(amic acid)s were isolated as white fibrous materials and were readily soluble in polar organic solvents.

For comparison purposes, *p*-xylylenediamine was also used for polymerization with PMDA, but the inherent viscosity was as low as 0.21 dL/g probably owing to the difficulty in handling of the diamine and poor solubility of the resulting polymer.

Conversion of Poly(amic acid)s into Polyisoimides. The poly(amic acid)s were then converted into polyisoimides (Scheme 3). Although thermal cyclization at 200 °C resulted in the quantitative formation of the corresponding polyimides, chemical cyclization with appropriate dehydrating agents should lead to the formation of polyisoimides. Reaction was first conducted in NMP solution with acetic anhydride at 0 °C, but as shown in Table 4, imide formation was preferred. With DCC, the isoimide content increased markedly.

The model reaction studies suggested that toluene was a suitable solvent for isoimide formation, but the poly(amic acid)s were insoluble in toluene. Mixed solvents of NMP and toluene were thus used, and the isoimide content could be raised to 91%. The other poly(amic acid)s were treated in a similar manner to give polyisoimides containing about 90% isoimide and 10% imide rings. Water-soluble carbodiimide, 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride, afforded almost the same results as DCC. The resulting polyisoimides were obtained as white powdery materials. For comparison, the poly(amic acid) prepared from *p*-xylylenediamine and PMDA was treated with DCC under similar conditions, but no isoimide formation was observed, indicating the importance of the bis(oxyamine) structure in the isoimide ring formation.

The IR spectra unambiguously support the structures of the polymers as illustrated in Figure 1. In the spectrum of the polyisoimide, no absorption bands due to carboxyl groups were observed as a result of complete cyclization. The strong band at 1809 cm^{-1} is characteristic of the isoimide ring, and the weak one at 1738 cm^{-1} is ascribable to the imide ring, and based on a calibration curve, the polyisoimide consisted of 91% isoimide and 9% imide.

Isomerization of Polyisoimides to Polyimides. The resulting polyisoimides were easily converted into polyimides on heating at 200 °C for 30 min (Scheme 3). As suggested from the studies on the model isoimides, catalytic isomerization would also be efficient. The polyisoimides were thus treated with triethylamine at room temperature in dichloromethane. IR spectroscopy confirmed that all the polyisoimides were transformed into polyimides completely in quantitative yields.

The IR spectra of the polyimides obtained by catalytic isomerization of the polyisoimides were identical with those obtained by heating the poly(amic acid)s or polyisoimides, and no bands due to carboxyl groups and

Table 4. Cyclization of Poly(amic acid)s to Polyisoimides[a]

poly(amic acid)					product	
dianhydride	diamine	solvent, mL (NMP/toluene)	cyclization agent	yield, %	isoimide	imide
PMDA	**5p**	5/0	Ac_2O	53	17	83
PMDA	**5p**	5/0	DCC	86	84	16
PMDA	**5p**	2/3	DCC	68	91	9
PMDA	**5m**	2/3	DCC	72	85	15
BTDA	**5p**	2/3	DCC	80	91	9
BTDA	**5m**	2/4	DCC	74	90	10
6FDA	**5p**	1/3.5	DCC	58	93	7
6FDA	**5m**	1/3.5	DCC	53	89	11

[a] Poly(amic acid), 50 mg; temperature, 0 °C; time, 24 h.

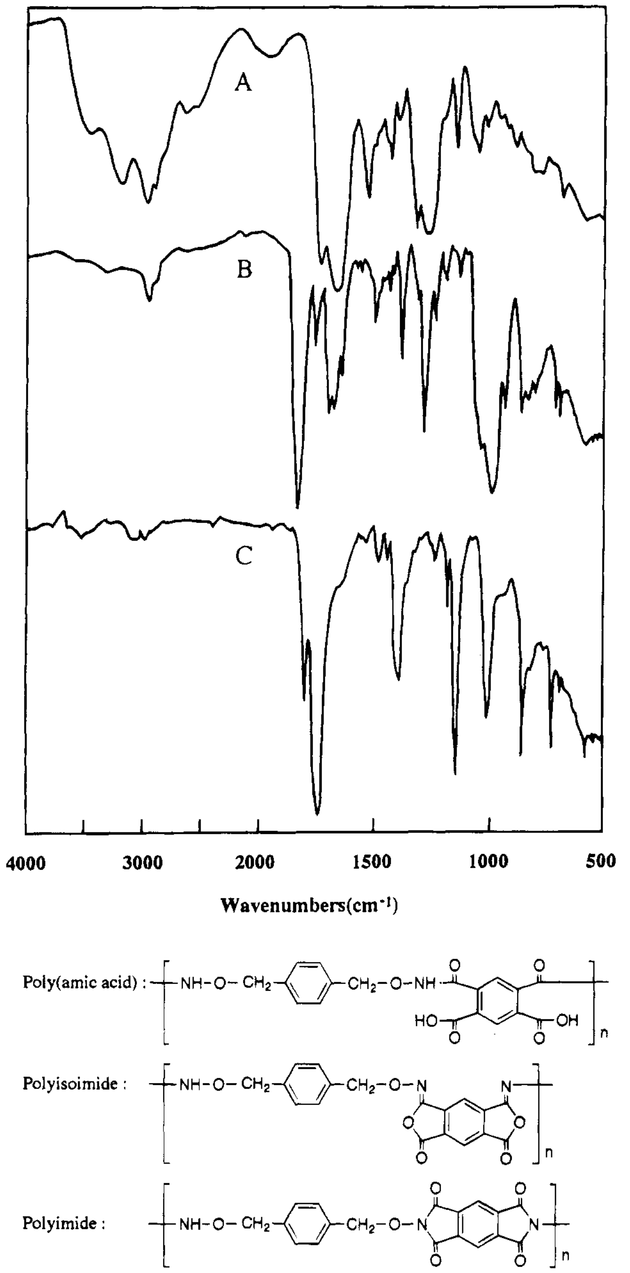


Figure 1. IR spectra of (A) poly(amic acid), (B) polyisoimide (isoimide/imide = 91/9), and (C) polyimide derived from **5p** and PMDA (KBr method).

Table 5. Solubility of Polyisoimides and Polyimides[a]

	polyisoimide						polyimide					
	PMDA		BTDA		6FDA		PMDA		BTDA		6FDA	
solvent	**5p**	**5m**	**5p**	**5m**	**5p**	**5m**	**5p**	**5m**	**5p**	**5m**	**5p**	**5m**
$CHCl_2CO_2H$	±	+	+	+	+	+	−	−	−	−	+	+
m-cresol	±	+	+	+	+	+	−	−	−	−	+	+
DMSO	±	+	+	+	+	+	−	−	−	−	+	+
DMAc	±	+	+	+	+	+	−	−	−	−	+	+
NMP	±	+	+	+	+	+	−	−	−	−	+	+
THF	±	±	±	±	+	+	−	−	−	−	+	+
CH_2Cl_2	±	±	±	±	+	+	−	−	−	−	+	+
benzene	±	±	−	−	+	+	−	−	−	−	±	±

[a] +, soluble; ±, partially soluble or swelled; −, insoluble.

isoimide rings are found as shown in Figure 1, indicating complete transformation.

Table 6. Thermal Characteristics of the Polyisoimides and Polyimides

		polyisoimide		polyimide	
dianhydride	diamine	T_g,[a] °C	T_{iso},[b] °C	T_g,[a] °C	T_{10},[c] °C
PMDA	**5p**	155	230	230	321
PMDA	**5m**	128	207	197	311
BTDA	**5p**	154	219	199	338
BTDA	**5m**	124	188	165	249
6FDA	**5p**	158		198	326
6FDA	**5m**	142		163	253

[a] Determined by DSC (20 °C/min in air). [b] Isomerization temperature determined by DTA (5 °C/min in air). [c] Temperature at which 10% weight loss was recorded by TG (5 °C/min in air).

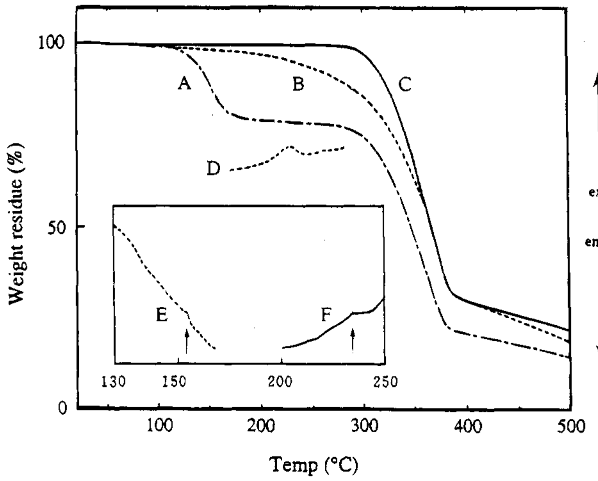


Figure 2. Thermal analysis curves for polymers derived from **5p** and PMDA: (A–C) TG curves for the poly(amic acid), polyisoimide (isoimide/imide = 91/9), and polyimide (5 °C/min in air); (D) DTA curve for the polyisoimide (5 °C/min in air); (E and F) DSC curves for the polyisoimide and polyimide (20 °C/min in air). See Figure 1 for the polymer structures.

Characteristics of Polymers. Table 5 lists solubility data of the polyisoimides and polyimides synthesized here. All the polyimides from PMDA and BTDA were insoluble, but those from 6FDA were soluble. In sharp contrast to the polyimides, polyisoimides showed much improved solubility as expected. Although the polyisoimide from **5p** and PMDA was only partially soluble or swelled, the other polyisoimides showed high solubility, and this is one of the more favorable characteristics of the polyisoimides.

Thermal properties of the polyisoimides as compared with those of the polyimides are summarized in Table 6. Glass transition temperatures (T_g) of the polyisoimides from **5p** were around 155 °C, and those from **5m** were a little lower. These values were much lower than those of the polyimides. DTA curves of the polyisoimides showed a small exothermic peak at 190–230 °C, implying that the isomerization to the polyimides was taking place. T_{10} stands for the 10% weight loss temperature determined by TG, and they were 250–340 °C. Typical examples of the TG, DTA, and DSC curves are shown in Figure 2.

Crystallinity was examined by X-ray diffractiometry. All the poly(amic acid)s, polyisoimides, and polyimides synthesized from **5p** and **5m** showed no distinct crystalline peaks and were considered to be amorphous.

Conclusion

Influence of substituents on the properties of isoimides has been shown to be important, and the benzyloxy group may be more appropriate for polymer formation than benzyl and phenyl groups due to its facile isoimide formation, high hydrolytic stability, and quantitative conversion into imides. Polyisoimides can be synthesized easily from xylylenebis(oxyamine)s. They are characterized by high solubility, low glass transition temperatures, and quantitative conversion into polyimides without producing water. Although this route to polyimides requires an additional step compared to the conventional direct cyclization of poly(amic acid)s, the advantages of these characteristics would be of importance in many high-technology applications.

References and Notes

(1) Kreuz, J. A. U.S. Patent 3,413,267, 1968.
(2) Wallace, J. S.; Tan, L.-S.; Arnold, F. E. *Polymer* **1990**, *31*, 2411.
(3) Kailani, M. H.; Sung, C. S. P.; Huang, S. J. *Macromolecules* **1992**, *25*, 3751.
(4) (a) Landis, A. L.; Naselow, A. B. *Natl. SAMPE Tech. Conf. Ser.* **1982**, *14*, 236. (b) Landis, A. L. U. S. Patent 4,438,273, 1984.
(5) Trade name of National Starch Co.
(6) Swanson, S. A.; Fleming, W. W.; Hofer, D. C. *Macromolecules* **1992**, *25*, 582.
(7) (a) Tsou, K. C.; Barrnett, R. J.; Seligman, A. M. *J. Am. Chem. Soc.* **1955**, *77*, 4613. (b) Roderic, W. R.; Bhatia, P. L. *J. Org. Chem.* **1963**, *28*, 2018.
(8) Cotter, R. A.; Sauers, C. K.; Whelan, J. M. *J. Org. Chem.* **1961**, *26*, 10.
(9) Hedaya, E.; Hinman, R. L.; Theodoropulos, S. *J. Org. Chem.* **1966**, *31*, 1311.
(10) Kurita, K.; Suzuki, Y.; Enari, T.; Kikuchi, M.; Nishimura, S.; Ishii, S. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 393.
(11) (a) Kurita, K.; Yamakawa, M.; Koyama, Y. *Chem. Lett.* **1987**, 2337. (b) Kurita, K.; Yamakawa, M.; Iida, K.; Susa, E.; Koyama, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 4297.
(12) Hoogewerff, S.; van Drop, W. A. *Recl. Trav. Chim. Pays-Bas* **1894**, *13*, 93.
(13) van der Meulen, P. H. *Recl. Trav. Chim. Pays-Bas* **1896**, *15*, 282.
(14) Hamor, G. H.; Breslow, D. M.; Fisch, G. W. *J. Pharm. Sci.* **1970**, *59*, 1752.
(15) Ishii, S.; Watabe, S.; Nishimura, S.; Kurita, K. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 577.

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