Preparation and Properties of Polyisoimide as a Polyimide-Precursor

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ABSTRACT: The reactions of *N*-phenylphthalamic acid with various dehydrating agents have been investigated. *N,N'*-dicyclohexylcarbodiimide (DCC) and trifluoroacetic anhydride with triethylamine (TEA) were found to be suitable dehydrating agents for the formation of *N*-phenylphthalisoimide. The isomerization of isoimide to imide was catalyzed by acids or bases, where 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) was most effective and a quantitative yield of imide was obtained quickly. Various polyisoimides were prepared by the cyclization of polyamic acids using DCC. These polyisoimides were relatively stable above their glass transition temperature (T_g), but easy to convert to corresponding polyimides by high thermal treatment ($>250^\circ\text{C}$). Furthermore, there was a change of $20\text{--}70^\circ\text{C}$ in T_g due to isomeric conversion.

KEY WORDS Dehydrating Agent / Isomerization / Polyamic acid / Polyisoimide / Polyimide /

High-performance plastics are currently receiving considerable attention for their potential uses in aerospace, automotive, electronic and related industries. In particular, polyimide (PI) has been widely used as an insulation material for microelectronic devices because of their excellent properties, such as thermal and chemical stability, and low dielectric constants.¹

Most of them are prepared by the reaction of aromatic dianhydrides with aromatic diamines. The reaction proceeds through a soluble polyamic acid (PAA) intermediate, which upon further heating undergoes a cyclization reaction leading to imide formation and the evolution of water.

The aromatic PI is usually intractable because of its insolubility to organic solvent and high melting. In most cases, PAA is prepared first, processed into shaped objects and then PI is formed by thermal cyclization reaction. However, this processing method in PAA form has some significant limitations. During the thermal cyclization reaction of

PAA, the loss of solvent and the release of water take place. These limitations are associated with improper curing of PAA, which make it a pronounced effect on the electrical and mechanical properties of PI film, such as rising dielectric constant, causing electromigration and decreasing tensile strength.

On the other hand, a polyisoimide (PII) has a lower glass transition temperature (T_g) than that of corresponding PI and converted easily to PI without elimination of volatile compounds. The thermal isomerization of an isoimide to imide group is well known process. This process induces resin flow and thereby enhances the processability. Commercial acetylene-terminated isoimide, IP-600, is an example of using such an approach to improve processability.²

Since the first report of the existence of isoimide was suggested by Hoogewerff and van Dorp in 1892,³ a number of synthetic route for producing isoimide and wide array of reactions of isoimide intermediate have been described in the literatures.^{4,5} These aspects are re-

presented by chemical cyclization reaction of PAA to PII^{6,7} and ring opening polyaddition reaction of *N*-substituted maleisoimide.⁸ However, the detailed study on the synthetic method of isoimide and the properties of PII as polymeric materials has not been reported.

This paper will provide full details of the preparation and properties of PII including the selection of optimal condensing agent for the isoimide synthesis from amic acid and the acid- or base-catalyzed isomerization of isoimide to imide.

EXPERIMENTAL

Materials

Dichloromethane, tetrahydrofuran (THF), *N,N*-dimethylacetamide (DMAc), triethylamine (TEA) was purified by distillation. Phthalic anhydride (from chloroform), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**5c**) (from 2-propanol), 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (**5b**) (from cyclohexane), and 4,4'-oxydianiline (**5a**) (from THF) were purified by recrystallization.

Pyromellitic dianhydride (**4a**), 4,4'-oxydiphthalic anhydride (**4b**), 1,3-bis(3,4-dicarboxyphenyl)-1,1,3,3,-tetramethyldisiloxanedianhydride (**4c**) (supplied by Toshiba silicone Co., Ltd.), and 1,3-bis(4-aminophenoxy)benzene (**5d**) were used without further purification. Other reagents and solvents were obtained commercially and used as received.

N-Phenylphthalamic acid (**1a**)

A solution of aniline (1.80 ml, 20.0 mmol) in dichloromethane (20 ml) was cooled with an ice-water bath. To this solution was added with stirring phthalic anhydride (2.96 g, 20.0 mmol). The mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure. The yield was 4.8 g (99%). mp 169–172°C (lit.⁹ 169°C). IR (KBr): ν 3320 cm^{-1} (N–H), 1653 cm^{-1} (C=O).

Dehydration of **1a**

Ethylchloroformate-TEA. Ethylchloroformate (0.21 ml, 2.2 mmol) was added dropwise to an ice-cooled solution of **1a** (0.48 g, 2.0 mmol) and TEA (0.28 ml, 2.0 mmol) in THF (3 ml). The mixture was stirred at room temperature for 2 h. Then, the mixture was filtered to remove TEA–HCl. The filtrate was diluted with dichloromethane and the organic solution was washed with water and dried with anhydrous magnesium sulfate. After evaporation of dichloromethane, the mixture of *N*-phenylphthalisoimide (**2a**) and *N*-phenylphthalimide (**3a**) was obtained. The yield was 0.34 g (77%). The product ratio of **2a** and **3a** was determined by IR spectroscopy.

Thionyl Chloride. A solution of **1a** (0.48 g, 2.0 mmol) in thionyl chloride (4 ml) was refluxed for 3 h and cooled. The precipitate was collected by suction filtration and washed with *n*-hexane. The yield was 0.37 g (84%).

DCC. To a solution of **1a** (0.48 g, 2.0 mmol) in dichloromethane (4 ml) was added dropwise with stirring a solution of DCC (0.41 g, 2.0 mmol) in dichloromethane (2 ml). The mixture was stirred at room temperature for 3 h. *N,N'*-dicyclohexylurea formed was removed by filtration, and the filtrate was evaporated under reduced pressure. The yield was 0.43 g (96%).

Acetyl Chloride. A solution of **1a** (0.24 g, 2.0 mmol) in acetyl chloride (4 ml) was stirred at 40°C for 3 h. The precipitate was isolated by filtration, washed with *n*-hexane and dried. The yield was 0.40 g (89%).

Trifluoroacetic Anhydride-TEA. A solution of **1a** (0.48 g, 4.0 mmol) and TEA (0.56 ml, 4.0 mmol) in dichloromethane (3 ml) was cooled with an ice-water bath. To this solution was added dropwise with stirring trifluoroacetic anhydride (0.28 ml, 2.2 mmol). The mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure to give **2a**. The yield was 0.76 g (85%). Recrystallization from diethyl ether yielded pale-yellow needles. mp 120°C (lit.¹¹ 119–121°C).

IR (KBr): ν 1790 cm^{-1} (C=O), 920 cm^{-1} (C–O).

N-Phenyl phthalimide (3a)

This compound was prepared by reaction of phthalic anhydride with aniline in boiling acetic acid. It was purified by recrystallization from acetic acid. mp 211°C (lit.¹¹ 209°C). IR (KBr): ν 1700 cm^{-1} (C=O), 1380 cm^{-1} (C=N).

N-(*p*-Methoxy) (2b) and *N*-(*m*-Nitro)phenylphthalisoimide (2c)

These compounds were prepared by treatment of corresponding amic acids with DCC in THF, and purified by recrystallization from diethyl ether and dichloromethane, respectively. (2b), mp 138°C (lit.¹⁰ 134°C). IR (KBr): ν 1800 cm^{-1} (C=O), 920 cm^{-1} (C–O), (2c), mp 140°C (lit.¹⁰ 138°C). IR (KBr): ν 1800 cm^{-1} (C=O), 930 cm^{-1} (C–O)

Polymer synthesis

A typical example is as follows.

Polymer (6b) from (4b) and (5b). To a solution of 5b (1.04 g, 2.0 mmol) in DMAc (5.3 ml) was added 4b (0.62 g, 2.0 mmol). The mixture was stirred at room temperature for 4 h, giving a polyamic acid solution. The resulting viscous solution was diluted with DMAc (53.3 ml), and to the polyamic acid solution was added with stirring DCC (0.80 g, 4.0 mmol). The mixture was stirred for 12 h at room temperature and poured into 2-propanol (800 ml). The polymer precipitated was filtered off and fibrous polymer was collected and dried *in vacuo* at 40°C. The yield was 1.51 g (95%). The inherent viscosity of the polymer in DMAc was 0.50 dl g^{-1} at a concentration of 0.5 g dl^{-1} at 30°C. IR (KBr): ν 1805 cm^{-1} (C=O), 930 cm^{-1} (C–O). Anal. Calcd for $(\text{C}_{43}\text{H}_{22}\text{N}_2\text{O}_7\text{F}_6)_n$: C, 65.15%; H, 2.79%; N, 3.53%. Found: C, 65.13%; H, 3.05%; N, 3.35%.

Measurement

The infrared spectra were recorded on a Hitachi I-5020 FT-IR spectrophotometer, and

UV-Visible spectra on a Shimadzu UV-2200 spectrophotometer. The NMR spectra were obtained on a JEOL EX270 (270 MHz) spectrometer. Viscosity measurements were carried out by using an Ostwald viscometer at 30°C. Thermal analysis were performed on a Seiko SSS 5000-TG/DTA 200 instrument at a heating rate of 10°C min^{-1} for TG and a Seiko SSS 5000 DSC220 at a heating rate of 10°C min^{-1} for differential scanning calorimetry (DSC) under nitrogen.

Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using JASCO HPLC system equipped with Shodex KD-80M column at 40°C in DMF.

RESULTS AND DISCUSSION

Selection of Dehydrating Agents

The selection of a suitable dehydrating agent is very important for the preparation of polyisoimides from corresponding amic acids. Although many dehydrating agents have been proposed for the preparation of isoimides from amic acids,⁴ it has not been clear which reagent would be the best. Therefore, to determine the suitable dehydrating agents we investigated on the synthesis of *N*-phenylphthalisoimide (2a) from *N*-phenylphthalamic acid (1a) using various dehydrating agents (eq 1). The reaction products were a mixture of 2a and *N*-phenylphthalimide (3a) which molar ratios were determined by comparing the absorptions of isoimide (920 cm^{-1}) and internal standard compound *p*-dicyanobenzene (2200 cm^{-1}). The results summarized in Table I indicate that ethyl chloroformate, *N,N'*-dicyclohexylcarbodiimide (DCC), and trifluoroacetic anhydride are suitable dehydrating agents and give excellent mole percentages (>90 mol%) of 2a under mild conditions. Exclusive isoimide formation occurred using trifluoroacetic anhydride with triethylamine (TEA). Acetyl chloride, on the contrary, yielded 90 mol% imide.

Several groups studied the mechanism of

R = H : 2a
 p-MeO : 2b
 m-NO₂ : 2c

Table I. Dehydration of **1a** using various dehydrating agents

Reagent	Yield/%	Content/mol%	
		2a	3a
EtCOOCl-TEA	77	93	7
SOCl ₂	84	21	79
DCC	96	92	8
(CF ₃ CO) ₂ O-TEA	85	99	1
AcCl	82	4	96

amic acid cyclization.^{4,5} The dehydration of phthalamic acid with dehydrating agent has been postulated to occur by way of the mixed anhydride followed by ring closure to isoimide and imide. The formation of mixed anhydride has been shown by IR and NMR studies.^{5c} Differences in the ratios of imide/isoimide formation depends both on the basicity of amines and the ability of dehydrating agents.^{5b} The yield of imide is larger when substituent groups (R) in the ring attached to nitrogen atom are electron-withdrawing. Because, the contribution to the amide resonance hybrid of structure A (Scheme 1) would be less important when R is the electron-withdrawing group.

Furthermore, Sauers *et al.*^{5a} proposed isoimides as the kinetic products of dehydration based on the mechanistic study of the cyclization of amic acids in the presence of acetic anhydride. Therefore, when the dehydrating agent with a good leaving group is used, the formation of isoimide appears to be exclusive. That is, the intermediates of amic acid cyclization are mixed anhydrides, which rapidly cyclize by the kinetically favored path of intramolecular *O*-acylation, giving greater concentration of isoimides relative to imides. Our results also supported this mechanism, where the formation of isoimide may be roughly correlated with the reactivity of mixed anhydrides with greater stability of the leaving group anions, that is, the pK_a of the leaving groups.

Acid or Base-Catalyzed Isomerization of Isoimide

Isoimide has been observed to undergo isomerization to imide in the presence of base, such as TEA and sodium acetate.¹¹ These nucleophilic catalysts of the isoimide-imide transformation may involve attack at the activated carbonyl group of the isoimide to

Polyisoimides

Scheme 1

Scheme 2

Table II. Acid- or base-catalyzed isomerization of **2a** to **3a**^a

Catalyst	Conversion/%
None	12
DBU	100
TEA	86
Py	13
<i>p</i> -Tol-SO ₃ H	60
CF ₃ COOH	85

^a Isomerization reaction was carried out in sealed tube at 120°C for 15 min.

yield an acyl-activated amic acid which undergoes ring closure to the imide (Scheme 2). This reaction would be applied as a new approach for the development of photosensitive PI which is based on chemically on the propensity for PII to isomerize rapidly in the presence of catalytic quantities of acid or base. Therefore, we studied the acid- or base-catalyzed isomerization of **2a** in more detail in the presence of various acid and base catalysts. Acid and base catalysts would be expected to enhance the electrophilicity of carbonyl carbon

and act as nucleophilic catalyst, respectively. First the reaction was carried out in a sealed tube at 120°C for 15 min in the presence of 10 wt% of catalyst (eq 2). The results were listed in Table II. The reaction temperature was chosen above the melting point of **2a**. A base catalyst, such as pyridine, TEA, and DBU, and an acid catalyst, such as *p*-toluenesulfonic acid and trifluoroacetic acid were used. Among them, DBU was found to be most effective and a quantitative yield of imide was obtained quickly.

To estimate the isomerization quantitatively, the reaction was subsequently performed in a DMAc solution of **2a** at 25°C in the presence of DBU. The reaction was followed by the decrease in absorbance at 328 nm. The results are shown in Figure 1. We found that isomerization in the presence of DBU was completed within 5 min, and the rate of its first order isomerization was $2.15 \times 10^{-2} \text{ s}^{-1}$. On the other hand, the reaction was very slow in the absence of DBU, and no trace of imide formed even after 2 h later.

Substituent Effects for *N*-Phenylphthalisoimide (2) on Thermal Isomerization

We showed that the isomerization of **2a** was accelerated by acid and base-catalysts in the preceding section. This isomerization will be also affected by the electron density of nitrogen and carbon atom in carbonyl group in isoimide group. Therefore, thermal isomerization behavior of **2a** having various substituents was investigated to clarify the effect of structure on isomerizability. The reaction was carried out at 150°C for 5 min, and proceeded in molten state (eq 3). The results are listed in Table III. As

Figure 1. DBU catalyzed isomerization of **2a** to **3a**.

would be expected, the incorporation of electron-donating substituents in *N*-phenyl ring markedly facilitated the isomerization because of the increased electron density on the nitrogen atom.

Synthesis of Polyisoimides (PII's) (6)

On the basis of these results, we prepared the polyisoimides (PII's) (**6**) using DCC to investigate their properties, such as the solubility, glass transition temperature (T_g), and thermal isomerization temperature (T_i). In order to obtain the soluble PII, tetracarboxylic dianhydrides (**4**) and diamines (**5**) having ether, isopropylidene, dimethylsiloxane, and *m*-phenylene linkages were used. We found that

Table III. Substituent effect on thermal isomerization of **2** to **3**^a

Substituents	
R	Conversion/%
H	35
<i>p</i> -MeO	92
<i>m</i> -NO ₂	32

^a Thermal isomerization of **2** was carried out in sealed tube at 150°C for 5 min.

Table IV. Synthesis of polyisoimide **6**^a

Dianhydride	Diamine	Polymer	Yield/%	$\eta_{inh}/dl\ g^{-1\ b}$
4a	5a	6a	99	—
4b	5b	6b	91	0.50
4b	5c	6c	96	0.63
4b	5d	6d	89	0.52
4c	5c	6e	86	0.85
4c	5d	6f	85	0.74

^a Ring-opening polyaddition was carried out with 2 mmol of each monomer in DMAc at room temperature.

^b Measured at a concentration of $0.5\ g\ dl^{-1}$ in DMAc at 30°C.

trifluoroacetic anhydride-TEA was a good dehydrating agent for the formation of isoimide, however, this system caused unfavorable reactions with solvent such as DMAc. Thus, DCC as dehydrating agent was used. The ring-opening polyaddition of **4** with **5** was carried out in DMAc for 4 h at room temperature (eq 4). PII **6** was isolated by pouring into isopropanol. Table IV indicates that PII's **6** were produced in excellent yields with inherent viscosities up to $0.85\ dl\ g^{-1}$ except for polymer **6a** because of low solubility of the corresponding PII.

Polymer Characterization

Polymers **6** were confirmed to be the corresponding PII's by means of infrared spectroscopy and elemental analysis. The IR spectra exhibited characteristic absorptions at $1800\ cm^{-1}$ due to the isoimide carbonyl. Imide contents determined by IR spectroscopy were less than 10% for all polymers. Elemental analyses also supported the formation of expected polymers **6**.

Polymers **6** were yellow solids and soluble in dipolar aprotic solvents except polymer **6a**. Polymer **6e** was soluble even in cyclohexanone, dichloromethane, tetrahydrofuran, and toluene, and swelling in acetone and methyl ethyl ketone. Transparent yellow films were cast from the solution of the polymers. The molecular weight of the polymer **6e** having

Figure 2. TG curves of polymer **6c**. —, N_2 ; ---, air.

inherent viscosity of $0.85\ dl\ g^{-1}$ was determined by GPC. Relative $\bar{M}_n$ and $\bar{M}_w$ values were 122000 and 250000, respectively, for standard polystyrene, and $\bar{M}_w/\bar{M}_n$ was 2.0. The thermal stability of the polymer was examined by thermogravimetry (TG). A typical trace of TG for polymer **6c** is shown in Figure 2. The polymer showed a 10% weight loss at $510^\circ C$ in nitrogen. The T_g of PII would be expected to differ from that of corresponding PI due to different chemical structure. In order to study the thermal properties of PII, DSC measurement was performed. The sample was dried under reduced pressure for 12 h at the specified temperature, which is $50^\circ C$ lower than T_g of sample, and subsequently subjected to DSC analysis.

DSC curves of polymer **6c** are shown in Figure 3. Polymer **6c** exhibited an endotherm at about $175^\circ C$ and a large exothermic peak at around $270^\circ C$ in the first heating process. In the second heating process, these peaks were not observed and a new endothermic peak appeared at $225^\circ C$. After the large exothermic peak, the IR spectrum of polymer **7c** showed strong imide carbonyl absorptions at 1780 and $1740\ cm^{-1}$, while the absorption bands characteristic of isoimide group at 1800 and $910\ cm^{-1}$ had entirely disappeared, suggesting that polymer **6c** was immediately converted to PI **7c**. Furthermore, no TG weight loss was

Figure 3. DSC curves of polymer **6c** in nitrogen.Table V. Thermal behavior of polyisoimide **6**

Polymer		TG ₁₀ /°C ^a	<i>T_i</i> /°C ^b	<i>T_g</i> /°C	
Isoimide	Imide			6	7
6a	7a	580	313	—	—
6b	7b	540	298	223	242
6c	7c	510	270	175	225
6d	7d	490	255	143	212
6e	7e	505	280	118	155
6f	7f	510	210	99	141

^a Temperature at which 10% weight loss was recorded with TG at heating rate of 10°C min⁻¹ in nitrogen.

^b Temperature at which exothermic peak was recorded by DSC measurement.

observed at around 270°C.

Based on these data, the first endotherm at 175°C and a large exothermic peak at around 270°C observed in the first heating process are assigned to *T_g* and *T_i* of polymer **6c**, respectively. And the endothermic peak at 225°C in second heating process reflects *T_g* of PI **7c**. The thermal behavior of polymers are listed in Table V. The introduction of flexible linking units into the main polymer chain decreases the *T_g* and isomerization temperature of polymers. Furthermore, Table V indicates that *T_g*'s of PII's are about 20–70°C lower than those of corresponding PI's.

Thermal Stability of PII

PII's are believed to isomerize rapidly to PI's

Figure 4. Isoimide-imide conversion versus curing time of polymer **6c** and **6e** at different temperatures: **6c** (—○—, —□—, —△—); **6e** (—●—, —■—).

above their *T_g*'s. The isothermal cure treatment of **6c** and **6e** above their *T_g* was carried out to clear the thermal stability of PII's. The conversion (%) of isoimide to imide was represented in normalized conversion value, since these polymers included approximately 10% of imide form. Figure 6 shows the isoimide-imide conversion versus curing time of polymers **6c** and **6e** at different temperatures. Polymer **6c** (*T_g* = 175°C) was stable at 150°C, and isomerized to imide about 40% for 2 h at 180°C. On the other hand, polymer **6e** (*T_g* = 118°C) was quite stable for 2 h even at 125°C, and isomerized to imide about 60% at 220°C. These quenching of isomerization may occur because the *T_g* of polymer increases with increasing imide content. However, at 345°C, the conversion was very near to completion after 10 min in each cases. These results indicate that PII's are relatively stable at a temperature a little above their *T_g*'s, but easy to convert to corresponding PI's by high thermal treatment close to *T_i*'s.

CONCLUSION

In summary, our studies indicate that PII's are successfully prepared from corresponding polyamic acids using DCC as a dehydrating

agent, and are relatively stable above their T_g 's, but easy to convert to PI's by high thermal treatment. Furthermore, dehydrating agents with good leaving groups are found to be suitable for the preparation of phthalisoimide from phthalamic acid. Therefore, PII is very advantageous as the polyimide-precursor and applicable to thermoplastic type adhesive, photosensitive PI precursor and other high functional PI materials.

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