Synthesis and Characterization of Polyimide Derivatives Prepared by Different One-Step Methods

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SYNOPSIS

Homo- and copolyimides with high molecular weight could be synthesized from three dianhydrides and three diamines following two different one-step methods. Solubility behavior with structural effect, viscosity, kinetics of solution imidization, synthesized method, mechanical and thermal properties, and effect of azeotroping agent are discussed. Results indicate that homo- and random copolyimides were only prepared from a one-step method; on the other hand, copolyimide with different arrangement, such as random, block, and alternating, could be synthesized by a modified one. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Most polyimides are intractable materials; therefore, their uses are limited. The most developed synthesis method for polyimide derivatives is the classic two-step method.[1,2] A polyamic acid as a soluble intermediate polymer is obtained in the first step and then the polyamic acid, formed into the desired shapes, is converted into polyimide by the thermal treatment of precursor in the solid state. The complete dehydrocyclization is usually achieved after full cure under high temperature. Thus, the thermal treatment with high temperature is needed for a high degree of imidization.

Recently, it was found that the soluble polyimide with large molecular weight can be produced in a single step.[3,4] The cyclodehydration into imide form is completed in the solution state, and a relatively mild reaction temperature is used, for instance, 160–200°C, which might avoid several possible side reactions that might occur during the curing process in high-temperature solid phase.[5–7]

We describe the synthesis and characterization of soluble polyimide derivatives by two single-step polymerizations. Polyimide derivatives were prepared by utilizing one-step imidization techniques in the solution without precipitation before it grows to maturity. In the present study, three series of polyimide derivatives are synthesized: the H series is homopolyimides, the A series is prepared from single dianhydride and two diamines, and the B series is yielded from two dianhydrides and a diamine.

EXPERIMENTAL

Reagents

Pyromellic dianhydride (PMDA, Aldrich Chemical Co.), 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (DMCA, Tokyo Kasei Co.), and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA, Aldrich Chemical Co.) were recrystallized from 4-methyl-2-pentanone followed by vacuum drying and stored in a desiccator over $CaCl_2$ and silicagel. α,α'-Bis(4-aminophenyl)-1,4-diisopropylbenzene (BADB, Tokyo Kasei Co.), 4,4'-oxydianiline (ODA, Aldrich Chemical Co), and bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS, Wakayama Seika Kogyo Co.) were purified by recrystallization in ethanol and followed by vacuum drying at 60°C for 4 h and stored in a drying oven. The chemical structures and abbreviation of monomers are summarized in Table I.

N,N'-dimethylacetamide (DMAc, bp 166°C), *N,N'*-dimethylformamide (DMF, bp 160°C), 1-methyl-2-pyrrolidone (NMP bp 202.2°C), and *m*-cresol (bp

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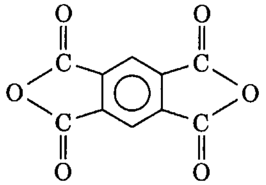
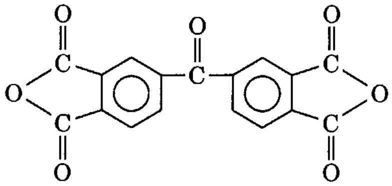
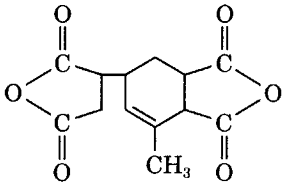
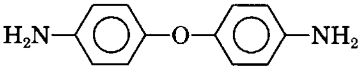
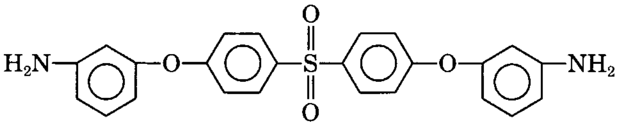
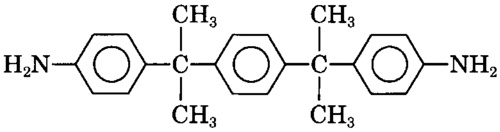
Table I Chemical Structures and Abbreviation of Monomers

Chemical Structure	Abbreviation	MW
	PMDA	218.1
	BTDA	322.2
	DMCA	264.2
	ODA	200.0
	BAPS	432.5
	BADB	344.5

202°C) were obtained from Aldrich Chemical Co. Those solvents were dehydrated with CaH_2 and then distilled before being stored in 4 Å molecular sieves. Benzonitrile (bp 190.7°C) and nitrobenzene (bp 210.8°C) were obtained from Janssen Chemical Co. They were dried with $CaCl_2$ and treated in the same manner as above. Other laboratory-grade reagents were used without further purification.

Measurements

The viscosity of polyimide (PI) derivatives solution was measured with a ubbelohde viscometer at a concentration of 0.5 g/dL in NMP at 30°C. IR spectrum was recorded in film using a Hartman & Braun model BOMEM DA 8.16. The extent of imidization could be calculated according to eq. (1)[3,8]:

Degree of Imidization

$$= \frac{[\{A(1)/A(s)_t\} - \{A(1)/A(s)_{t=0}\}]}{[\{A(1)/A(s)_\infty\} - \{A(1)/A(s)_{t=0}\}]} \quad (1)$$

where $A(1)$ is the absorbance of imide peak at about 1780 cm^{-1}, $A(s)$ is the standard reference peak at about 1500 cm^{-1}, and $t = \infty$ is taken as the time beyond which no further change is seen in the imide peak.

The kinetics of imide formation could be evaluated according to the first- and second-order kinetic equation[6,8]:

$$\ln(1 - P) = -kt \quad (2)$$

$$1/(1 - P) = kt + 1 \quad (3)$$

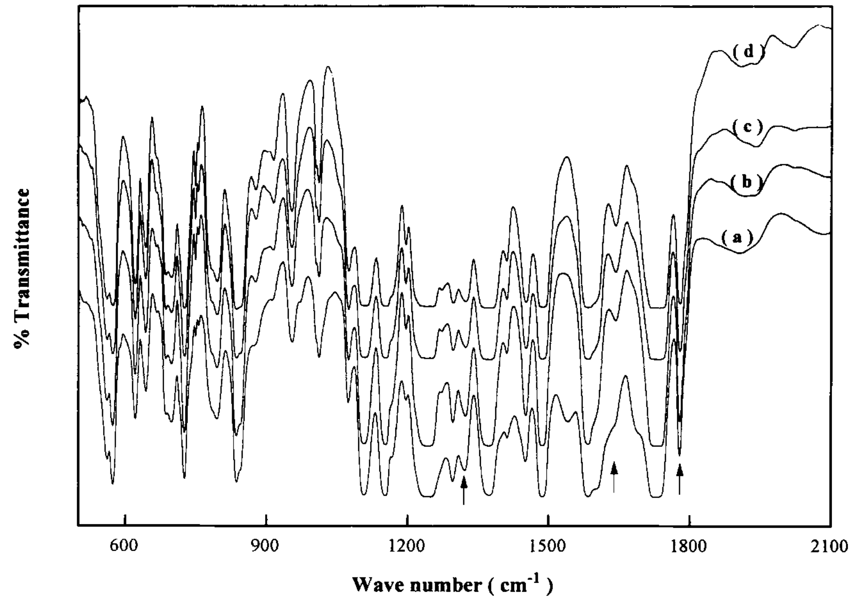


Figure 1 IR spectra of H-1 PI prepared from one-step polymerization at (a) 220°C, (b) 200°C, (c) 180°C, and (d) 150°C.

where P is the extent of imidization and k is rate constant.

The thermal properties were measured by using differential scanning calorimetry (DSC, Dupont 2100) and a thermogravimetric analysis (TGA, Perkin-Elmer TGA7). The tensile strength and elongation were measured at room temperature using an instron testing machine model TT-C. This test was used on the PI film with 150-μm thickness, 10-mm width, and 50-mm length.

To determine the solubility, polymer samples were immersed in the various solvents and allowed to shake for 7 days. If the sample was only partially dissolved or swelled, it was heated at 70°C for 24 h.

Preparation of PI by Different One-Step Polymerizations

Synthesis of Polymer by the One-Step Method

PIs that were soluble in organic solvents could be synthesized by the one-step or the single-step method. In this procedure, the flask was warmed at 130°C in an oil bath to the homogeneous mixture. Next, the contents of the flask were warmed to 160–220°C with stirring under flow of nitrogen in a high-boiling organic solvent. Under these conditions, dehydrocyclization into PI was completed in the solution without producing precipitation and the by-product, water, liberated from the reaction medium, was completely eliminated by the flow of nitrogen.

Homopolyimide. Equivalent dianhydride and diamine and solvent were placed in a four-neck flask equipped with a mechanical agitator, a nitrogen inlet tube, distilling receiver having a reflux condenser, and thermometer. The flask was gradually warmed at 130°C in an oil bath to prepare the homogeneous reaction-solution and was maintained for 1 h. When the temperature increased, the contents of the flask turned into the homogeneous solution with brown color. Next, the bath was further heated up to 160–220°C under flow of nitrogen and kept at this condition until no more increasing viscosity. The by-product, water, was evolved, which was the evidence of the dehydrocyclization. On completion of the reaction, the viscose polymer solution was cooled under nitrogen atmosphere and poured into a large quantity of methanol in which the polymer deposited. The precipitate was filtered off, washed free of used solvent by repeated use of methanol, and dried *in vacuo* at 70°C.

Copolyimide. The same flask as described before was charged with equivalent dianhydrides and diamines and solvent. The reaction was treated in the same manner as above.

Synthesis of Polymer by the Modified One-Step Method

To obtain the copolyimide with variously structural arrangement, the modified one-step polymerization

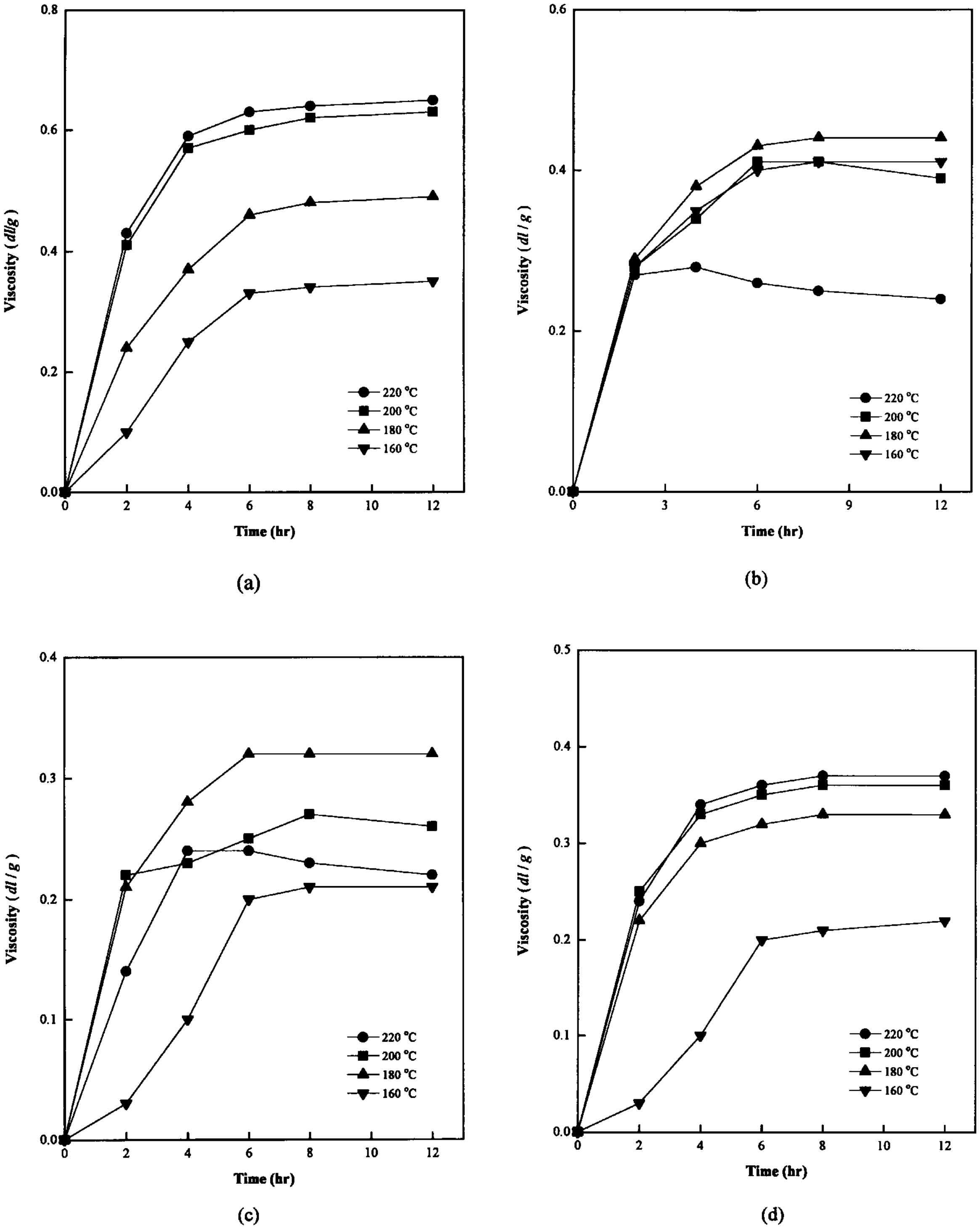
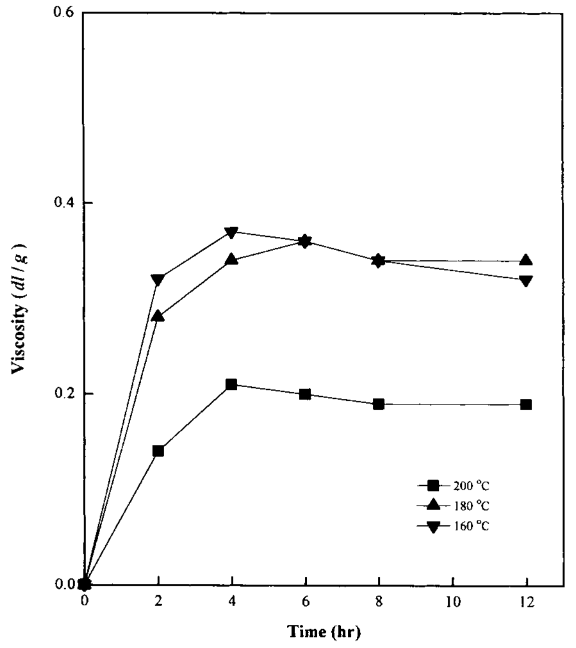


Figure 2 The viscosity of H-1 PI prepared from the one-step method as functions of time and temperature in (a) nitrobenzene, (b) NMP, (c) benzonitrile, (d) *m*-cresol, and (e) DMAc. Reaction was carried out with 15 wt % of monomers concentration in solvent.

reaction was introduced. Previously, the polyamic acid (PAA) with different arrangement was synthesized at a moderate temperature in the NMP with the same way as in the classic two-step method,[1,2] and subsequently the dehydrocyclization was completed in the solution without intermediating pro-



(e)

Figure 2 (*Continued from the previous page*)

cess. *p*-Xylene as an azeotroping agent was used for enhancing the elimination of the byproduct.

Homopolymer. A four-neck flask equipped with a mechanical stirrer, a nitrogen inlet tube, thermometer, and drying tube was charged with diamine and NMP at 20°C. Under nitrogen conditions, equivalent dianhydride was added into the flask with stirring, and the reaction mixture was kept at this condition to obtain PAA with high molecular weight. When the reaction was completed, the azeotroping agent, *p*-xylene, was added, and the drying tube in the flask was exchanged with a distilling receiver having a reflux condenser. The mixture was rapidly heated up to 180°C until no more increased viscosity was seen in the flow of nitrogen. The water liberated by dehydrocyclization was removed. PI was then obtained as above.

Alternating Copolymers. The same flask as described above was charged with diamine and NMP at 20°C. Unequivalent dianhydride was added to the solution to yield a prepolymer terminated with anhydride or amine groups. After the reaction was complete, another diamine or dianhydride was added to the reaction mixture to complete the unbalanced stoichiometry. If the reaction was completed, the yielded PAA was dehydrocyclized and separated as above.

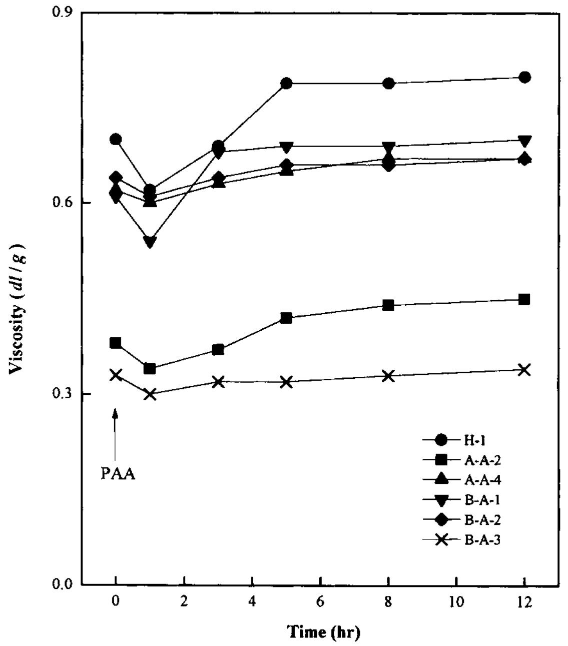


Figure 3 The viscosity change of PI derivatives during modified one-step polymerization. (a) Reaction for preparation of PAA was carried out 15 wt % of monomers concentration in NMP at 20°C for 4 h under flowing nitrogen atmosphere. (b) Reaction for solution imidization was carried out at 180°C under the same conditions as in PAA.

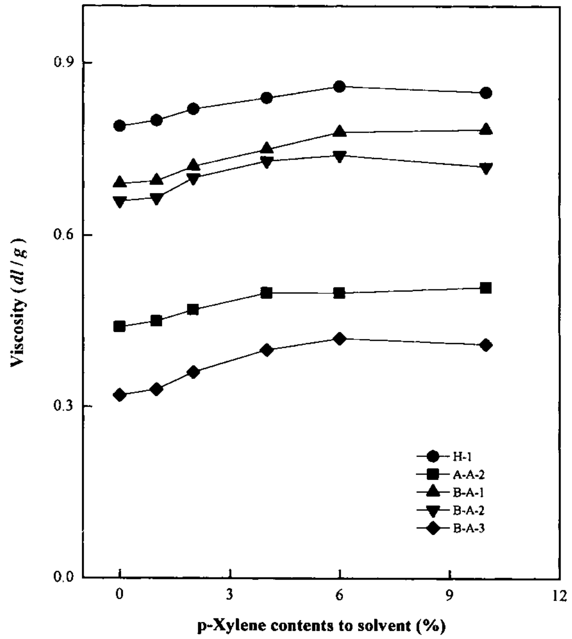


Figure 4 Evolution of the viscosity of PI derivatives versus amount of azeotroping agent in the modified one-step method. Reaction for solution imidization was carried out 15 wt % of monomers concentration in NMP at 180°C for 7 h under flowing nitrogen atmosphere.

Table II Viscosity and Yield of PI Derivatives Prepared by the One-Step Polymerization

No.	Dianhydride (mol ratio)	Diamine (mol ratio)	Viscosity[a] (dL/g)	Yield (%)	Remarks[b]
H-1	PMDA	BAPS	0.60	> 98	S
H-2	BTDA	BAPS	0.40	> 98	S
H-3	DMCA	BAPS	0.21	> 98	S
	PMDA	ODA : BAPS			
A-R-1		2 : 1	—	—	P
A-R-2		1 : 1	—	—	PP
A-R-3		1 : 2	0.43	> 98	S
		BADB : BAPS			
A-R-4		2 : 1	—	—	P
A-R-5		1 : 1	0.32	> 98	S
A-R-6		1 : 2	0.35	> 98	S
		BADB : ODA			
A-R-7		1 : 1	—	—	P
	BTCA	BADB : BAPS			
A-R-8		2 : 1	—	—	P
A-R-9		1 : 1	—	—	P
A-R-10		1 : 2	0.33	> 98	S
	DMCA	BADB : BAPS			
A-R-11		2 : 1	0.22	> 98	S
A-R-12		1 : 1	0.26	> 70	S
A-R-13		1 : 2	0.22	> 70	S
	PMDA : BTCA	BAPS			
B-R-1	2 : 1		0.47	> 98	S
B-R-2	1 : 1		0.43	> 98	S
B-R-3	1 : 2		—	—	P
	PMDA : DMCA	BAPS			
B-R-4	2 : 1		0.20	> 98	S
B-R-5	1 : 1		0.22	> 98	
B-R-6	1 : 2		0.20	> 98	S

Polymerization was carried out with 15 wt % of monomers concentration in nitrobenzene at 200°C for 7 h under flowing nitrogen.

[a] Measured at contents of 0.5 g/dL polyimide in NMP at 30°C.

[b] Where S is not deposited, PP is partially deposited, and P is deposited in the reaction medium.

RESULTS AND DISCUSSION

Figure 1 represents the IR spectra of H-1 PI yielded from one-step methods. It was possible when soluble PI derivatives, which were a basic component in the pretest, were prepared in the used solvent. The absorption peaks that identified PAA with amide I, II, and III bands at about 1650, 1520, and 1300 cm^{-1}, respectively, rapidly disappeared with reaction temperature but exhibited strong bands at about 1780 and 1710 cm^{-1}, which are assigned to the stretch vibration of C=O linkage of cyclic imide, and a band at 1370 cm^{-1}, which is due to the C—N stretch vibration of cyclic imide groups. It could be deduced from the spectra that the polymers obtained by the one-step polymerization at above 180°C were mostly PI.

The Figure 2 series shows the viscosity of H-1 PI as the function of reaction time and temperature for each solvent. The influence of reaction temperature was worked over a temperature range from 160 to 220°C in the one-step polymerization. The temperature was limited to the temperature at which the homogeneous reaction medium could be prepared and the boiling point of nitrobenzene. Nitrobenzene has the highest boiling point among used solvents. As a result, the viscosity values of the polymers increased as the reaction temperature increased at below the boiling temperature of each solvent. Those values with reaction time increased rapidly in the first 2 h, and after that time the values slightly rose to complete the reaction. However, the values of viscosity obviously reduced with time, when the reaction was carried out above the boiling point of

Table III Viscosity and Yield of PI Derivatives Prepared by the Modified One-Step Polymerization

No.	Dianhydride (mol ratio)	Diamine (mol ratio)	Viscosity[a] (dL/g)	Yield (%)	Remarks[b]
H-1	PMDA	BAPS	0.79	> 98	S
	PMDA	ODA : BAPS			
A-A-1		2 : 1	—	—	PP
A-A-2		1 : 1	0.44	> 98	S
A-A-3		1 : 2	0.43	> 98	S
		BADB : BAPS			
A-A-4		1 : 2	0.67	> 98	S
	BTCA	BADB : BAPS			
A-A-5		1 : 1	0.48	> 98	S
A-A-6		1 : 2	0.45	> 98	S
	DMCA	BADB : BAPS			
A-A-7		1 : 2	0.23	> 98	S
	PMDA : BTCA	BAPS			
B-A-1	2 : 1		0.69	> 98	S
B-A-2	1 : 1		0.66	> 98	S
B-A-3	1 : 2		0.32	> 98	S
	PMDA : DMCA	BAPS			
B-A-4	1 : 1		0.27	> 98	S
B-A-5	1 : 2		0.25	> 98	S

Polymerization was carried out with 15 wt % of monomers concentration in NMP at 180°C for 7 h under nitrogen.

[a] Measured at contents of 0.5 g/dL polyimide in NMP at 30°C.

[b] Where S is not deposited and PP is partially deposited in the reaction medium.

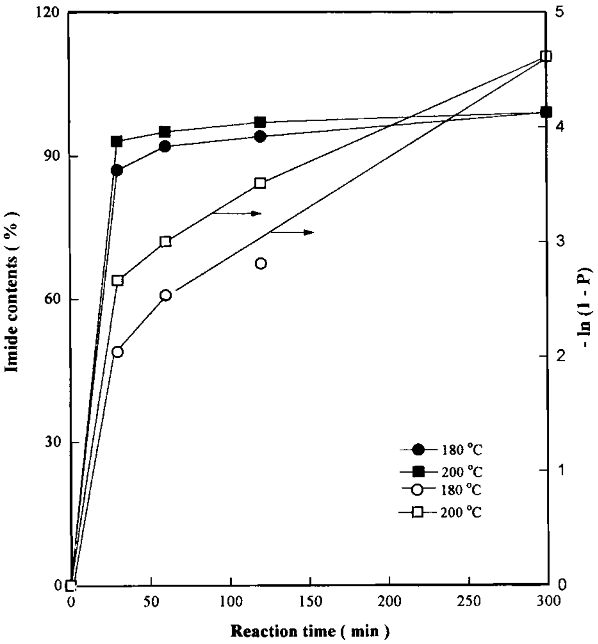


Figure 5 Extent of imidization and first-order kinetic plot of $-\ln(1 - P)$ versus time for H-1 PI as functions of reaction time and temperature in the one-step polymerization.

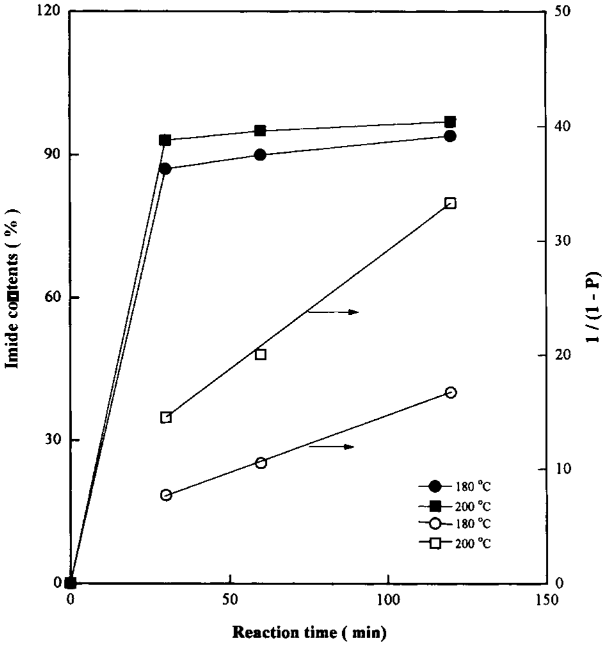


Figure 6 Extent of imidization and first-order kinetic plot of $1/(1 - P)$ versus time for H-1 PI as functions of reaction time and temperature in the one-step polymerization.

Table IV Kinetic Parameters Derived From First- and Second-Order Kinetics for H-1 PI Prepared by One-Step Methods

Kinetic Order	k ($\times 10^2$ min^{-1}) 180°C	k ($\times 10^2$ min^{-1}) 200°C	A (min^{-1})
First	4.2	5.0	2.0
Second	10.0	21.0	1.4×10^6

k, rate constant; A, Arrhenius frequency factor.

each solvent. As could be deduced from those results, PI could be formed almost with a quantitative molecular weight even after 2 h reacting, and nitrobenzene, NMP, and *m*-cresol with high boiling temperatures were suitable solvents, whereas DMAc, which has been one of the typical solvents in use in the two-step method,[1,2] might be an unsuitable one. The extent of one-step polymerization significantly depended on the solvents[3,4] that might have powerful solvent action on the monomers and the polymer. Particularly, the solvent has a strong dissolving power to propagate a polymer with high molecular weight. Otherwise, the polymers might deposit in the reaction mixture during propagating reaction, and the preparation of PI from the one-step polymerization fails. In general, degradation of PI derivatives may occur at elevated temperature in a solvent of amide type such as NMP, DMAc, and so on because of acceleration of the alkaline hydrolysis of PI.[4,9] Although the polymer was probably susceptible to the alkaline hydrolysis of overheated solvents of the amide type, the viscosity value of the polymer prepared in NMP was slightly reduced as that seen with nitrobenzene below NMP boiling temperature. It could be explained by the solubility of reagents. Even though overheated NMP might hydrolyze PI derivatives, the dissolving power of NMP to monomers and polymers was superior to that of nitrobenzene. All dianhydride monomers showed the insoluble nature in nitrobenzene and *m*-cresol below 130°C.

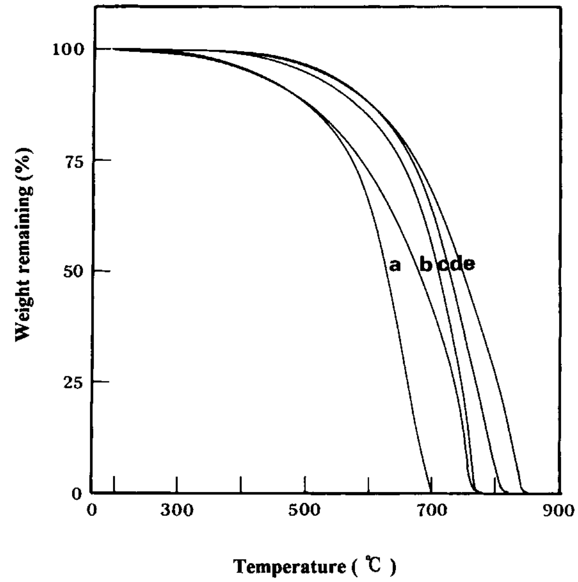


Figure 7 TGA thermograms of (a) H-1, (b) B-A-3, (c) B-A-1, (d) A-A-3, and (e) A-A-2 PI.

To prepare the copolyimide with high molecular weight and various molecular arrangements, the modified one-step polymerization was introduced. NMP was used in this reaction because the used monomers exhibited a good soluble nature at room temperature and the design for molecular arrangement was easy. Figure 3 represents the fluctuation of viscosity on the modified one-step polymerization as a function of reaction time. Previously, PAA with the high molecular weight and different molecular arrangements was prepared in NMP at 20°C for 4 h under nitrogen atmosphere, and subsequently the temperature of reaction medium was rapidly elevated to 180°C for the dehydrocyclization of PAA and the elimination of liberated water. PAA with high molecular weight could be synthesized because the monomers and the propagating polymer were dissolved well in NMP at 20°C, and after heating at 180°C, the value of viscosity slightly decreased in the first 1 h, but the viscosity immediately retrieved its initial value and rose with time. A direct comparison of viscosity was not possible because the

Table V Activation Parameters for Solution Imidization of H-1 PI at 453 K

Kinetic Order	E_a (kJ mol^{-1})	A (min^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (kJ^{-1} mol^{-1})	ΔG^* (kJ mol^{-1})
First	14.6	2.0	10.8	−289.4	141.9
Second	10.0	1.4×10^6	58.7	−177.1	139.0

E_a, Arrhenius activation energy; ΔH^*, activation enthalpy; ΔS^*, activation entropy; ΔG^*, activation Gibbs free energy.

Table VI Thermal Behavior of PI Derivatives Prepared From One-Step Polymerization in TGA Traces

No.	T_i (°C)	T_{10} (°C)	$T_{\max}$ (°C)	T_f (°C)
H-1	400	470	600	700
A-A-2	430	570	725	830
A-A-3	450	570	700	830
B-A-1	420	540	650	720
B-A-3	400	510	640	700

Measured at a heating rate of 20°C/min in nitrogen. T_i, initial decomposition temperature; T_{10}, 10% weight loss temperature; $T_{\max}$, temperature of maximum rate of weight loss; and T_f, final decomposition temperature.

molecular structure changed from the amic acid group to the imide form, but the temperature effect on the viscosity could be observed. The implication of those phenomenon was that the proper imidization conditions were required to ensure the recombination of the degradation chains, the reaction of residual monomers, and their subsequent dehydrocyclization reaction.

Figure 4 shows the influence of azeotroping agent in the modified polymerization. For enhancing the elimination of the byproduct from the reaction zone, *p*-xylene as azeotroping agent was used. On the basis of previous studies,[3,4] it was suggested that the complete elimination of water liberated by dehydrocyclization reaction may be necessary and the minimum alkaline hydrolysis of PI derivatives from overheated NMP may also be requisite to obtain high-molecular-weight polymers. From the result, the azeotroping agent might enhance the elimination of the byproduct and therefore the viscosity values of polymers increased.

The characteristics of polymers yielded by the one-step and the modified polymerizations are summarized in Tables II and III. The extent of polymerization reaction might be strongly dependent on the electron affinity of carbonyl carbon atoms of dianhydride and the nucleophilicity of nitrogen atoms of diamine since that was processed by the nucleophilic substitution at the carbonyl carbon atoms of anhydride.[3,5,6,10–14] In the one-step polymerization, homopolymer and random copolyimides could only be prepared since all the dianhydride reagents used showed an insoluble nature in nitrobenzene at below 130°C. The values of viscosity increased in the following order: DMCA, BTDA, PMDA. Those results might relate to the electron deficiency of carbonyl carbon atoms in dianhydride. From the literature,[2,5,13] the electron affinity increased DMCA < BTDA < PMDA. The values of viscosity for the reaction of diamines with given dianhydride increased with increasing the portion of the following order: BADB, ODA, BAPS. The extent of reaction also increased as the electron sufficiency of amino nitrogen atoms in diamine increased. The nucleophilicity of diamines has known the function of a chemical structure.[6,15] On the basis of the chemical structure, the following order could be given for the nucleophilicity of diamines: BADB > ODA > BAPS. From the results, the extent of polymerization was only influenced by the reactivity of monomers. On the other hand, in the modified one, the PAA, which had different structural arrangement and high molecular weight, could be previously prepared in NMP at room temperature since the reagents and prepolymers were dissolved well in NMP. In the case of the A series, the viscosity increased with increasing proportion of more nucleophilic diamine. The prepolymer terminated with anhydride groups might be destroyed by the residual water in the reaction

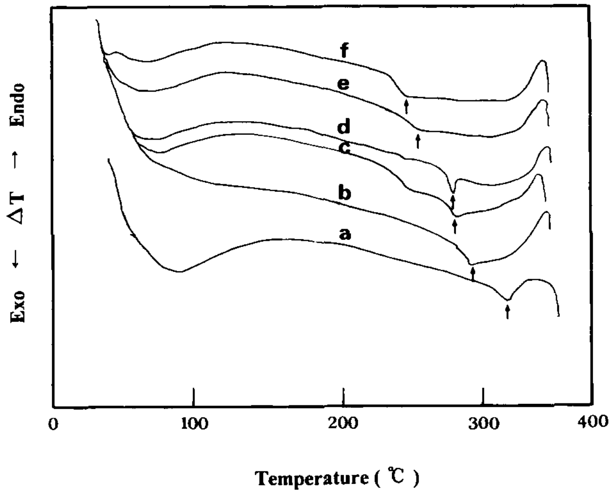


Figure 8 DSC thermograms of (a) A-A-1, (b) A-A-2, (c) A-A-3, (d) A-R-3, (e) B-A-3, and (f) H-1 PI.

Table VII Tensile Strength and Elongation of PI Derivatives Prepared From One-Step Polymerization

No.	Tensile Strength (kg/mm^2)	Elongation (%)
H-1	7.2	7.7
A-A-1	3.3	7.0
A-A-3	5.1	15.0
Ultem −1000[a]	5.6	6.7

Measured at room temperature.

[a] Purchased from General Electric Specialty Plastics.

Table VIII Solubility of PMDA/BAPS Homopolyimide

No.	Solvent	δ_d	δ_p	δ_h	δ_t	Remarks[a]
1	Acetic acid	7.1	3.9	6.6	10.5	IS
2	Acetic anhydride	7.8	5.7	5.0	10.9	IS
3	Acetone	7.6	5.1	3.4	9.8	IS
4	Chloroform	8.7	1.5	2.8	9.3	IS
5	*m*-Cresol	8.8	2.5	6.3	11.1	S
6	Diethyl ether	7.1	1.4	2.5	7.7	IS
7	*N,N*-Dimethylacetamide	8.2	5.6	5.0	11.1	S
8	*N,N*-Dimethylformamide	8.5	6.7	5.5	12.1	S
9	Dimethyl sulfoxide	9.0	8.0	5.0	13.0	S
10	1,4-Dioxane	9.3	0.9	3.6	10.0	IS
11	Formamide	8.4	12.8	9.3	17.9	IS
12	Formic acid	7.0	5.8	8.1	12.2	SW
13	Glycerol	8.5	5.9	14.3	17.6	IS
14	Methanol	7.4	6.0	10.9	14.5	IS
15	*N*-Methyl-1-pyrrolidone	8.8	6.0	3.5	11.2	S
16	Nitrobenzene	9.8	4.2	2.0	10.9	S
17	1-Propanol	7.8	3.3	8.5	12.0	IS
18	Pyridine	9.3	4.3	2.9	10.7	SW
19	Tetrahydrofuran	8.2	2.8	3.9	9.5	IS
20	Toluene	8.8	0.7	1.0	9.1	IS

Heated continuously at 25°C for 7 days, when the sample was partially soluble in the solvent, then heated at 70°C for 24 h.
[a] Where S is soluble, SW, swell, and IS, insoluble in solvent.

medium; therefore, the next reaction probably did not go on smoothly. The anhydride groups belonging to prepolymer and monomer were more serious destructions as they stayed in the reaction medium. The dimension of a propagation polymer also affected the extent of reaction. It was reported by several authors[14] that the viscosity decreased with increasing flexibility of the prepared polymer. According to them, the viscosity of the polymers derived from BAPS was lower than that of others. In the case of B series, the distinctive feature of this process was not to leave unreacted anhydride groups but only amine groups. The amine groups belonging to amine-terminated prepolymer were more stable than the anhydride groups belonging to the anhydride-terminated one; therefore, the extent of polymerization could be raised. As given in Table III, it could clearly be observed that the extent of polymerization was influenced by the reactivity of reagents and the effect of structure. The viscosity of copolymers decreased as the proportion of BAPS increased in the backbone. In the modified one, the polymerization reaction might be dependent on the reactivity of reagents as well as the reaction procedure, and the molecular weight of the polymer was slightly higher than that of the polymer synthesized from the one-step procedure.

On the basis of the degree of imidization, the kinetics of solution imidization was estimated. Figure 5 shows both the imide content plot and the first-order kinetic plot of H-1 PI as a function of time at 180 and 200°C. It could be found that the dehydrocyclization reaction went on rapidly up to high conversion. The linear relationship was initially obtained up to high conversion, but the deviation from the first-order reaction was observed after 1 h, as above 90% conversion. Figure 6 represents both the extent of imidization and the second-order kinetic plot as a function of time at each temperature. It seemed that the second-order kinetics was followed up to high conversion (ca. above 90%). The first- and second-order rate constant (k), the activation energy (Ea), Arrhenius frequency factor (A), and the activation energy parameters were measured in the same manner as stated previously[6,8,15] and are summarized in Tables IV and V. The kinetics of the one-step polymerization could be described by the first-order reaction up to relatively high conversion as compared with that for the general solid-phase imidization processes.[6] It was difficult to explain clearly. However, those results might be related to the following reasons. First, the dehydrocyclization process was not affected by the T_g effect due to the unchanged mobility of reacting polymer[3,6,16] and by the residual solvent effect since the solvent was excessive[5]; therefore, kinetically nonequivalent conformations was avoided in the solution at elevated temperatures. Second, a solution imidization process could be defined as a chemical process[3,6,15] where kinetics was governed by chemical reactivity of the amic acid groups. Thus, that was characterized by auto-acid-catalyzed reactions.[3,6] In explaining the auto-acid-catalyzed reaction, it was necessary to assume that all the PAA groups in different chemical environments hold the equal reactivity and the side reaction and unimolecular degradation of PAA takes no practical effect on the kinetics. In conclusion, dehydrocyclization probably occurred either simultaneously with propagation or very quickly thereafter.[5]

Figure 7 shows curves of PI derivatives, and the results are listed in Table VI. All the polymer samples degraded a similar pattern in TGA. The stability gradually decreased with increasing flexible portion, BAPS. Those results might be due to the influence of molecular weight and the asymmetric structure of BAPS.

The glass transition temperatures (T_g) were calculated from the DSC thermograms in Figure 8. The thermal behavior in the DSC thermogram was mostly similar to the results of TGA. These results could be explained in the same way as in the TGA case. The crystalline melting temperature (T_m) was absent on the DSC thermograms.

The mechanical properties of polyimides are listed in Table VII. The samples yielded revealed good mechanical properties. Elongation was a function of the structure that was increased as the portion of a more flexible component, BAPS, increased. The effect of the composition and the structure was observed.

The solubility of PI derivatives prepared from two different one-step polymerizations in organic solvents are shown in Table VIII. All the polymers were dissolved well in some aprotic polar solvents. The better solubility of PI derivatives derived from one-step methods might be due to the relatively mild imidization temperature. In general, the solubility of the PIs produced by the thermal solid-phase imidization process was inferior to that of polymers produced by the one-step methods because the dehydrocyclization in the solution state might avoid several side reactions that occurred during the curing process in the solid-phase imidization.[3,5-7] Good solubility was advantageous in the processability of polymers and expended the practical application.

CONCLUSIONS

PI derivatives with different arrangements were synthesized by two different one-step methods. In the one-step polymerization, nitrobenzene was the suitable solvent, but the polymers with different structural arrangement were not prepared because all dianhydride monomers showed the insoluble nature in that solvent at below 130°C. In the modified one, NMP was the proper solvent. The polymers with various molecular arrangements could be synthesized in NMP due to the reagents and propagating polymer good soluble in NMP at room temperature.

Relatively mild reaction temperature could be used to complete imidization, which might avoid possible side reactions that might occur at much higher temperature.

PI derivatives exhibited good soluble characterization in several solvents such as NMP, DMF, DMAc, nitrobenzene, and *m*-cresol. The polymers prepared by the one-step polymerizations improved the solubility and processability to avoid several side reactions in the solid-phase imidization. The soluble polymers with large molecular weights sufficient to form strong films could be produced. The azeotroping agent, *p*-xylene, enhanced the elimination of byproduct.

All polymers showed good thermal and mechanical properties and outstanding chemical stability. T_g was observed in the temperature range of 245–310°C on DSC traces. T_g was influenced by the molecular structure and the chain arrangement. Those PIs were almost amorphous compounds in the DSC. In the TGA, the loss in weight below 400°C had not been observed. A weight loss of 10% was observed in the temperature range of 470–570°C, whereas the major weight loss was observed in the temperature range of 600–725°C.

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