Preparation of Soluble Poly(amide imide) Derivatives with Metal Salts and Phosphorous Compounds

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ABSTRACT: Soluble poly(amide imide) derivatives were prepared through the direct polycondensation of 1,2,4-benzenetricarboxylic acid and three diamines—bis[4-(3-aminophenoxy)phenyl]sulfone, bis(4-aminophenyl)-1,4-diisopropylbenzene, and 4,4′-oxydianilne—in the presence of metal salts and phosphorous compounds. Phosphonium salt, which was used as the initiating species and was prepared by the reaction of the metal salts and phosphorous compounds, reacted with 1,2,4-benzenetricarboxylic acid to form acyloxy phosphonium salt, and then the salt was reacted with a diamine for the preparation of the prepolymers. The prepolymers were converted into the corresponding poly(amide imide)s in a homogeneous solution state at 180°C. The poly(amide imide)s showed good thermal and mechanical properties. Glass-transition temperatures were observed from 240 to 270°C in differential scanning calorimetry traces. A melting endotherm was not observed for the polymers with differential scanning calorimetry. The initial decomposition occurred around 400°C according to thermogravimetric analysis, and major weight loss was observed from 610 to 680°C. The poly(amide imide)s had comparatively good solubility in aprotic polar solvents at concentrations high enough (~30%) for the fabrication of various forms. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1399–1407, 2002

Key words: poly(amide imide); direct polycondensation; phosphorous compound; solubility; thermal properties; chemical properties

INTRODUCTION

Polyimide derivatives have found a wide range of applications as high-performance engineering materials in the aerospace and electronics industries because of their excellent electrical, thermal, and high-temperature mechanical properties.[1,2] Their uses, however, are limited because they are intractable materials that do not dissolve in common organic solvents and do not melt before thermally decomposing. Therefore, soluble polyimide derivatives are highly desirable to facilitate processing. For improved characteristics, polyimides have been modified by the incorporation of various functional moieties into the polymer backbone.[3–5] Many attempts have been made to minimize the shortcomings of polyimides but also preserve their excellent properties to the largest possible extent. Many researchers have investigated methods of preparing polyimides with amide structures in the main linkage and have also studied the structure–property relationship of copolyimides.[6–8] Polyimide derivatives with amide structures in the backbone deserve particular attention because they more closely resemble polyimides in their properties.

A modified polymerization was developed to obtain polyimides from the reaction of a carboxy-

lic acid and an amine,[9] with phosphoration being the important reaction. The use of phosphorous compounds and metal salts has been investigated for the direct synthesis of high molecular weight polyamides from a dicarboxylic acid compound and a diamine.[10–14]

The objectives of this investigation were to relate characteristics of poly(amide imide)s (PAIs) to their chemical compositions and to apply direct polycondensation to the synthesis of PAI derivatives with a tricarboxylic acid compound and diamines in the presence of metal salts and phosphorous compounds.

EXPERIMENTAL

Reagents

1,2,4-Benzenetricarboxylic acid (BTCA; Aldrich Co., USA) was recrystallized from acetic acid before use. Bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS; Wakayama Seika Kogyo Co., Japan), 4,4′-oxydianilne (Aldrich Co., USA), and bis(4-aminophenyl)-1,4-diisopropylbenzene (Tokyo Kasei Co., Japan) were purified by recrystallization in ethanol. N-Methyl-2-pyrrolidone (NMP) was dried with CaH_2 and distilled before use. LiCl and $CaCl_2$ were recrystallized from methanol, vacuum-dried, and stored in a vacuum oven. Phosphorous compounds and other laboratory-grade reagents were used without further purification.

Measurements

The viscosity was measured for a 0.5 g/dL NMP solution at 25°C in an automated Ubbelohde viscometer. The analysis of gel permeation chromatography (GPC) was carried out with a Waters model 150 C (USA) equipped with micro-Styragel columns [1.0~10-Å, with dimethylformamide (DMF) as the solvent]. The thermal properties were investigated with differential scanning calorimetry (DSC; DuPont 910, USA) and thermogravimetric analysis (TGA; DuPont 951, USA). All samples were tested under nitrogen at a heating rate of 10°C/min. The second-run TGA curve was considered after the first run up to 300°C for the elimination of remaining materials. The IR spectrum was recorded in a film with a PerkinElmer Paragon 500 Fourier transform infrared spectrometer (USA). Mechanical properties were obtained at room temperature with an Instron model TTC testing machine (Japan). This test used a film 200 μm thick, 10 mm wide, and 50 mm long. For the determination of solubility, the polymer film was immersed in the solvent and shaken at room temperature for 12 h.

PAI Preparation through Direct Polymerization

A metal salt was dissolved in NMP in a four-necked, round flask equipped with a sealed Teflon stirrer, a nitrogen gas inlet tube, a reflux condenser, and a thermometer. Under flowing nitrogen, a phosphorous compound was added to the solution. The mixture was kept under these conditions for 1 h for conformation to a phosphonium salt (**I**), and then BTCA was added to the mixture. When the organic salt (**II**) was completely prepared, the equivalent amount of the diamine was slowly added to the mixture with a stirrer to obtain the prepolymer (**III**). The solid content was 5–30% (w/w) in NMP. On completion of the reaction, the viscous polymer solution was poured into a large quantity of methanol, in which the polymer deposited. The precipitate was filtered off, washed several times with methanol for the removal of the metal salt and with ethanol for the removal of residual phosphorous compounds, and then vacuum-dried at 70°C for 2 h. The prepared polymer chip was dissolved in NMP to approximately 25% (w/w). The polymer solution was placed in a round flask equipped with a distilling receiver with a reflux condenser. Next, the temperature of the reaction system was rapidly elevated to 180°C with a stirrer under flowing nitrogen. The reaction system was kept under these conditions until there was no more of the liberated byproduct, water, which was confirmed with CaH_2. The yielded polymer was treated in the same manner as previously, and then PAI was obtained. The typical reaction proceeded according to Scheme 1.

RESULTS AND DISCUSSION

Figure 1 represents the IR spectra of PAI-1. The spectrum of the prepolymer exhibited characteristic absorption peaks around 1650, 1520, and 1300 cm^{-1}, which are peculiar to amides **I**, **II**, and **III**. The band, at about 2400–3200 cm^{-1}, was due to the stretching of —O—H of carboxylic acid. The peak around 1660 cm^{-1} was related to the stretching vibration of the —C=O linkage of carboxylic acid, and the band around 3300 cm^{-1} was assigned to —N—H of the amide. In the spectrum
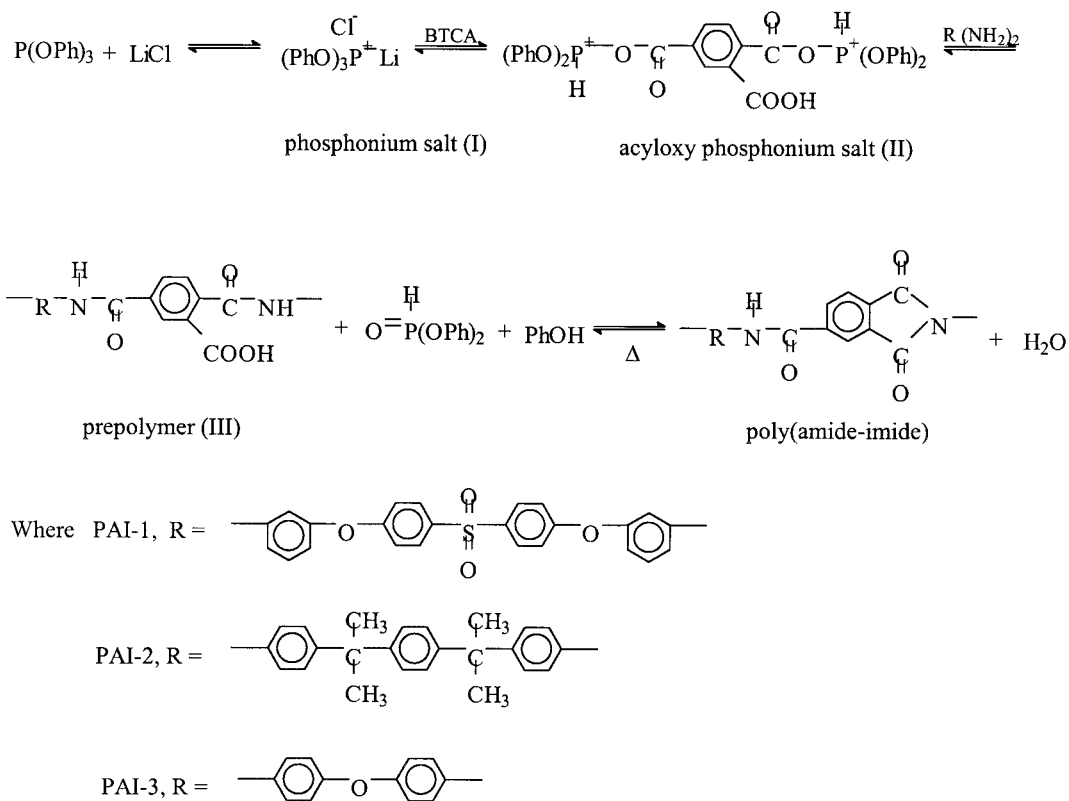
Scheme 1

of the corresponding PAI prepared by dehydrocyclization in solution, the peaks that were characteristic bands of carboxylic acid disappeared, and the intensity of the characteristic absorption peaks of amide decreased. However, new absorption bands appeared around 1720 and 1780 cm^{-1}
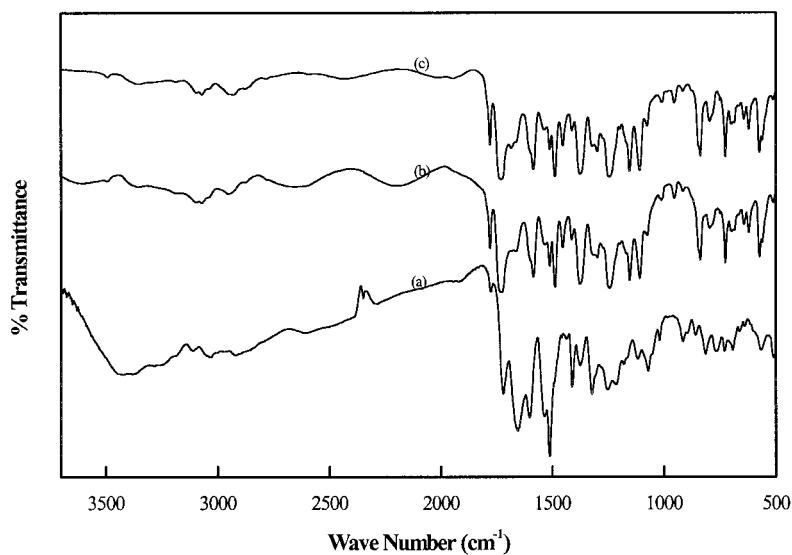

Figure 1   IR spectra of (a) the PAI-1 prepolymer, (b) PAI-1 at 180°C for 2 h, and (c) PAI-1 at 180°C for 6 h.

Table I   Effect of the Monomer Concentration on the Viscosity and Yield

Concentration (wt %)	Viscosity (dL/g)			Yield (%)		
	PAI-1	PAI-2	PAI-3	PAI-1	PAI-2	PAI-3
5	0.64	0.77	0.93	95 ± 2	95 ± 2	95 ± 2
10	0.84	0.92	1.25	95 ± 2	95 ± 2	95 ± 2
15	0.87	1.12	1.37	95 ± 2	95 ± 2	95 ± 2
20	0.86	1.14	1.35	90 ± 2	90 ± 2	85 ± 2
25	0.74	0.85	0.75	85 ± 2	85 ± 2	80 ± 2
30	0.62	0.73	0.52	85 ± 2	80 ± 2	75 ± 2

The reactions were carried out with equal molar amounts of TPP and the monomer and 4 wt % LiCl to the solvent in NMP at 100°C for 4 h under nitrogen. Measurements were made at a 0.5 g/dL polymer concentration in NMP at 25°C.

that were related to the stretching vibration of the —C≡O linkage of the imide ring and around 1380 and 720 cm^{-1} that were assigned to the —C—N stretching vibration of that ring. It could be deduced from the spectra that the prepolymer was polyamide containing carboxylic acid, and the final product yielded from dehydrocyclization in solution was PAI.

Table I explains the effect of the monomer concentration on the viscosity and yield. The solid
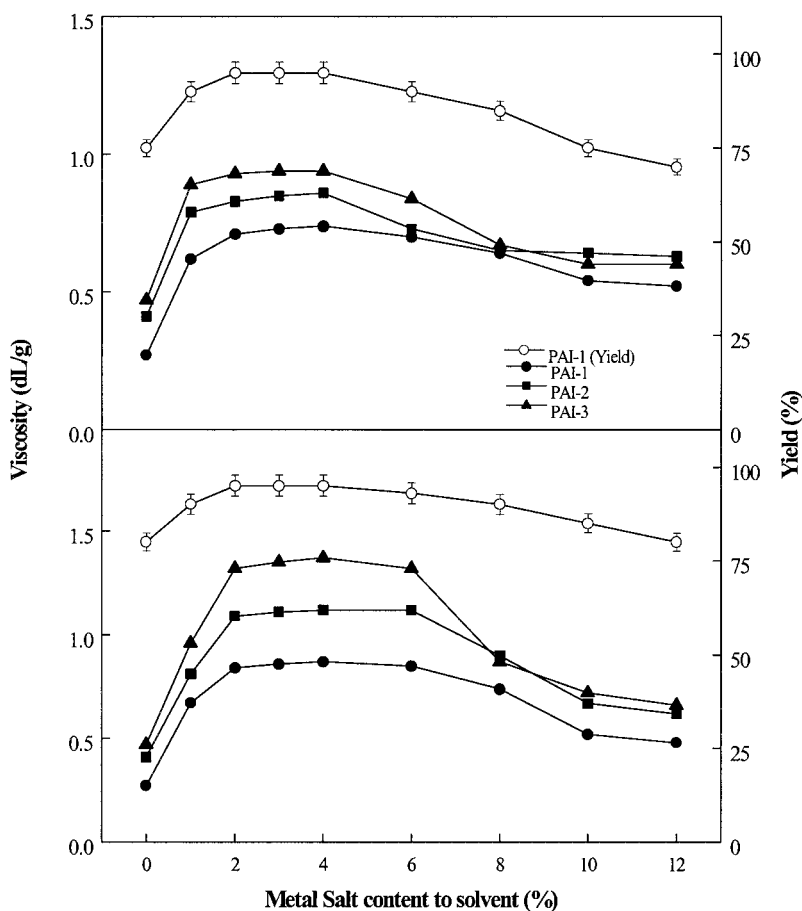

Figure 2   Viscosity and yield of PAIs against the metal salt content [(top) CaCl$_2$ and (bottom) LiCl]. The reactions were performed with a 15 wt % solid content and equal molar amounts of P(Oph)$_3$ and BTCA at 100°C for 4 h.
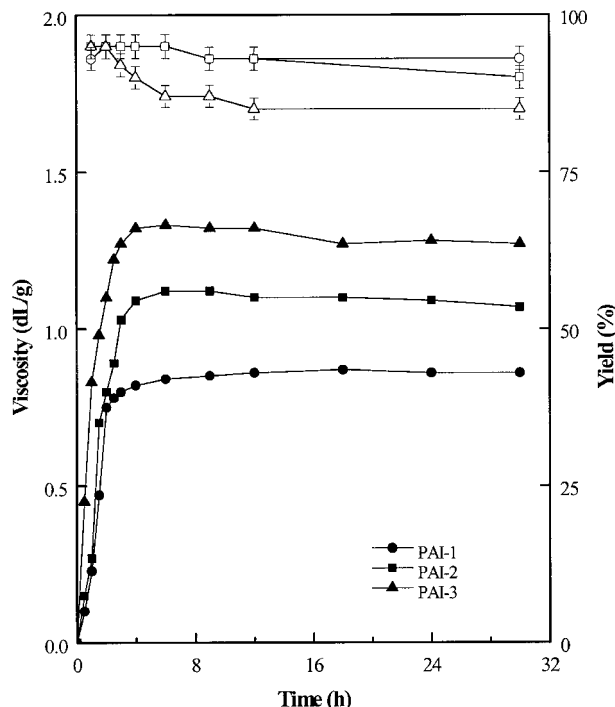
Figure 3 Viscosity (filled symbols) and yield (open symbols) of PAIs against the reaction time. The reactions were performed with a 15 wt % solid content, 2 wt % LiCl to NMP, and equal molar amounts of P(Oph)$_3$ and BTCA at 100°C.

content affected the molecular weight. The viscosity increased with the monomer content increasing up to 15% (w/w) in NMP, apparently reaching a maximum value, whereas the viscosity decreased gradually in proportion to the increasing monomer content. The result could be explained by a gel effect.[15,16] Below 15%, the probability of the impingement of each monomer increased with increasing monomer content for the forward reaction. However, for contents above 15%, the probability of contact between reagents increased, but the reactant mobility could drop because of the rapidly increased viscosity, which took place before the viscosity reached a higher value.[15,16] The rate of the initial reaction increased with the proportion of reagents, but the mobility rapidly decreased because of increasing viscosity.

Figure 2 represents the viscosity and yield as a function of the metal salt content. The polymerization was carried out with a 15 wt % solid content and equal molar amounts of triphenylphosphite (TPP) and BTCA in NMP at 100°C for 4 h. LiCl and CaCl$_2$ were used in this reaction because they, among many known metal salts, are well known for increasing the solvating power of

aprotic solvents such as NMP and dimethylacetamide (DMAc).[9,10,12,17] The reaction between a carboxylic acid and an amine appeared to be enhanced by metal salts. In the absence of metal salts, a polymer with low viscosity was obtained. The viscosity gradually increased with an increasing amount of added metal salts up to about 2% (w/w) in NMP. However, after that amount, the viscosity nearly remained the same up to 6% and then gradually decreased. A relatively satisfactory result was obtained by the addition of about 2% (w/w) LiCl in NMP. These behaviors could be explained by the fact that metal salts took part in the formation of **I** and improved the dissolution power of the solvent, but the excess amount of metal salts, more than 4%, partially precipitated. The hypersaturated amount of metal salts retarded the synthesis of **I**. LiCl and CaCl$_2$ could improve the dissolution power of NMP. With the dissolution power of NMP increasing, the stability of yielded salts as propagating species was increased, and the solubility of the intermediates was also increased.[15,16] Therefore, the propagating reaction proceeded more easily.
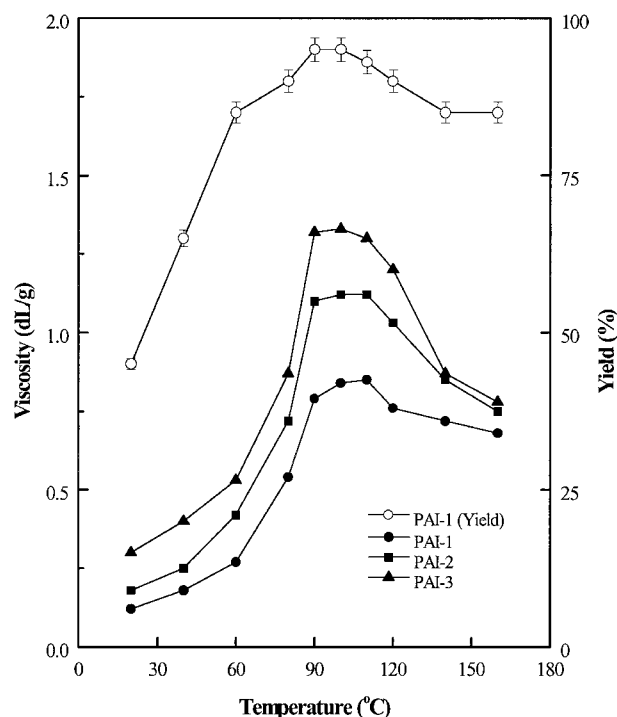

Figure 4 Effect of the reaction temperature on the viscosity and yield of PAIs. The reactions were performed with a 15 wt % solid content, 2 wt % LiCl to NMP, and equal molar amounts of P(Oph)$_3$ and BTCA for 6 h.
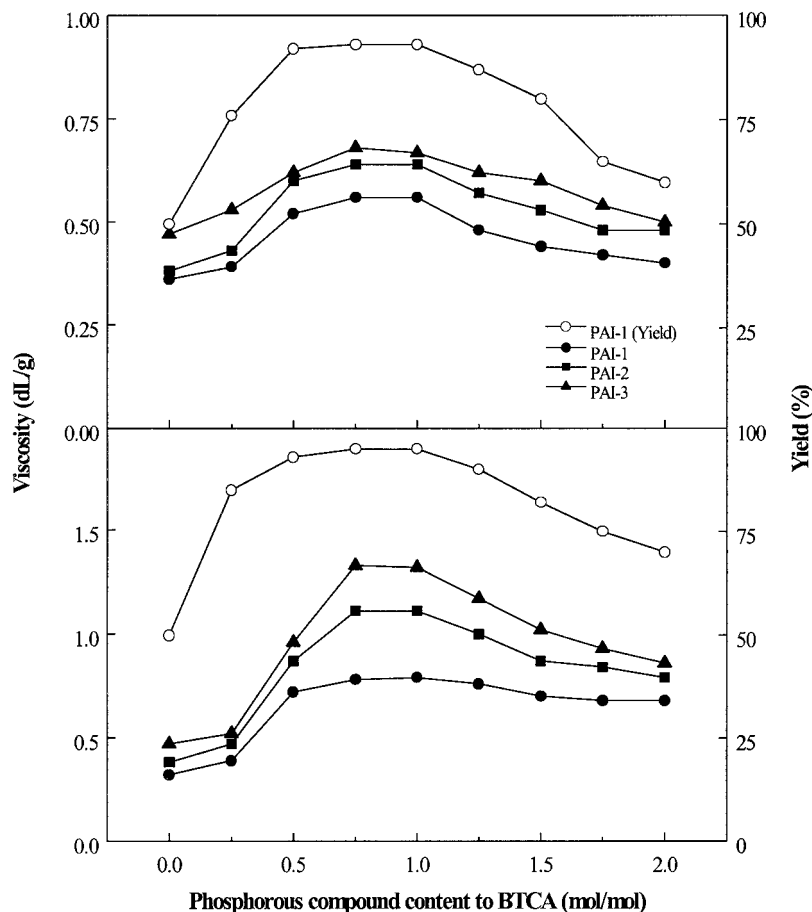
Figure 5 Effect of the amount of the phosphorous compound on the viscosity and yield [(upper) diphenylphosphite and (bottom) triphenylphosphite]. The reactions were performed with a 15 wt % solid content and 2 wt % LiCl to NMP at 90°C for 6 h.

Figures 3 and 4 represent the effects of the reaction time and reaction temperature. The extent of polymerization increased with reaction time. The viscosity was nearly unchanged after 6 h; it leveled off at a certain valve. The result might relate to the equilibrium between the propagating reaction and depolymerization.[15,16] When the rates of polymerization and depolymerization became equal, the extent of polymerization apparently did not proceed after that state. The polycondensation reaction was propagated step by step, and the molecular weight gradually increased as time went by, reaching an equilibrium state. An efficient method of removing byproducts was necessary for the forward reaction to proceed smoothly in the condensation reaction. In this reaction, a phosphorous compound, phenol, and water yielded by the partial cyclization were produced as byproducts. They might have given rise to the inverse reaction. The viscosity was rela-

tively high from 90 to 110°C. When the reaction was carried out below 60°C, a satisfactory result was not obtained, and above 120°C, the viscosity obviously dropped. The result was related to the conformation of the quaternary phosphonium salt (**I**), which was prepared by the reaction of a metal salt and a phosphorous compound and a small amount of water yielded from partial dehydrocyclization into the imide ring. The salt might have been previously conformed for the preparation of **II**, which reacted with an amine. Sufficient energy might have been supplied to the reaction systems for active metal salts and phosphorous compounds.[15,16,18] If the supplied energy as activation energy was not sufficient, the salt (**I**) did not conform and the forward reaction could not proceed. The temperature of the reaction system was the function of energy. Partial dehydrocyclization from amic acid to an imide ring is known occur above 75°C, and the water as a byproduct is
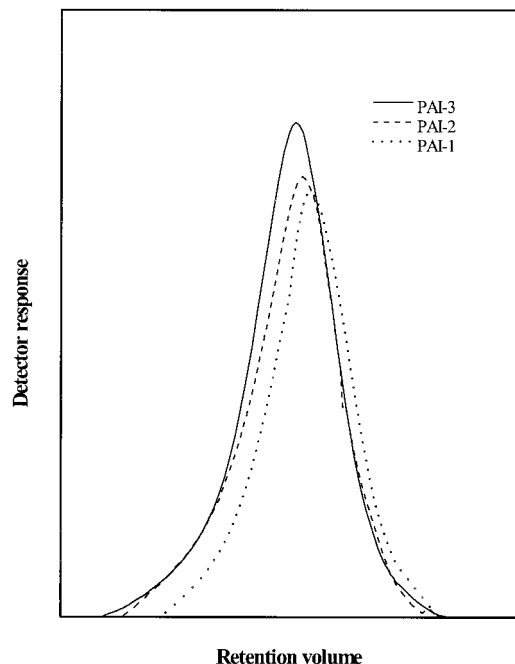
Figure 6 GPC chromatograms of PAIs.

liberated.[1,2,5] The liberated water could induce an inverse reaction. The extent of the forward reaction was dependent on the stability of the activated propagating species and byproducts. In this reaction, a high molecular weight polymer could be obtained above 75°C. As a result, the reactive species might maintain their activity for the forward reaction, and the rate of the forward reaction might be greater than that of the yielded byproducts.

Figure 5 shows the effect of the additive amount of a phosphorous compound in the presence of 2% (w/w) LiCl in NMP. Phosphorous compounds are well known as effective condensing agents for the preparation of high molecular weight polyamide derivatives synthesized by the direct reaction of a carboxylic acid compound and a diamine in the presence of metal salts.[12,13,15,16] On the basis of a previous study,[9] TPP and diphenylphosphite were examined in the reaction. The reaction in the absence of the compounds was not satisfactory. The viscosity of the polymer increased as the amount of the added phosphonium compound increased up to 0.75 mol/mol of BTCA. The viscosity apparently leveled off at this value. Above that additive amount, the viscosity was maintained and gradually decreased with an increasing amount of the phosphonium compound. The results were similar to those of a previous study.[9] This was explained by the steric effect and

the amounts of the byproducts. The conformation of **I** and **II** increased as the proportion of the phosphonium compound increased in the reaction mixture, and the amounts of the yielded byproducts also increased. The excess amount of byproducts could induce an inverse reaction and potentially obstruct the extent of polymerization. All the carboxylic acids that belonged to BTCA were able to react with **I** to conform the acyloxy phosphonium salt (**II**), but only partial groups took part in the conformation reaction of the organic salt because steric hindrance was induced by the bulky substitutions.

Figure 6 shows GPC chromatograms of PAIs. In this diagram, the molecular weight distribution exhibits a similar polydispersity index of 2.2–2.4.

Thermal properties were investigated with DSC and TGA. The initial decomposition temperature (T_i), the 10% weight-loss temperature (T_{10}), and the maximum rate of decomposition (T_{max}) for each step were observed on TGA thermograms. T_i was taken to be the onset temperature when the fastest weight loss began, and T_{max} was confirmed with differential thermogravimetric traces. The results are summarized Table II. T_i's of 380–410°C and T_{10}'s of 450–490°C clearly qualified all the PAIs as thermally stable materials. PAI-3 was slightly more stable than the other PAIs. All the PAIs showed a similar thermal stability pattern in nitrogen. The thermal stability is related to the chemical structure in the backbone. The introduction of bulky substitutes and/or flexible linkages in the main chain might lead to loose packing strength and less thermal stability.

The glass-transition temperature (T_g) was calculated from the DSC thermograms. The T_g's were 240–270°C. There was no significant difference. T_g's were also related to the chemical structures of PAIs, and the results can be explained in the same way as the TGA case was. Figure 7 represents an evaluation of T_g versus the treatment time in a homogeneous solution state at 180°C. The T_g value of the polymer gradually increased with time up to a limiting value. However, the changed value of T_g was less than that of polyimide derivatives with a similar chemical structure.[5,9] This behavior might be related to the density of the imide ring in the main chain. The density of the imide ring was reduced by the separation of the imide structure in the repeating unit of the PAI. The polymer, which had a lower density in the imide structure in the main chain, showed a tendency to reduce the effect of the

Table II   Thermal Behavior of the Copolyimide Derivatives

Polymer	T_i (°C)[a]	T_{10} (°C)[a]	T_{max} (°C)[a]	T_g (°C)[b]
PAI-1	380	450	610	240
PAI-2	380	460	620	247
PAI-3	410	520	680	270
Polyimide[c]	400	470	600	240

[a] From TGA measurements at a heating rate of 10°C/min in nitrogen.
[b] From DSC thermograms at a heating rate of 10°C/min.
[c] Prepared by the reaction of pyromellic dianhydride and BAPS (ref. 5).

Table III   Tensile Strength and Elongation of PAI Films at Break[a]

Polymer	Tensile Strength (kg/mm^2)	Elongation (%)
PAI-1	7.2 ± 0.3	19.0 ± 0.5
PAI-2	7.4 ± 0.3	14.0 ± 0.5
PAI-3	9.0 ± 0.3	12.0 ± 0.5
Polyimide[b]	7.4 ± 0.3	8.3 ± 0.5
Ultem-1000[c]	5.6 ± 0.3	6.7 ± 0.5

[a] Measured at room temperature.
[b] Prepared by the reaction of pyromellic dianhydride and BAPS (ref. 5).
[c] Obtained from General Electric Specialty Plastics.

degree of imidization on T_g. The crystalline melting temperatures of PAIs were absent from the DSC curves. The behavior was probably attributable to the essentially amorphous character of the PAIs.

The mechanical properties of PAIs are given in Table III. A tensile strength at break of about 7–9 kg/mm^2 and an elongation at break of 12–19% were typical. The tensile strength of PAI-3 was somewhat superior to the tensile strengths of the rest. This result was related to the effects of the composition and chemical structure. Elongation
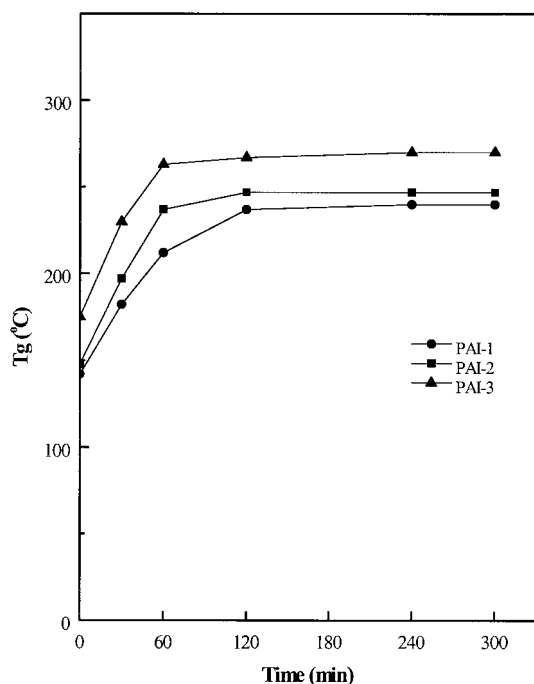
was also the function of the chemical structure in the backbone. All the polymers exhibited good mechanical properties.

Table IV shows the soluble characteristics of the PAIs. The PAIs exhibited good solubility in aprotic polar solvents such as NMP, dimethyl sulfoxide (DMSO), and nitrobenzene at concentrations high enough (~30%) for the fabrication of various forms. PAI-3, containing a less flexible linkage, showed the lowest solubility. However, the solubility of the PAIs was somewhat improved over that of the polyimide derivatives with similar chemical structures in the main chains.[5] Those soluble behaviors could be advantageous for fabricating and extending practical applications.

Figure 7   Evaluation of T_g against the treatment time in a homogeneous solution at 180°C.

Table IV   Soluble Behavior of PAI Derivatives[a]

Solvent	Polymer		
	PAI-1	PAI-2	PAI-3
Acetic acid	IS	IS	IS
Acetone	IS	IS	IS
Chloroform	IS	IS	IS
m-Cresol	S	S	S
DMAc	S	S	S
DMF	S	S	S
DMSO	S	S	S
Formic acid	PS	PS	SW
NMP	SS	SS	S
Nitrobenzene	SS	SS	S
Pyridine	PS	SW	SW
Tetrahydrofuran	IS	IS	IS
Toluene	IS	IS	IS

[a] With shaking at 25°C for 12 h. S = soluble; PS = partially soluble; SW = swell; IS = insoluble in the solvent.

CONCLUSIONS

The PAIs, which were high in their molecular weight for the fabrication of strong films, were synthesized by direct polycondensation between BTCA and diamines in the presence of phosphorous compounds and metal salts in NMP at moderate temperatures. The extent of polymerization was dependent on the reaction temperature and time, the amount and kind of added metal salts and phosphorous compounds, and the monomer content.

All the PAIs had comparatively good solubility without much loss in the outstanding properties of polyimide derivatives with similar chemical structures. The solubility of the PAIs was also improved over the solubility of those polyimides.

The PAIs showed good thermal and mechanical properties and chemical stability. T_g's were observed from 240 to 270°C in DSC traces. The crystalline melting temperature of all the polymers was absent in the DSC traces. The initial decomposition occurred around 400°C according to TGA, and a major weight loss was observed between 610 and 680°C.

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