Synthesis and Characterization of Polyimides by Use of Metal Salts and Phosphorous Compounds in the Presence of Solvent

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SYNOPSIS

Polyimide precursors and polyamic acid were synthesized by direct polycondensation reaction of the 1,2,3,4-butanetetracarboxylic acid (BTCA) and diamines in the presence of metal salts and phosphorous compounds. The BTCA was reacted with an initiating species, which is the phosphonium salt of metal salts and phosphorous compounds, to form acyloxy phosphonium salt building up at moderated temperatures. The salt reacts with diamine to form polyamic acid. The reaction was markedly affected by several factors: reaction temperature and time, solvent, metal salts, phosphorous compounds, and tertiary amine. The polyamic acid was converted into polyimide by chemico-thermal or thermal methods. The polyimide with a high molecular weight can be prepared from BTCA and diamines and was soluble in polar aprotic solvent. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The most widespread route for the preparation of polyimide is a two-step method[1-4]: the ring-opening polyaddition of a diamine to a dianhydride in an aprotic polar solvent at room temperature yielding polyamic acid, which was converted to the polyimide.

Recently, some modified methods of the polyimide preparation were developed.[5-10]

The direct polycondensation was developed to polyimide yielded from tetracarboxylic acids and diamines, among them the important phosphoration reaction. The use of phosphorous compounds and metal salts has been reported[11-16] for the synthesis of condensation polymers. Triphenylphosphite among phosphorous compounds has been shown to be an effective condensing agent for synthesis of high molecular weight polyamides directly from dicarboxylic acids and diamines.[11,12] Phosphite compounds reacted with alkyl halides to form quaternary phosphonium halides, which were capable of halo-genating alcohols to give the corresponding halides and phosphonate compounds.[13] These phosphonium halides could promote the reaction of carboxylic acids and amines. Metal halides were capable of halogenation of alcohols and production of phosphonium salts by reacting with phosphite compounds, and phosphite compounds can activate carboxylic acids in the presence of tertiary amine via acyloxy N-phosphonium salts of tertiary amines.[14-16]

The main objective of this investigation was the successful application of the reaction to the synthesis of polyimide by using BTCA and diamines in the presence of metal salts and phosphorous compounds in the solvent.

EXPERIMENTAL

Reagents

1,2,3,4-Butanetetracarboxylic acid (BTCA, Aldrich Chemical Co.) was recrystallized from acetic acid before use. 4,4'-Dianimodiphenyl-methane (DADM, Aldrich Chemical Co.) and 4,4'-oxydianiline (ODA, Aldrich Chemical Co.) were recrystallized from

ethanol. *N,N'*-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), and *N,N'*-dimethylformamide (DMF) were obtained from the Aldrich Chemical Co. All the solvents were dried by using calcium hydrate and distilled before being stored in 4Å molecular sieves. The metal salts used were recrystallized from methanol before use. Phosphorous compounds were used without further purification. Other laboratory grade reagents were used without further purification: among them were acetic acid, benzene, calcium hydrate, ethanol, methanol, pyridine, imidasole, 2,3-, 2,4-, 2,6-lutidines, and α-, β-, γ-picolines.

Measurements

The viscosity of the polyamic acid solution was determined with a ubbelohde viscometer at a concentration of 0.5 g/dL in DMAc at 30°C.

Gel permeation chromatograms (GPC) were measured by a Water model 150C high-performance liquid chromatograph apparatus (column: μ-styragel 10–10 Å, solvent: DMF).

IR spectrum was recorded in film using a Diglab-FTS-600FT–IR spectrometer, and ^{1}H-NMR spectrum was performed using a Bruker AM 100 spectrometer in dimethyl sulfoxide-δ_6 at room temperature.

The thermal properties of polymers were measured by using a differential scanning calorimetry (DSC, Du Pont 910), thermogravimetric analysis (TGA, Du Pont 951), and derivative thermogravimetry (DTG, Du Pont 951).

The tensile strength and elongation were measured at room temperature using an Instron testing machine (Model TT-C). This test was used on polyimide film with 150 μm thickness, 10 mm width, and 50 mm length.

In order to measure solubility, polyimide samples were placed in the various solvents and allowed to stand for 7 days. When the sample was only partial dissolved or swelled, it was heated at 70–90°C for 24 h and then tested. By using this test, the solubility parameter can be calculated by the second-hand method.[29]

Model Reaction

Model reaction was performed to examine the possibility of the direct polycondensation between a tetracarboxylic acid and a diamine in the presence of metal salts and phosphorous compounds.

When a mixture of equimolar amounts of BTCA, diamine, and triphenylphosphite (TPP) in the presence of 4 wt % LiCl and/or pyridine was heated at 100°C for a few hours in DMAc and then poured into methanol, polyamic acid could be obtained. However, in the absence of LiCl, polymer was not obtained in this reaction. The reaction was assumed to proceed as follows (Scheme 1); similar to the reaction with alkyl halides, TPP was capable of react with LiCl to conform a phosphonium salt (I), which then reacts with BTCA to give the organic salts form, acyloxy (R — CO — O — R') phosphonium salt (II). This mechanism was proposed by some authors.[14-18] This organic salt was reacted with amine to form amic acid. When pyridine was used instead of LiCl, the reaction of TPP with carboxylic acid and amine may proceed via the *N*-phosphonium salts (III) of pyridine.

Synthesis of Polyimide

A four-necked 250 mL round-bottomed flask equipped with a seal Teflon stirrer, nitrogen gas inlet tube, reflux condenser with CaCl$_2$ guard tube, and thermometer, respectively, was charged with metal salts and solvent. To the solution was added a phosphorous compound. After the mixture had been stirred at a moderated temperature for 1 h to conform to a phosphonium salt (I), BTCA was added
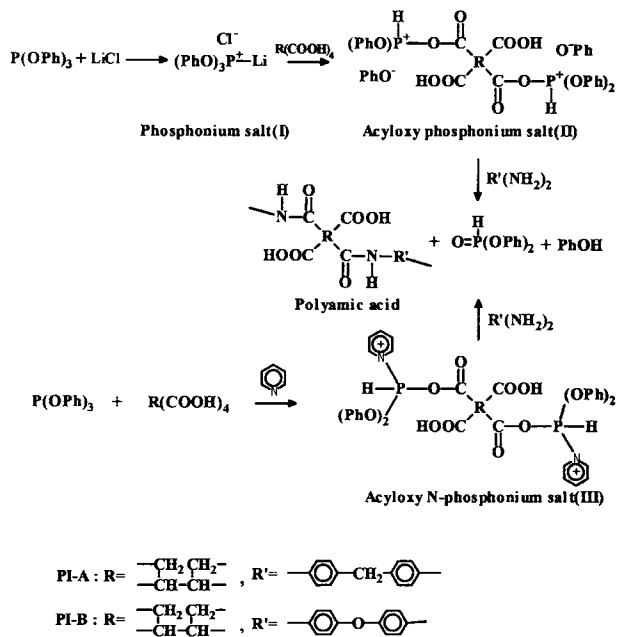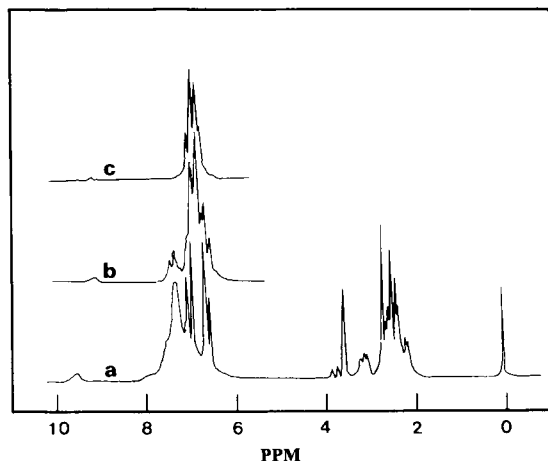
Scheme 1.

Figure 1 NMR Spectra of BTCA/DADM polyamic acid. (a) Polyamic acid; (b) polyamic acid during chemical conversion; and (c) polyimide.

into the mixture with a stirrer. When the organic salt (II) was completely prepared, the stoichiometric amount of the diamine that was dissolved in solvent was slowly added. The residual reagents were washed with the used solvent and then the reaction mixture was kept at the temperature for several hours with a stirrer to obtain high molecular weight polyamic acid. The total weight of reactant monomers is 5–20% (w/w) in solvent. If the reaction was complete, the mixture was poured into methanol in which the polyamic acid was deposited as a pale brown product. The precipitate was separated by filtration, washed several times with methanol to be free of metal salts and with ethanol for removing residual phosphorous compounds, and then vacuum dried at 70°C. The prepared polyamic acid, powder or chip form, was dissolved in DMAc to ca 30% (w/w). The solution was cast on a glass plate. The major amount of solvent was removed in a dried oven at 70°C for 2 h. The resulting film partially dried could be peeled from the glass plate and then clamped to the steel frame. Next, the film was dehydrocyclized by the chemical and/or thermal conversion method.

RESULTS AND DISCUSSION

Figure 1 represents the NMR spectra of BTCA/DADM polyamic acid and corresponding polyimide with different conversion methods. In both the spectra of polyamic acid and polyimide, the absorption peaks of alkane protons were observed at 2.0–3.0 ppm (R_2CH — H), 2.5–3.5 ppm (R_3 — C — H), and 3.4–4.0 ppm (Ar_2 — CH — H), respectively. The
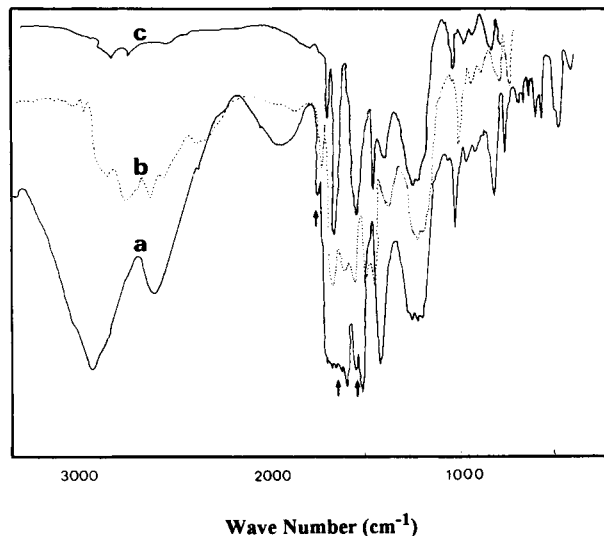
Figure 2 Infrared spectra of BTCA/DADM polyamic acid. (a) Polyamic acid; (b) polyamic acid during chemical conversion at 20°C; and (c) polyimide.

peak of aromatic ring protons (Ar — H) also appeared at 6.0–8.5 ppm. In the spectrum of polyamic acid, the characteristic peaks of amic acid owing to the residual carboxylic acid protons (— COOH) and the secondary amine protons (— CONH —) was detected at 10.5–12.0 ppm and 5.0–8.0 ppm, respectively, but the absorption peak of primary amine (NHH) belonging to the monomer reagent was not detected at 1.0–5.0 ppm. Those are means by which the functional groups of the polyamic acid might consist of carboxylic acids and secondary amines, the amide bond. In spectra (b) and (c), which rep-

Table I   Effect of the Solvent on the Viscosity and Yield of Polyamic Acid[a]

Solvent	Polymer[b]	Viscosity[c] (dL/g)	Yield (%)
DMAc	PI-A	0.44	95
	PI-B	0.52	95
NMP	PI-A	0.42	95
	PI-B	0.46	95
DMF	PI-A	0.38	90
	PI-B	0.40	90

[a] Polymerization was carried out with 10 wt % of monomers content, equimol of P(OPh)₃ to BTCA, and 4 wt % LiCl to solvent at 100°C for 7 h under nitrogen.
[b] PI-A (BTCA/DADM) and PI-B (BTCA/ODA).
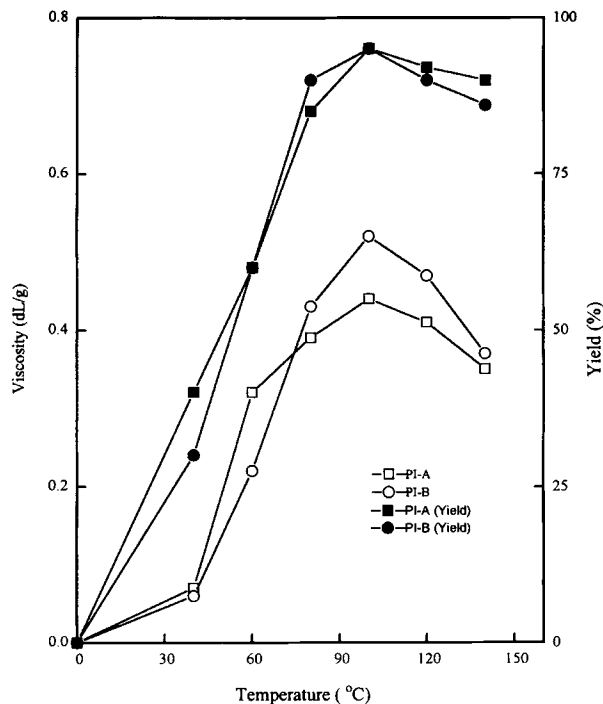[c] Measured at content of 0.5 g/dL polyamic acid in DMAc at 30°C.

Figure 3 Effect of the reaction temperature on the viscosity and yield of polyamic acid: PI-A (BTCA/DADM) and PI-B (BTCA/ODA). 1) Reaction was carried out with 10 wt % monomers content, equimol of P(OPh)$_3$ to BTCA, and 4% (w/s) LiCl in DMAc for 7 h.
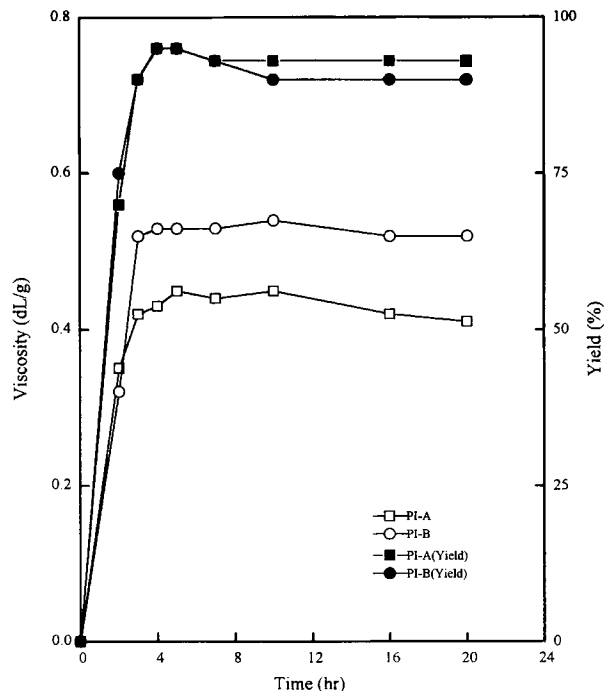

Figure 4 The viscosity and yield of polyamic acid against reaction time: PI-A(BTCA/DADM) and PI-B (BTCA/ODA). 1) Reaction was carried out with 10 wt % monomers content, equimol of P(OPh)$_3$ to BTCA, and 4% (w/w) LiCl in DMAc at 100°C.

resent the polyimide structures according to the conversion methods, the absorption peaks of the represented polyamic acid, carboxylic acid, and secondary amine proton were detected only in the spectrum of the polyimide yielded by the chemical conversion. The intensity of those peaks was gradually decreased during the chemical treatment. This reaction occurred at the conversion-stop state at which dehydrocyclization no longer occurred. The spectra indicate that the polyimide prepared by the chemical conversion method consists of the imide as well as some amount of unconverted amic acid. In view of the fact that the amic acid only partially converted into imide ring during chemical treatment. On the other hand, in the spectrum of polyimide yielded by the thermal conversion, the carboxylic acid and secondary amine proton peaks disappeared. Figure 2 shows the IR spectra of the polymers: the spectra of polyamic acid showed characteristic peaks at about 1650, 1520, and 1300 cm^{-1} for amide I, II, and III, respectively; 1660 cm^{-1} for C=O stretching of carboxylic acid; and about 3300 cm^{-1} for N—H of the amide. In the spectrum of polyimide prepared by the thermal conversion method, the absorption

bands at about 1780 and 1730 cm^{-1} were related to symmetry and asymmetry of C=O linkage of cyclic imide group, respectively, and the absorption peaks at about 1370 and 720 cm^{-1} were due to the C—N stretch vibration of imide structure. On the other

Table II Effect of Monomer Concentration on the Viscosity and Yield of Polyamic Acid[a]

Polymer[b]	Concentration (wt %)	Viscosity[c] (dL/g)	Yield (%)
PI-A	5	0.24	85
	10	0.43	95
	15	0.40	95
	20	0.25	90
PI-B	5	0.34	90
	10	0.52	95
	15	0.48	95
	20	0.40	90

[a] Polymerization was carried out with equimol of P(OPh)$_3$ to BTCA, and 4 wt % LiCl to solvent in DMAc at 100°C for 4 h under nitrogen.
[b] PI-A (BTCA/DADM) and PI-B (BTCA/ODA).
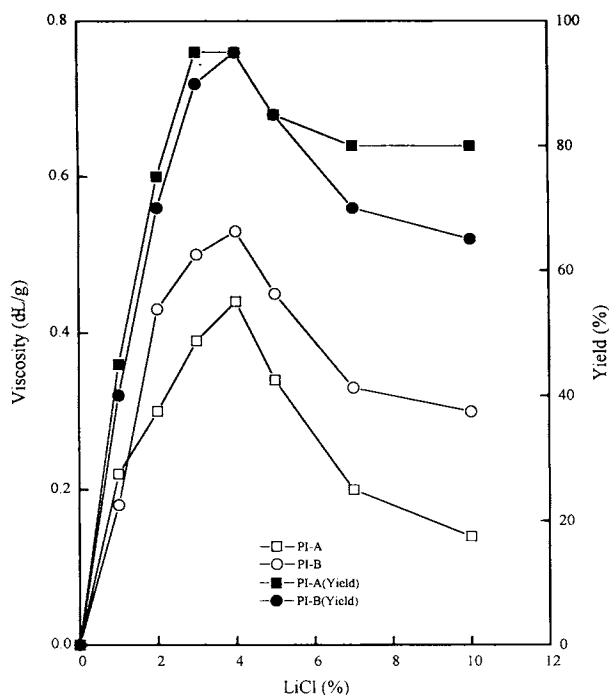[c] Measured at content of 0.5 g/dL polyamic acid in DMAc at 30°C.

Figure 5 The viscosity and yield of polyamic acid against LiCl content in DMAc: PI-A (BTCA/DADM) and PI-B (BTCA/ODA). 1) Reaction was carried out with 10 wt % monomers content, and equimol of P(OPh)₃ to BTCA at 100°C for 4 h.

hand, the peaks that were polyamic acid characteristic peaks disappeared. It can be deduced from those spectra that the product obtained at the first step is mostly polyamic acid, and the final product, generated by thermal and/or chemical treating, consisted mostly of polyimide.

Table I represents viscosity and yield of polymers obtained from various solvents. It is found that the viscosity of polymer obtained in DMAc was larger than that obtained in other solvents. A significant solvent effect on the molecular weight of the polymer produced has been observed in many condensation reactions.[19-21,30] It is difficult to explain clearly, but the results may be related to the change of the reactivity of propagating species by the solvent affect.[19-21,30] During polymerization, counterions are present in the reaction medium to electrical neutrality. The reaction may be strongly influenced by the counterions, depending on the whether they are strongly or weakly associated with the propagating species.[31,32] The strength of association between propagating species and counterion depends on several factors, such as the dielectric strength of the solvent, monomer reactivity, the catalyst effect, the solvent's ability to coordinate the counterion, and

so on.[31,32] The strength is decreased with increasing the solvent polarity so that a charged species is more easily generated. In general, the stronger the association, the lower the propagating rate. As a result, the solvent was able to dissolve the intermediate and generate free-ion and/or solvent-separated ion pairs. Hydrogen bonds take an active part in polyamic acid and solvent.[33] They were formed between the solvent and — OH and/or — NH — groups of the polyamic acids. Polymerization reaction was also influenced by the hydrogen bonding strength.

Figures 3 and 4 show the effects of the reaction temperature and the reaction time, respectively. As a result, it shows that the relatively high viscosity of polymer was obtained at 100°C for 2–3 h. When the reaction was carried out below 60°C, it did not proceed. The reason might be explained by the fact that the quaternary phosphonium salt (I) conformed from TPP and metal salt might be previously prepared for the propagating reaction.[24,25] For the conformation of the salt, sufficient energy must be supplied to the reagent in order to activate. When the supplied energy was not enough, the forward reaction could not occur. Reaction medium temperature is the function of energy.

In the common polyimide synthesis,[1-4] above 75°C, partial dehydrocyclization into imide ring occurred during synthesis of the polyamic acid, and the molecular weight became markedly decreased. But in this reaction, polymerization was performed

Table III The Viscosity and Yield of Polyamic Acid against Various Metal Salts[a]

Metal Salt	Viscosity[b] (dL/g)		Yield (%)	
	PI-A	PI-B	PI-A	PI-B
LiCl	0.43	0.52	95	95
LiBr	0.21	0.20	75	85
KCl	0.18	0.38	75	90
KBr	0.10	0.14	60	80
CaCl₂	0.40	0.42	85	90
KSCN	0.09	0.07	35	50
ZnCl₂	0.27	0.22	50	60
MgCl₂	0.35	0.36	60	70
KF	—	—	—	—

[a] Polymerization was carried out with 10 wt % of monomers content, equimol of P(OPh)₃ to BTCA, and 4 wt % of metal salt to solvent in DMAc at 100°C for 4 h under nitrogen. PI-A (BTCA/DADM) and PI-B (BTCA/ODA).
[b] Measured at content of 0.5 g/dL polyamic acid in DMAc at 30°C.

Table IV Effect of the Various Tertiary Amines on the Viscosity and Yield of Polyamic Acid[a]

Tertiary Amine	K^b	Viscosity $(dL/g)^c$		Yield (%)	
		PI-A	PI-B	PI-A	PI-B
Pyridine	5.62×10^{-6}	0.56	0.62	95	95
β-Picoline	2.09×10^{-6}	0.50	0.56	90	90
α-Picoline	1.07×10^{-6}	0.46	0.53	90	85
γ-Picoline	9.55×10^{-7}	0.45	0.53	90	85
2,4-Lutidine	1.02×10^{-7}	0.40	0.53	80	80
2,3-Lutidine		0.37	0.48	75	60
2,6-Lutidine	1.02×10^{-7}	0.32	0.41	50	50
Imidasole	1.11×10^{-7}	—	—	—	—

[a] Polymerization was carried out with 10 wt % of monomers content, equimol of P(OPh)$_3$ to BTCA, and 4 wt % of LiCl to solvent in t-amine/DMAc ($\frac{1}{4}$ wt) at 100°C for 4 h under nitrogen. PI-A (BTCA/DAPM) and PI-B (BTCA/ODA).
[b] The equilibrium constants were obtained from ref. 36.
[c] Measured at content of 0.5 g/dL polyamic acid in DMAc at 30°C.

at those temperatures. As a consequence, the propagating species might maintain their activating states (activity).

Polycondensation reaction is processed step by step, that is to say, molecular weight increases as time gones by.[31,32] From the results, the viscosity of polymer gradually increased with reaction time to reach a limited value. After that state the values slightly changed. Because this polymerization is a reversible process, it is necessary in this case to provide an efficient means of removing by-products, using ultrapurified reagents, and so on to obtain high molecular weight polymers. In this polymerization, diphenylphosphite and phenol, which were produced from the condensation reaction, a small amount of water, which was the result from partial cyclization from polyamic acid to polyimide, and residual impurities in reagents may give rise to the inverse reaction.

Table II explains the effect of the monomer concentration on viscosity and yield of the polymers. It can be clearly observed that the content of reagents affects the molecular weight. The viscosity of the polymers increased with increasing monomer content up to 10% (w/w) in solvent, where a limiting value apparently was reached; however, the viscosity decreased gradually with increasing monomer content. It seems that, in the case of a low content of 5%, the probability of impingements of each monomer is extremely low for favorable progress. On the other hand, in the case of a higher reactant concentration, the lower viscosity of the polymers is at-

tributable to reduced reactants mobility due to the rapidly increased viscosity, which takes place before the viscosity reaches a higher value.[31,32,34]

The viscosity and yield as a function of LiCl content are shown in Figure 5. The reaction seemed to be catalytically enhanced by LiCl. The amount of LiCl is an important factor to the extent of polymerization, and the most satisfactory result was obtained by the addition of 4% (w/w) LiCl in DMAc. The reaction did not occur in the absence of LiCl,

Table V The Viscosity and Yield of Polyamic Acid Prepared in Pyridine/DMAc Mixed Solvent[a]

Py./DMAc (w/w)	Viscosity[b] (dL/g)		Yield (%)	
	PI-A	PI-B	PI-A	PI-B
0/5	0.43	0.52	95	95
0.5/4.5	0.48	0.57	95	95
1/4	0.56	0.62	95	95
2/3	0.46	0.60	90	90
1/1	0.32	0.29	70	80
3/2	0.25	0.27	45	50
4/1	0.15	0.10	40	50
5/0	—	—	—	—

[a] Polymerization was carried out with 10 wt % of monomers content, equimol of P(OPh)$_3$ to BTCA, and 4 wt % of LiCl to solvent at 100°C for 4 h under nitrogen. PI-A (BTCA/DADM) and PI-B (BTCA/ODA).
[b] Measured at content of 0.5 g/dL polyamic acid in DMAc at 30°C.

Table VI   The Viscosity and Yield of Polyamic Acid Prepared using Various Phosphorous Compounds[a]

Phosphorous Compound	Viscosity[b] (dL/g)		Yield (%)	
	PI-A	PI-B	PI-A	PI-B
Triphenylphosphite	0.56	0.62	95	95
Triphenylphosphate	0.23	0.22	75	70
Diphenylphosphite	0.34	0.40	85	85
Diphenylphosphate	—	—	—	—
Diethylphosphate	—	—	—	—

[a] Polymerization was carried out with 10 wt % of monomers content, equimol of phosphorous compound to BTCA, and 4 wt % of LiCl to solvent in pyridine/DMAc ($\frac{1}{4}$ wt) at 100°C for 4 h under nitrogen.
PI-A (BTCA/DADM) and PI-B (BTCA/ODA).
[b] Measured at content of 0.5 g/dL polyamic acid in DMAc at 30°C.

and no polymer was obtained. The viscosity gradually increased with increasing content of LiCl, reaching about 4% (w/w) LiCl in DMAc. However, further addition retarded the reaction to give a lower viscosity of the polymer. This effect suggested that LiCl takes part in the formation of phosphonium salt (I) and in the improvement of the dissolution power of the solvent,[11,13] but further addition, which was more than 4%, was partially precipitated. The precipitated LiCl might retard the propagating re-

Table VII   Effect of the Amount of Triphenylphosphite on the Viscosity and Yield of Polyamic Acid[a]

| P(OPh)₃ Added mol/mol BTCA	Viscosity (dL/g)[b]		Yield (%)	
	PI-A	PI-B	PI-A	PI-B
0	—	—	—	—
0.25	0.20	0.35	50	50
0.50	0.27	0.42	70	85
0.75	0.41	0.57	95	95
1.00	0.56	0.62	95	95
1.25	0.56	0.57	90	90
1.50	0.50	0.52	75	90
2.00	0.43	0.45	50	60

[a] Polymerization was carried out with 10 wt % of monomers content, and 4 wt % of LiCl to solvent in pyridine/DMAc ($\frac{1}{4}$ wt) at 100°C for 4 h under nitrogen.
PI-A (BTCA/DADM) and PI-B (BTCA/ODA).
[b] Measured at content of 0.5 g/dL polyamic acid in DMAc at 30°C.
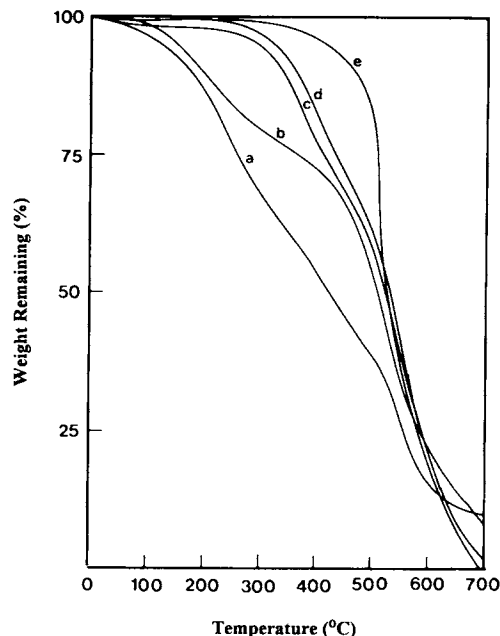
Figure 6   TGA traces of BTCA/DADM polyamic acids with different imidization. (1) Polyamic acid; (b) about 20%; (c) about 30%; (d) about 50%; and (e) polyimide.

action. LiCl could improve the dissolution power of the solvent.[13] Increasing the dissolution power of solvent, the stability of propagating species is probably increased and the solubility of intermediate is
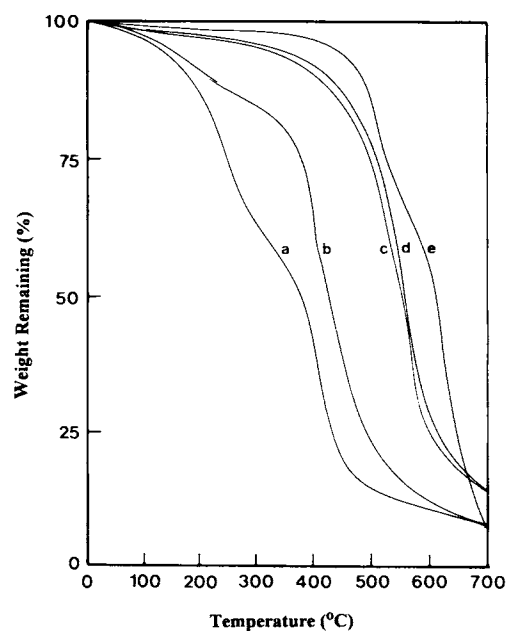
Figure 7   TGA traces of BTCA/ODA polyamic acids with different imidization. (a) Polyamic aicd; (b) about 20%; (c) about 30%; (d) about 50%; and (e) polyimide.
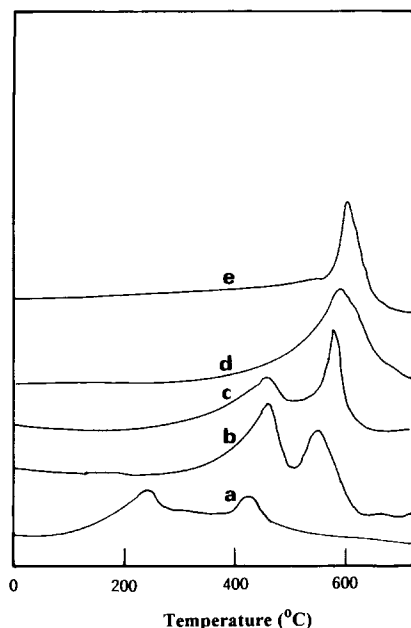
Figure 8 DTG traces of BTCA/DMDA polyamic acids with different imidization. (a) Polyamic acid; (b) about 20%; (c) about 30%; (d) about 50%; and (e) polyimide.

also increased.[31,32] Therefore, the propagating reaction can more easily proceed.

Table III shows the result of the polymer prepared under carrying out at 100°C for 4 h using TPP in the presence of 4% (w/w) of several metal salts in DMAc. Among the metal salts used, LiCl and CaCl₂, whose presence is known to increase the solvating power of aprotic solvents such as DMAc, DMF, NMP, and so on,[13,35] showed relatively satisfactory

Table VIII **Thermal Behavior of Polyamic Acids in TGA Thermograms[a]**

Sample	Temperature[b] (°C)	T_i (°C)	T_{10} (°C)	T_{max} (°C)
PI-A	Polyamic acid	50	200	560
	10	300	460	570
	20	300	455	560
	40	200	275	590
PI-B	Polyamic acid	50	180	550
	10	350	430	610
	20	350	425	570
	40	210	310	580

[a] Measured at heating rate: 20°C/min under flowing air.
PI-A (BTCA/DADM) and PI-B (BTCA/ODA). T_i: initial decomposition temperature, T_{10}: 10% weight loss temperature, and T_{max}: the maximum rate of weight loss.
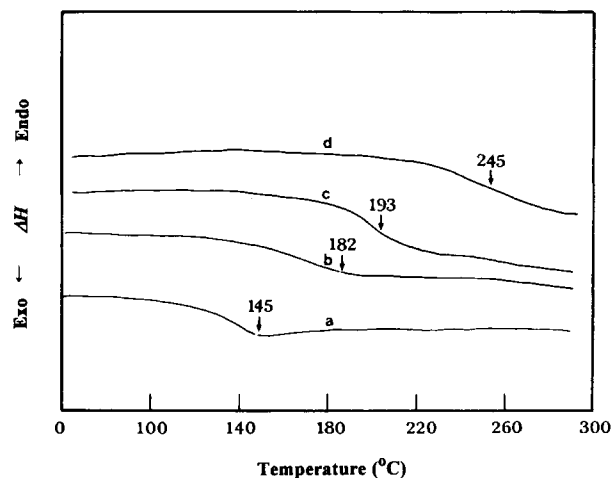[b] The treated temperature during chemical conversion.

Figure 9 DSC thermograms of BTCA/DADM polyamic acids with different imidization. (a) Polyamic acid; (b) about 20%; (c) about 50%; and (d) polyimide.

result on the viscosity and the yield of polymers. The use of KSCN was not effective in the reaction. MgCl₂, ZnCl₂, LiBr, KBr, and KCl could also facilitate the reaction, although results were not satisfactory, and KF did not give a polymer because the fluoride anion could probably conform to a strong ion bond with propagating species. The fluoride has the most electronegativity in all the atoms. The ef-
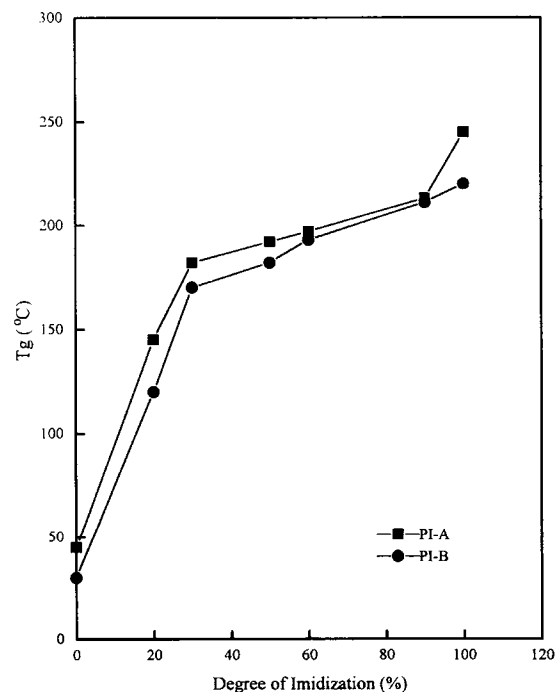

Figure 10 Evoluation of the T_g vs. the extent of imidization of polyamic acid on the chemical treatment.
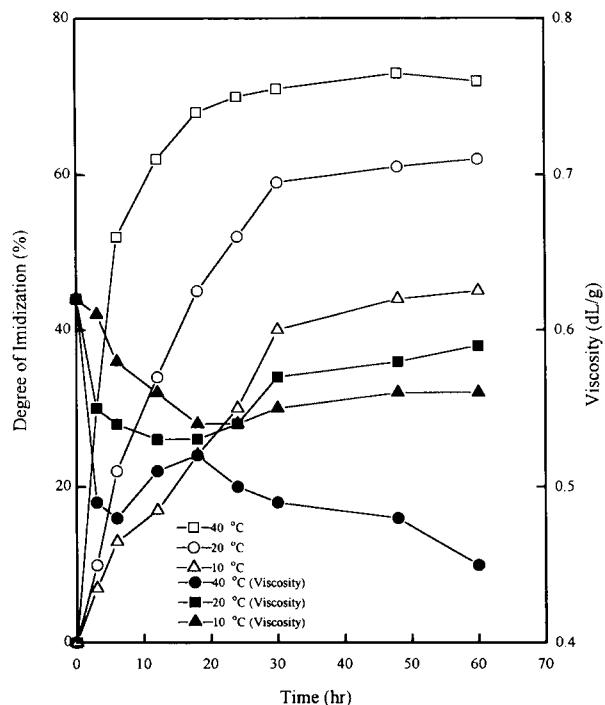
Figure 11 Degree of imidization and viscosity of BTCA/ODA polyamic acids as functions of temperature and time during chemical conversion.

fect of halides of metal salts was observed, chloride giving more satisfactory results than bromide and fluoride.

Recently, it was reported[13,37] that phosphorous compounds could be partially activated by tertiary amine. Based on this fact, it was attempted to used the tertiary amine for the promotion of the quaternary phosphonium salt formation. Table IV represents viscosity and yield of polymers obtained in a mixed solvent of various tertiary amines and DMAc. Among the various tertiary amines examined, pyridine was the most effective. These factors could be explained by the basicity and steric hindrance of used amines.[13,37,38]

Tertiary amine is a Lewis base, so that it can offer an electron pair to conform the acyloxy N-phosphonium salt (III) of that amine.[13,14,31,32] The salt functions as a propagating species in this reaction. The stability of the salt was strongly affected by the basicity of the used amine. A similar result is known,[13,37] that pyridine was the most useful acid acceptor, and was promoted as the formation of a more stable acyloxy N-phosphonium salt because pyridine is a relatively strong Lewis base.

Consequently, the activity of TPP is enhanced in the presence of pyridine. Other used amines gave

less favorable results because of their relatively low basicity and steric hinderance. Lutidines especially had a strong steric effect.[14,37]

The reaction was examined in a mixture solvent of pyridine and DMAc, and the results are represents in Table V. According to the result, a significant pyridine effect was observed in this reaction, where the reaction proceeded more favorably in the solvent of an increased amount of pyridine in DMAc, and the most satisfactory result was obtained in a mixed solvent consisting of a pyridine/DMAc (1 : 4 wt ratio). Increasing the relative amount of pyridine up to the 1 : 4 ratio (w/w) (pyridine/DMAc), the viscosity of polymer was increased, where a limiting weight ratio of mixed solvent was apparently reached. Above this limiting ratio, the extent of reaction gradually decreased with increasing amounts of pyridine; especially, it was conspicuously decreased in the equiweight ratio of pyridine and DMAc. This result could be explained by the reversible behavior and solubility.[13] The state of equilibrium between products including intermediate, polymer, by-product, and monomers existed because this reaction was a reversible reaction. Although, the formation of acyloxy N-phosphonium salt as an intermediate could be promoted by pyridine, the propagating reaction might be retarded by an excess
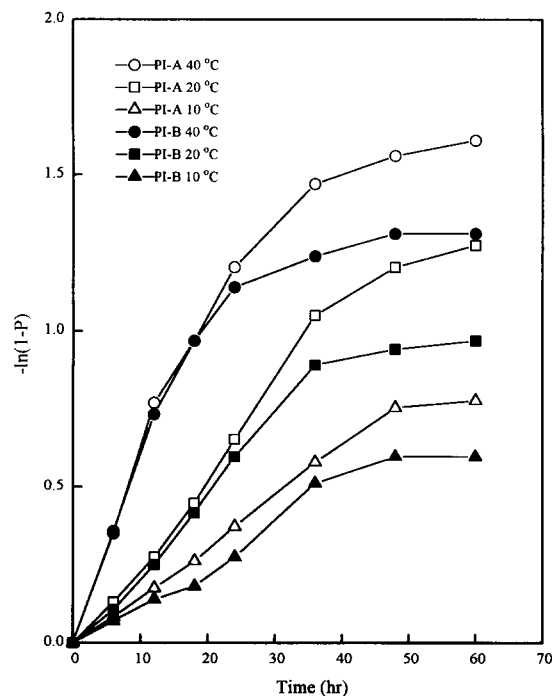

Figure 12 First-order kinetic plot of $-\ln(1-P)$ vs. time: PI-A (BTCA/DADM) and PI-B (BTCA/ODA).

amount of the salt. Where the excess amount of the salt was in a more favorably maintained salt state and/or an inverse reaction than the propagating reaction. It was apparently observed that the gradual precipitation of propagating polymer in the mixed solvent of an increased amount of pyridine occurred because the polymer is insoluble in pyridine. Especially, the reaction in only the pyridine could not be propagated because all the polymer was precipitated. The propagating species of the precipitated polymers may have lost their activity; therefore, the low molecular weight and low yield can be induced.

Phosphorous compounds have been shown to be effective condensing agents for the synthesis of high molecular weight polyamides directing from carboxylic acids and diamines.[5-10,13,14] Several phosphorous compounds were examined in the presence of LiCl and the pyridine/DMAc mixed solvent. The result is shown in Table VI. TPP was the most effective among the phosphorous compounds. Although diphenylphosphite as a by-product was partially catalyzed by pyridine, the result was not satisfactory. Others were also ineffective.

Table VII indicates the effect of the additive amount of TPP on viscosity and yield. The reaction, in the absence of TPP, gave no polymer. The optimal result was obtained in the equivalent of TPP and BTCA. But above this amount, the viscosity and yield of the resulting polymer did not improve. Those facts could be explained by the amount of by-product and steric effect. It was assumed that the amount of phosphonium salt (I) and acyloxy phosphonium salts (II and III) might increase with an increasing amount of TPP, and an equivalent diphenylphosphite was also produced as the by-product. Although the by-product catalyzed from tertiary amine took part in this reaction, the effect was insignificant. The reaction might be retarded by the excess amount
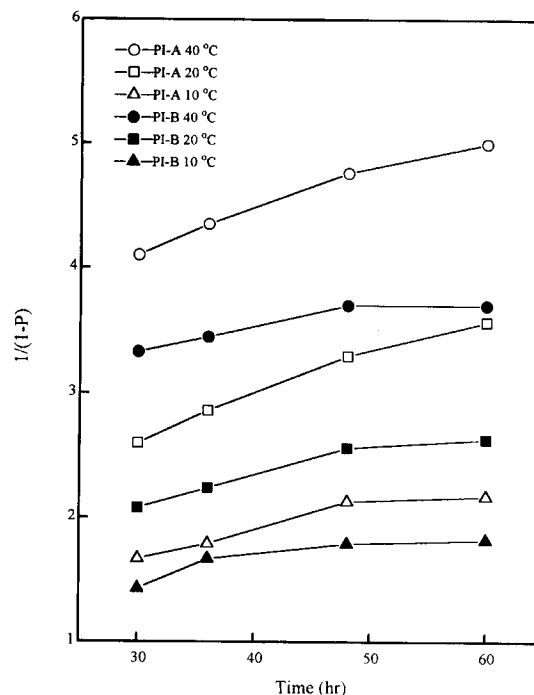

Figure 13 Second-order kinetic plot of 1/(1−P) vs. time: PI-A (BTCA/DADM) and PI-B (BTCA/ODA).

of by-product. In the formation of the acyloxy phosphonium salts, the four functional groups belong to BTCA were able to react with phosphonium salts, but only partial groups participated in the actual reaction because the steric hinderance occurred by bulky quaternary salts. Therefore, above the amount of the equivalence, the results did not improve.

The TGA curves of BTCA/DADM and BTCA/ODA polymers as a function of temperature are shown in Figures 6 and 7. In order to assess the relative thermal stability, the temperature of initial, T_i, 10% weight loss, T_{10}, and the maximum rate of

Table IX Kinetic Parameters Derived from First- and Second-Order Kinetics for the Polyimide System[a]

Polymer		k ($\times 10^4$ min^{-1})			Ea (kJ mol^{-1})	ln A (min^{-1})
		10°C	20°C	40°C		
PI-A	1st	2.3	4.2	8.9	36.5	7.1
	2nd	1.5	2.7	2.5	12.2	−3.6
PI-B	1st	1.7	3.9	8.9	44.0	10
	2nd	1.1	1.5	1.3	3.5	−7.6

[a] Where k is the rate constant, Ea is the activation energy, and A is the Arrhenius frequency factor. PI-A (BTCA/DADM) and PI-B (BTCA/ODA).

Table X   Activation Parameters for the Chemical Imidization of Polyamic Acid at 293 K[a]

Polymer		Ea (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})	ΔG^* (kJ mol^{-1})
PI-A	1st	36.5	34.1	−228.9	101.2
	2nd	12.2	9.8	−317.9	102.9
PI-B	1st	44.0	41.6	−204.0	101.4
	2nd	3.5	1.6	−351.1	104.5

[a] Where Ea is the activation energy, ΔH^* is the activation enthalpy, ΔS^* is the activation entropy, and ΔG^* is the activation Gibbs free energy.
PI-A (BTCA/DADM) and PI-B (BTCA/ODA).

weight loss, T_{max} were noted. The temperature of maximum rate of weight loss was confirmed in the DTG trace (Fig. 8). Those results are summarized in Table VIII.

There was nearly the same pattern between the BTCA/DADM and BTCA/ODA polyimide, according to the TGA curve. It could be observed that the thermal degradation showed a tendency to decrease with an increasing degree of imidization.

Endothermic transition was observed in the DSC curve (Fig. 9), and glassy transition temperature T_g could be obtained. Figure 10 shows the evaluation of T_g vs. the degree of imidization. The T_g of the polymer was increased with increasing content of

imide rings in the polymer. This behavior could be explained by the density of imide rings in the main chain.[23,41,42]

Polyamic acid was treated in the chemical conversion mixture at temperatures of 10, 20, and 40°C. The extent of imidization could be evaluated according to eq. (1).[43] The results are shown in Figure 11.

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 the imide peak at 1780 cm^{-1}, $A(s)$, the standard reference peak at about 1500 cm^{-1}, and $t = \infty$ was taken as the time
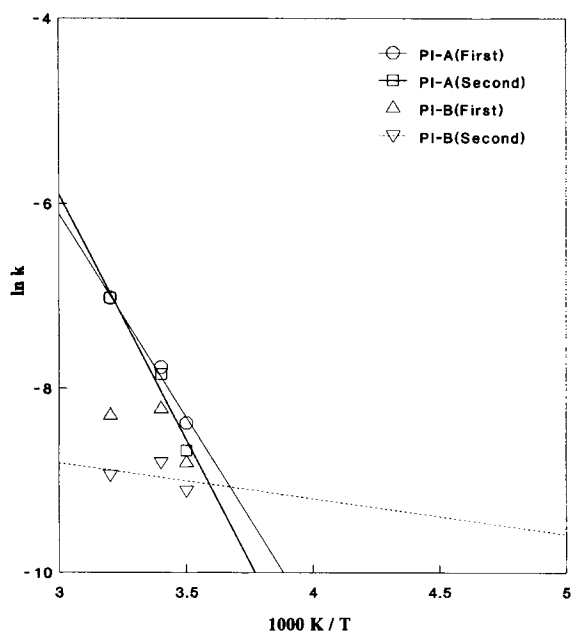

Figure 14 Arrhenius plot of first- and second-order kinetic data: PI-A (BTCA/DADM) and PI-B (BTCA/ODA). The slope gives $-Ea/R$ and the intercept at $1/T = 0$ gives $\ln A$.
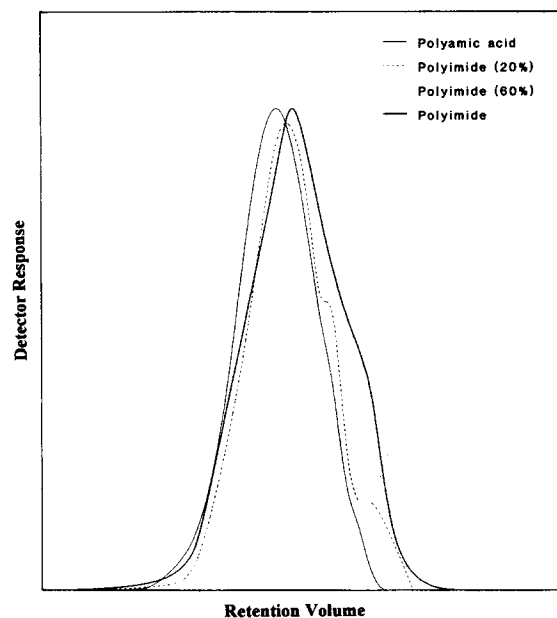

Figure 15 GPC chromatograms of the BTCA/DADM polyamic acid system with different imide content.

Table XI Solubility of BTCA/DADM and BTCA/ODA Polyimide[a]

No.	Solvent	δ_d	δ_p	δ_h	δ_t	Solubility
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	Benzene			2.2	9.2	IS
5	*l*-Butanol	7.8	2.8	7.7	11.3	IS
6	Chloroform	8.7	1.5	2.8	9.3	IS
7	*m*-Cresol	8.8	2.5	6.3	11.1	S
8	*N,N*-Dimethylacetamide	8.2	5.6	5.0	11.1	S
9	*N,N*-Dimethylformamide	8.5	6.7	5.5	12.1	S
10	Dimethyl sulfoxide	9.0	8.0	5.0	13.0	S
11	1,4-Dioxane	9.3	0.9	3.6	10.0	IS
12	Ethanol	7.7	4.3	9.5	13.0	IS
13	Formamide	8.4	12.8	9.3	17.9	IS
14	Formic acid	7.0	5.8	8.1	12.2	SW
15	Glycerol	8.5	5.9	14.3	17.6	IS
16	Methanol	7.4	6.0	10.9	14.5	IS
17	*N*-Methyl-2-pyrrolidone	8.8	6.0	3.5	11.2	S
18	Nitrobenzene	9.8	4.2	2.0	10.9	S
19	*l*-Propanol	7.8	3.3	8.5	12.0	IS
20	Pyridine	9.3	4.3	2.9	10.7	SW
21	Tetrahydrofuran	8.2	2.8	3.9	9.5	IS
22	Toluene	8.8	0.7	1.0	9.1	IS

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

beyond which no further change in the imide peak were observed at 270°C for 4 h.

The extent of dehydrocyclization was gradually increased with treating time up to a limit value, which was called the kinetic stop state.[28,44] The kinetic stop was significantly affected by the treating temperature.[28,44] Although the chemical conversion could be quantitative, a subsequent heat treatment had to be performed if higher imidization was desired.

During the chemical treatment, the viscosity of polymer was changed. This result is also described in Figure 11. At 40°C, the decrease of viscosity was rapid at first and slowed down, on the other hand, at below treating temperature, 10 and 20°C. The viscosity was also reduced in the initial stage, but it was gradually regained up to an approximate value of the initial state with extending dehydrocyclization. The result was related to the rate of reaction because this included reversible and irreversible reaction. The overall reactions that might simultaneously occur could be irreversible imidization as well as reversible resynthesis and decomposition.

The kinetics of imidization was also studied in the chemical treatment. Because both the carboxylic

acid and amide functional group belong to the same polyamic acid, almost all kinetics have been analyzed by using the first- and the second-order equation.[23,45]

If the degree of imidization is P at treating time t, the first-order kinetic equation can be expressed as eq. (2).

$$\ln(1 - P) = -kt, \qquad (2)$$

where k is the rate constant.

The first-order kinetic plots are presented in Figure 12. The kinetic plots show that the kinetics of imidization gradually deviated from the first-order kinetics up to a relatively high conversion. Those features have been interpreted in terms of decreased molecular mobility, kinetic nonequivalence, etc.[28,45] The first-order rate constant (k) was calculated for each temperature and listed in Table IX. The second-order kinetics are shown in Figure 13, and the kinetic constants are also listed in Table IX. It seems that this kinetic was followed to higher conversions. From these results, the rate of imidization was strongly affected by the treating temperature.

Using the Arrhenius equation and the absolute rate theory relation,[45] the Arrhenius plots (Fig. 14)

and the activation kinetic parameters such as activation Gibbs free energy, ΔG^*, enthalpy, ΔH^*, and entropy, ΔS^* are shown in Table X. Those parameters were not easily explained, but the reaction rates were related to the activation energy.

Figure 15 shows GPC chromatogram of polyimides. The distribution of polyimides produced lay in the range of 1.5–2.0.

The solubility of polyimide is summarized in Table XI. Polyimides have good solubility in some aprotic polar solvents, and the good solubility can have the advantages for a processing and for an enhanced application. Solubility parameter composed of a dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) force was represented with a weak polar and weak hydrogen force.

CONCLUSION

The polyimides with a high molecular weight could be prepared by the newly developed polymerization in the presence of equimol TPP to BTCA, 4 wt % LiCl to solvent in pyridine/DMAc (1 : 4 wt %) mixed solvent at 100°C for above 4 h.

The polyimides prepared by the newly developed polycondensation showed good thermal and mechanical properties and good solubility in some aprotic polar solvents.

Glass transition temperature was observed in the temperature range of 150–240°C according to the degree of imidization. The polyimides produced were mostly amorphous polymers in the DSC. In the TGA and DTG thermograms, the loss in weight below 200°C has not been observed. A weight loss of 10% was observed in the temperature range of 420–460°C. It indicates that the polyimides prepared are excellent thermally stable polymers.

In GPC, the molecular weight distribution lay in the range of 1.5–2.5.

The kinetics and energetics for chemical imidization of polyamic acid were determined. From the results, it is concluded: (1) imidization of polyamic acid occurred in the chemical conversion method and exhibited two kinetic regions in all the treating temperature, initial conversion kinetics, and final kinetic stop region. The first- and second-kinetic constant (k) could be calculated; (2) for the times longer than about 20 h, the extent of imidization was a function of temperature. Only small changes in the extent of imidization occurred at longer times; (3) the activation energy (first kinetic Ea: 36.5–44.0 and second kinetic Ea: 3.5–12.2 KJ mol^{-1}) and the

Arrhenius frequency factor (ln -7.6–10.0 min^{-1}) could be calculated in the Arrhenius plot. The activation energy parameters were also measured: ΔS^*: -351.1 to -204.0 J K^{-1} mol^{-1}, ΔH^*: 1.6–41.6 KJ mol^{-1}.

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