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A Water-Soluble Polyimide Precursor:
Synthesis and Characterization of Poly(amic acid) Salt

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Abstract: We have synthesized a water-soluble polyimide precursor, poly(amic acid) amine salt (PAD), from pyromellitic dianhydride (PMDA), 4,4'-oxydianiline, and *N,N'*-dimethylethanolamine (DMEA) and have investigated in detail its properties with respect to the degree of salt formation (D_{sf}). The maximum value of D_{sf} we obtained upon precipitation of the precursor solution into acetone was 79%. We synthesized a PAD having a D_{sf} of 100% (PAD100) by the solid state drying of an organic solution. The precursors showed different solubility depending on the D_{sf} to make up to 4 wt% solutions in water containing a small amount of DMEA. PAD100 is completely soluble in pure water. We investigated the imidization behavior of PAD in aqueous solution using various spectroscopic methods, which revealed that PAD100 has faster imidization kinetics relative to that of the poly(amic acid)-type precursors. The resulting polyimide films prepared from an aqueous precursor solution possess almost similar physical and thermal properties as those prepared from N-methyl-2-pyrrolidone(NMP) solution. Therefore, we have demonstrated that PAD can be used as a water-based precursor of polyimide; this procedure avoids the use of toxic organic solvents, such as NMP.

Keywords: polyimide precursor, poly(amic acid) salt, PMDA, ODA, FTIR spectroscopy, water-soluble, stepwise thermal imidization.

Introduction

Polyimides (PI), a class of high-performance materials, have been widely used as electrical insulators, coatings, adhesives, substrates for flexible printed circuits, and alignment films for liquid crystal displays due to their high temperature stability, excellent mechanical properties and good chemical resistance. Conventionally PI were prepared in two steps: First, aromatic dianhydride is added to a solution of aromatic diamine in a highly polar aprotic solvent such as dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), or N-methyl-2-pyrrolidone (NMP), until a highly viscous poly(amic acid) (PAA) solution was obtained. Second, poly(amic acid) is converted to polyimide by either thermal or chemical imidization. Since poly (amic acid)s are soluble only in strongly polar solvents as mentioned above, which are toxic, careful handling is necessary to avoid environmental problems. Moreover, due to the hydrolytic instability for PAAs over storage, there have been efforts to prepare other precursors of polyimides, such as poly(amic acid) esters,[1-2] and poly(amic acid) salts (PAAS),[3-6] which have no storage problem in solution. Especially, compared to poly(amic acid) and poly(amic acid) ester, PAAS is attractive because it is easy to synthesize and is soluble in water, which are beneficial for both the environmental and practical issues.

Despite such advantages, however, PAAS has not been studied systematically as a water-soluble precursor. In this paper, we described the synthesis and characterization of water soluble polyimide precursor, poly(amic acid) dimethylethanol amine salt (PAD). In addition, its properties and imidization behavior were also investigated.

Experimental

Materials. Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were purchased from Aldrich and used after careful vacuum sublimation. NMP was dried with calcium hydride and vacuum distilled before use. The salt-forming compound, N,N'-dimethylethanolamine (DMEA) (99 %) (Janssen Chimica), was used as received without further purification.

Preparation of poly(amic acid)s (PAA). Poly(amic acid)s

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(PAA) was prepared according to the typical procedure[7] in a round-bottom flask under nitrogen atmosphere. PMDA (0.015 mole) was added to 55 mL of dry NMP solution containing dissolved stoichiometric equivalent amount of ODA (0.015 mole). The mixture was stirred for 18 hrs at room temperature. With the gradual dissolution of PMDA, viscous and yellowish PAA solution was obtained.

For NMR measurements, PAA powder was obtained by precipitating the reaction mixture into acetone followed by subsequent drying at 40 °C in vacuum oven overnight.

Preparation of poly(amic acid) dimethylethanol amine salts (PAD) with different degree of salt formation (D_{sf}). PADs with various degree of salt formation (D_{sf}) were synthesized by adding different amount of DMEA (2.0, 1.5, 1.0, and 0.5 mole equivalent to PMDA, respectively) into the PAA solution. Typically, calculated amount of DMEA was added into PAA solution[8] at room temperature and the mixture was stirred for 45 min under nitrogen atmosphere. Upon the addition of DMEA, large increase of viscosity was observed with a local white precipitation of polymer as reported by Kreuz et. al.[5] The precipitated polymer was redissolved in NMP with stirring to give homogeneous and yellowish solution. The solution was poured into acetone, and the precipitated solid was filtered, dried in vacuum and pulverized in a mortar. Subsequent drying in vacuum at 40 °C for 24 hrs gave light yellow PAD powder. It should be noted that the highest D_{sf} achieved by precipitation was ca. 79%. PAD of 100% D_{sf} (PAD100) was prepared by casting 4 wt% PAD solution (D_{sf} = 79%) in 2% (v/v) DMEA/H_2O on a glass plate and dried at 40 °C in vacuum overnight. The complete elimination of free amine was confirmed by NMR spectrum in DMSO-d_6.

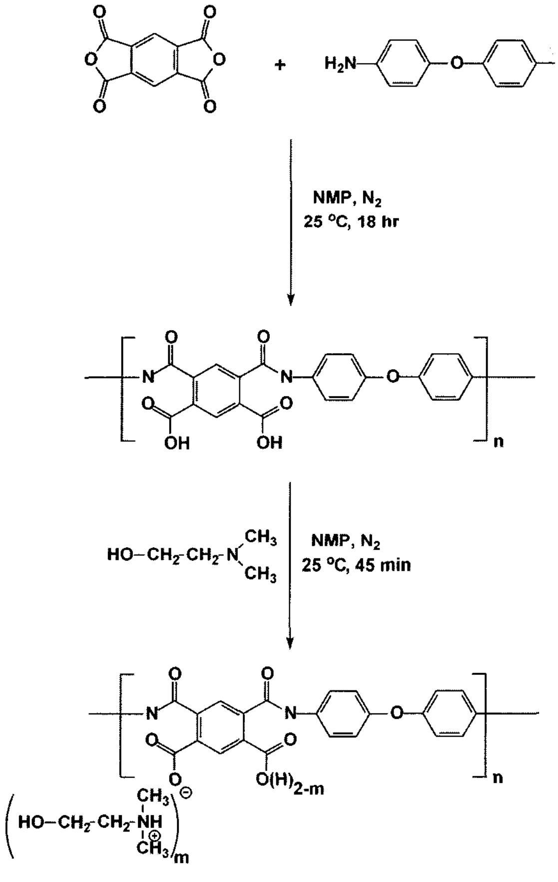

Figure 1. Reaction scheme for preparation of PAD from poly(amic acid) in NMP.

Preparation of polyimide films. In this study, polyimide films were prepared by casting aqueous PAD100 solutions (4.0 wt.%) onto a glass plate followed by multi-step thermal imidization processes as depicted in Figure 2. A polyimide film was also obtained from PAA for comparison. In this case, PAA solution in NMP was used with the same procedure. The thickness of the final films was ca. 20-35 μm.

Determination of degree of salt formation (D_{sf}). D_{sf} was determined by ^{1}H-NMR (in DMSO-d_6, JEOL-EX, 400 MHz). In the ^{1}H-NMR method, the integration value of methylene proton peak of DMEA centered at 3.7 ppm was compared to that of ODA aromatic proton at 7.0 ppm. The detailed calculation is discussed in the results and discussion section.

Viscosity Measurements. Inherent solution viscosities (η_{inh}) were measured for 0.14% (v/v) dilute aqueous solution of PAD100. To investigate the hydrolytic stability, two aqueous PAD solutions of different concentrations, 0.14 and 3.5% (v/v), were stored at 25 °C, and viscosity of the solution was measured periodically. It should be noted here that the 3.5% PAD100 aqueous solution was diluted to 0.14% solution before the viscosity test. All the tests were performed by using Cannon-Fenske type viscometers with capillaries sized to give flow rate in the 40-120 sec range in water bath with temperature controlled at 30 ± 0.05 °C.

Thermogravimetric Analysis. Dynamic thermal behavior of the polyimide films made from aqueous PAD100 solution and PAA solution in NMP were determined by measuring the weight losses while heating from 50 °C to 700 °C at 15 °C/min under nitrogen with gas flow rate of 40 mL/s by using thermogravimetric analyzer (TGA 2050, TA Instruments).

FT-IR Measurement. Infrared spectra were obtained with

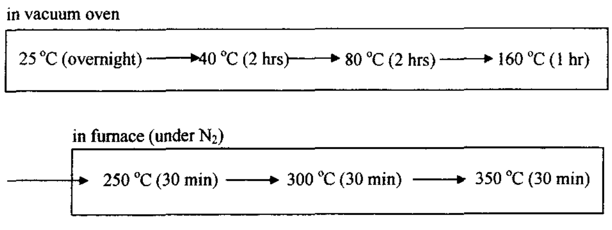

Figure 2. Stepwise thermal imidization procedure (Vacuum + Furnace).

JASCO Model 300E FT-IR spectrometer at a resolution of 2 cm^{-1} and 30 accumulations in order to study the stepwise curing temperature effect on the degree of imidization. Thin films were made by spin-coating 4% (g/mL) PAD100 aqueous solution and 5% (g/mL) in DMSO solution, respectively, onto small squared silicon wafers followed by a subsequent drying at room temperature in vacuum oven overnight. PAA film was also made in the same way from 10% (g/mL) NMP solution for comparison. The absence of solvent in the film before thermal curing was confirmed from the FT-IR spectra (Figure 7) in order to eliminate the solvent effect on the thermal imidization.[9,10]

Results and Discussion

Determination of D_{sf}. Degree of salt formation is calculated from ^{1}H-NMR spectrum (JEOL-EX ^{1}H-NMR spectrometer, 400 MHz). In Figure 3, ^{1}H-NMR spectrum of PAD salt was compared with those of free PAA and DMEA. H_e and H_f peaks shifted downfield due to the formation of ammonium salt. D_{sf} was obtained by comparing the integral values of H_e with that of H_a by the following equation:

$$D_{sf}(\ \%) = \frac{2m}{4} = \frac{A_e}{A_a} \qquad (1)$$

where, 2m and 4 denote the numbers of proton e and a, respectively, in one PAD molecule unit and A is the area under the corresponding peaks.

Syntheses of PADs. To investigate the effect of reaction condition on the salt formation degree (D_{sf}), the mole ratio of PAA and DMEA was varied from 1.0:0.5 to 1.0:4.0 (PAA : DMEA). The results were summarized in Table I. In the case of PADs prepared by precipitation, the highest D_{sf} of ca. 79% was obtained when the stoichiometric amount of DMEA was used to the PAA repeating unit. Larger amounts of DMEA did not have significant effect on the increase of salt formation degree (D_{sf}). In this experiment, PADs from PAD-1 to PAD-4 were used for further characterizations. In addition to these, the reaction time was varied, and the results are also shown in Table I. Reaction time did not affect the salt formation degree considerably. The low salt formation degree would be attributed to the elimination of amine molecules due to the equilibrium change between free amine and ammonium salt during the precipitation into acetone. The resulting polymers were insoluble in pure water, but soluble in 2% (v/v) DMEA/H_2O mixture to make a homogeneous solution of up to 4 wt% solid content. The higher D_{sf}, the faster dissolution was observed in DMEA/H_2O mixed solvent. When the above PAD samples (PAD-1 ~ PAD-4) were redissolved in 2% (v/v) DMEA/H_2O mixture, cast on a glass plate, and dried at 40 °C in vacuum for overnight, PADs of 100% D_{sf}(PAD100) were obtained. From the NMR spectra of PAD100 in DMSO-d_6, 100% salt formation degree was confirmed by the absence of peaks corresponding to free amine and exact agreement in integration values of other peaks. Therefore, it is not likely that the elimination of free amine occurred during the vacuum drying in the case of PAD-1~PAD-4. The resulting polymer was soluble in pure water as well as in DMSO, while the PADs (PAD-1~PAD-4) obtained from the precipitation method were only soluble in water containing extra DMEA.

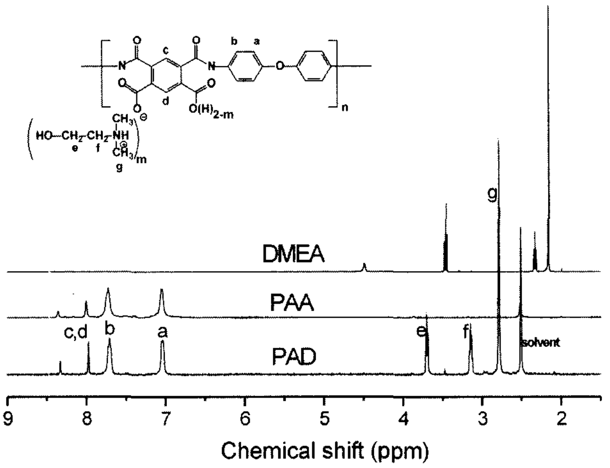

Figure 3. ^{1}H-NMR spectra of *N,N*-dimethylethanolamine (DMEA), free poly(amic acid) (PAA), and its corresponding ammonium salt (PAD).

Table I. Effects of PAA:DMEA Mole Ratio and Reaction Time on D_{sf} of PAD

Sample Number	PAA:DMEA (Mole ratio)[a]	Reaction time (hr)	D_{sf} (mole %)[b]	Dissolve time (min.) in DMEA/H_2O[c]
PAD-1	1:0.5	0.75	26	250
PAD-2	1:1.0	0.75	48	160
PAD-3	1:1.5	0.75	67	100
PAD-4	1:2.0	0.75	79	55
PAD-5	1:2.0	1.5	79	-
PAD-6	1:2.0	2.5	79	-
PAD-7	1:2.0	4	79	-
PAD-8	1:2.5	4	78	-
PAD-9	1:3.0	4	80	-
PAD-10	1:4.0	4	79	-

[a] Per one repeating unit of PAA.
[b] D_{sf} values are estimated from NMR spectra.
[c] 2.0 % (v/v) DMEA in DMEA/H_2O mixed solvent.

Hydrolytic stability of PAD100 in aqueous solution. In Figure 4, changes of the intrinsic viscosity of 0.14% (v/v) and 3.5% (v/v) aqueous PAD100 solutions stored at 25 °C were plotted against the storage time. Compared to the PAA in DMAc, which exhibits a fast decrease in viscosity due to

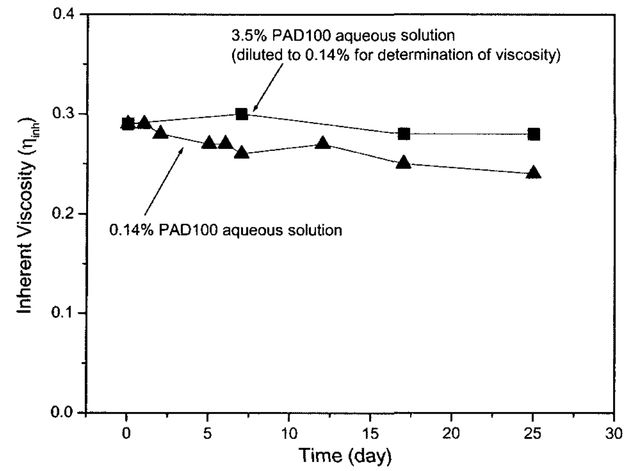

Figure 4. Effect of concentration and storage time on the stability of PAD100 in aqueous solution.

the acid-catalyzed hydrolysis as reported by Sroog *et al.*,[7] aqueous PAD solutions showed much slower decrease in viscosity for both cases. The more concentrated solution of 3.5% (v/v) PAD exhibited even better stability than the diluted solution. The improved stability of PAD may be attributed to that the acid-catalyzed hydrolysis to amine and unstable anhydride is suppressed by the presence of amine salts.[17]

FT-IR Experiment. Thermal imidization of the cast films was performed by stepwise heating for overnight at room temperature, 2 hrs at 40 °C, 2 hrs at 80 °C, 1 hr at 160 °C under vacuum condition, and then 30 min each at 250, 300, and 350 °C[11] in the furnace. To avoid possible water sorption,[12] the sample films were cooled in the furnace to 50 °C after each heating steps, and the FT-IR measurement was done as quickly as possible.

The infrared spectra of polymer films obtained from aqueous PAD100 solution, PAD100 solution in DMSO and PAA solution in NMP were compared during the stepwise thermal imidization. As seen in Figure 5(a), for the film made from aqueous PAD100 solution, the adsorption at 1550 cm^{-1} (amide I: C(=O)NH vibration) disappeared and the absorption peak at 1380 cm^{-1} corresponding to imide C-N stretching vibration[13] appeared after 80 °C. In comparison, for the film prepared from NMP solution of PAA, such phenomenon could only be observed after curing at 160 °C. This implies that PAD100 in aqueous solution starts to be imidized at 80 °C, which is much lower temperature than that of PAA in NMP.

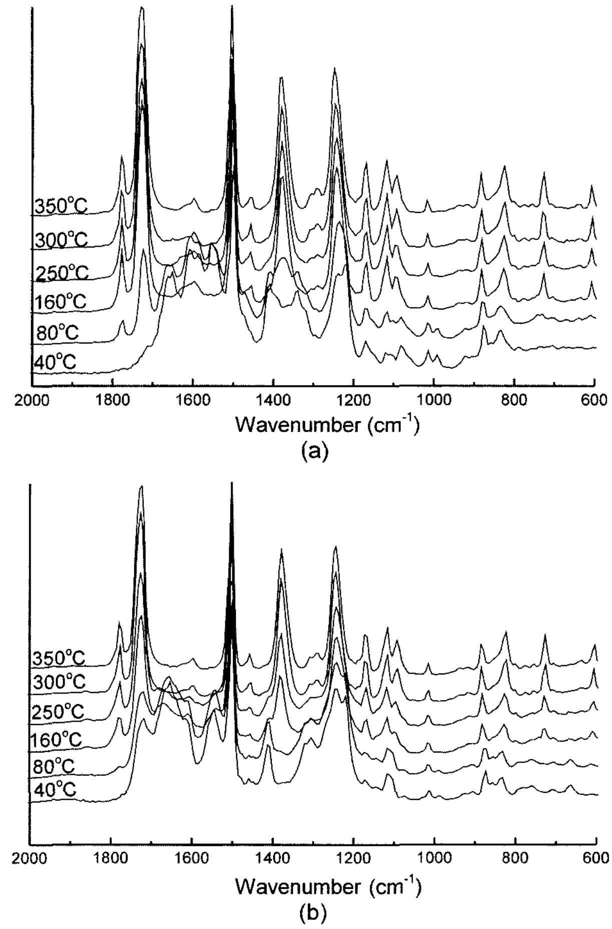

Figure 5. Effect of curing temperature on the FT-IR spectra of (a) PAD100 film made from PAD100 aqueous solution, and (b) PAA film from PAA (PMDA/ODA) in NMP solution.

The band appearing at 1500 cm^{-1} (C-C stretching of the p-substituted benzene) was used as an internal standard for the calibration purpose.[13] Among the bands indicative of the imide formation during the curing, the band at 1380 cm^{-1} (imide II: C-N stretching vibration), was used as the measure of imidization conversion percent since the two imide feature bands at 1720 and 1780 cm^{-1} fell in the region of anhydride absorption.[14] The conversion (%) to polyimide was calculated by the following equation[15]:

$$\text{Conversion to PI}(\%) = \frac{(D_{1380\text{cm}^{-1}}/D_{1500\text{cm}^{-1}})_T}{(D_{1380\text{cm}^{-1}}/D_{1500\text{cm}^{-1}})_{350^\circ\text{C}}} \times 100 \qquad (2)$$

where D is the optical density. Figure 6 summarizes the conversion (%) to polyimide at various curing temperatures for the films of from aqueous PAD100 solution (Figure 6a), from PAD100 in DMSO solution (Figure 6b), and from PAA in NMP solution (Figure 6c). Both films prepared from PAD100 solutions in water and DMSO showed more than 95% imidization at 160 °C under vacuum condition, while the film from PAA solution in NMP showed only 50% conversion. Furthermore, 50% of imidization was detected at 80 °C for the film from aqueous PAD100 solution, while almost no imidization was observed in either case of PAD100 in DMSO and PAA in NMP. Imidization degrees between 160 °C and

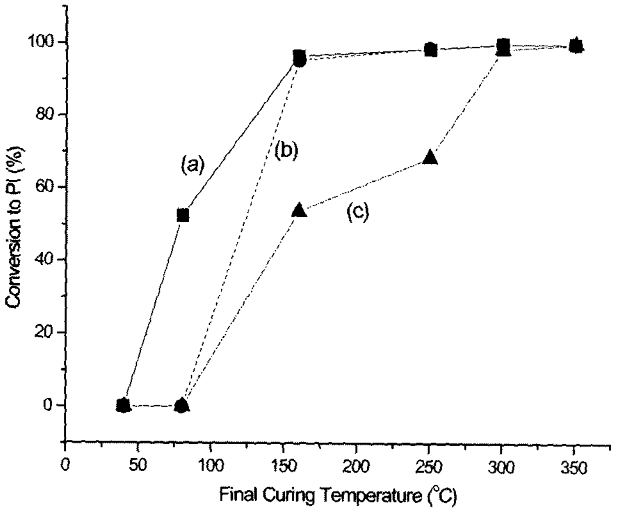

Figure 6. Conversion to PI (%) at various curing temperatures for (a) PAD100 in water, (b) PAD100 in DMSO, and (c) PAA in NMP.

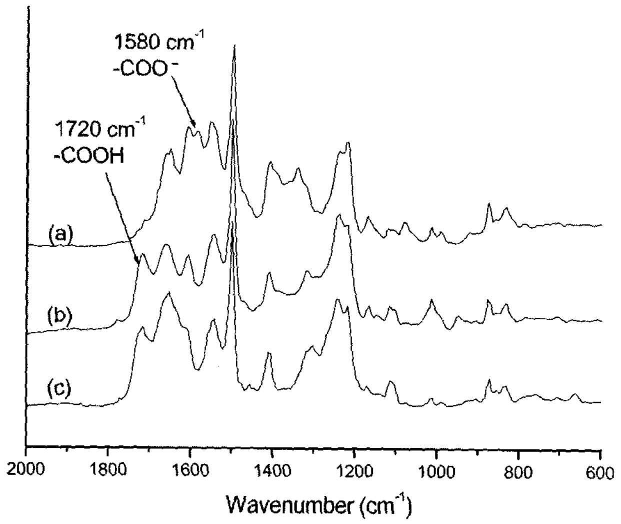

Figure 7. Different solvent effect on the IR spectra of (a) PAD100 film from 4.0% (v/v) PAD100 aqueous solution, (b) PAD100 film from 5.0% (v/v) PAD100 in DMSO solution, and (c) film from PAA solution in NMP. All are treated at 40°C for 2hrs under vacuum condition before test.

250°C for PAD100 films were also much higher than PAA film, which can be attributed to the different chemical structures of precursors. For the film from the aqueous PAD100 solution (Figure 7a), the characteristic band of COOH at 1720 cm^{-1} disappeared, and a band at 1580 cm^{-1} which is characteristic of carboxylate carbonyls appeared. This suggests all the carboxylic acid groups in PAD100 have been converted into carboxylate anions due to the ionization effect in water. In other cases (Figure 7b and 7c), however, the carboxylic acid group is still present. This suggests the formation of the carboxylate anion as the preferred precursor to the activated complex is important for the imide ring closure.[16]

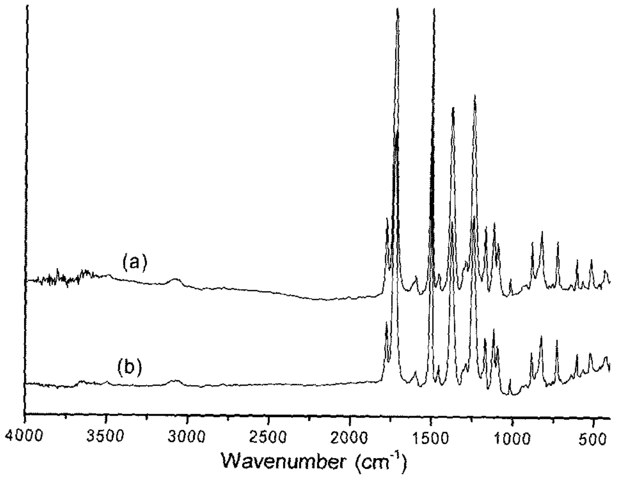

Figure 8. FT-IR spectra of PI films made from (a) PAD100 aqueous solution, and (b) PAA (PMDA/ODA) in NMP solution.

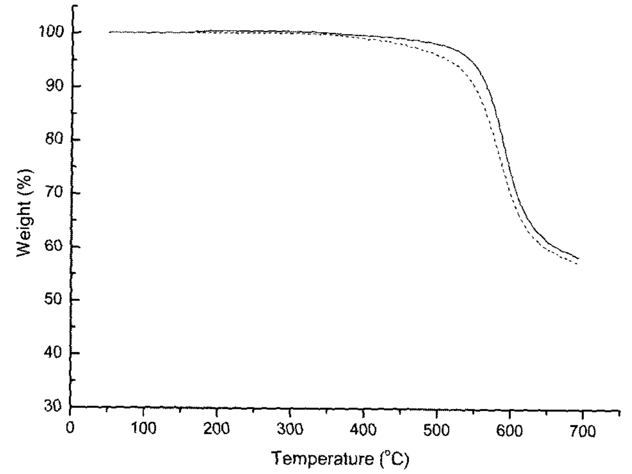

Figure 9. TGA of PI films from poly(amic acid) in NMP solution (solid line), and PAD100 aqueous solution (dashed line).

Thermal stability. The chemical structures of the final polyimide films obtained either from conventional PAA-NMP or PAD100 aqueous solution after the same thermal imidization procedure were almost identical as confirmed by FT-IR spectra shown in Figure 8. Thermal stability has been determined for both polyimide films by weight loss measurement. The results of thermal properties and physical properties, summarized in Figure 9 and Table II, show the polyimide film made from aqueous PAD100 solution still retains relatively high thermal stability, good hardness and toughness. There were slight losses of thermal stability and transparency compared with those of PI film obtained from conventional poly(amic acid). It is proposed that the small decrease of

Table II. Thermal and Physical Properties of final Polyimide Films

Sample Number	T_i^c (°C)	T_{d1}^c (°C)	T_{d2}^c (°C)	Residue at 700 °C (%)	Pencil Hardness
1[a]	370	468	545	58.45	HB~H
2[b]	345	417	515	57.25	HB~H

[a]Polyimide film prepared from PAA(PMDA/ODA) in NMP solution.
[b]Polyimide film prepared from aqueous PAD100 solution.
[c]T_i, T_{d1}, and T_{d2} are the initial decomposing temperature, 1% weight loss temperature, and 5% weight loss temperature, respectively.

molecular weight has occurred due to the presence of free DMEA which acted as a base catalyst for the decomposition of amide linkages during the curing process. This interpretation can explain the difference of thermal stability between the two polyimide films.

Conclusions

We reported the preparation of water-soluble poly(amic acid) salt (PAD) as a precursor for polyimide. In order to study the solubility of PAD in water, PAD samples with different amine fractions were prepared from the reaction of the corresponding free poly(amic acid) and dimethyl ethanol amine. The increase of the ion concentration in water was suggested to interpret the solubility increase of PAD with higher amine moiety. PAD having 100% degree of salt formation (PAD100) showed complete dissolution in pure water, which can be used as an aqueous precursor solution for making a polyimide film. The imidization behavior of the resulting PAD100 aqueous solution was first investigated by using FT-IR spectroscopy. The polyimide film prepared from aqueous PAD100 solution showed faster imidization kinetics compared to that made from PAA solution in NMP, which was explained by the presence of carboxylate anion acting as a preferred intermediate for the imide ring closure. The resulting polyimide film showed almost comparable physical and thermal properties as those of conventional polyimide prepared from NMP solution. In conclusion, we showed that PAD can be used as an water-based precursor of polyimide, which consequently can avoid the use of toxic organic solvents such as NMP.

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