Synthesis, characterization and kinetic study of hydrolysis of polyamic acid derived from ODPA and *m*-tolidine and related compounds

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Abstract

Polyamic acid (PAA) and polyimide, 4,4$'$-oxydiphthalamic acid of *m*-toluidine (amic acid 1) and bisphthalamic acid of 2,2$'$-dimethyl-4,4$'$-diaminobiphenyl (amic acid 2) were synthesized and characterized. In molecular fragmentation study, fast atom bombardment positive ionization mode was found to be suitable than electron impact (EI) ionization mode for detecting the molecular ion of amic acid compounds. EI ionization was found to cause imidization in amic acid compounds. Kinetic investigations were carried out for both amic acid compounds and PAA using potentiometric titration with tetramethyl ammonium hydroxide. At or below 60°C, the acid number was found to increase with increase in time which suggests that hydrolysis reaction is predominant. Acid number was found to decrease with increase in time at 80°C, indicating that imidization reaction is predominant. Rate constants were determined at different temperatures based on the second order rate equation for the hydrolysis reaction. Activation energy was found to be 10.28, 8.34 and 15.05 kcal/mol for the hydrolysis reaction of amic acid compounds 1 and 2 and PAA, respectively. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyamic acid; Polyimide; Potentiometry

1. Introduction

Aromatic polyimides (PI) have found widespread use in microelectronics and aerospace applications because of their excellent electrical properties, chemical resistance, high mechanical strength, high modulus and thermoxidative stability but often sold and used as solutions of the precursor, polyamic acid (PAA) [1]. These precursors can undergo many reactions such as hydrolysis of amide bonds or terminal anhydride groups and cyclization with the elimination of amine or water depending upon the synthesis and storage conditions [2]. These reactions not only affect the properties of PAA but also PI which has been prepared either thermally or chemically from PAA. To prevent or to minimize the degradation of PAA during storage, a clear understanding of the type of reaction whether hydrolysis or cyclization taking place is necessary. Hydrolysis of PAA derived from PMDA/ODA [3,4] and BPDA/PPD [4] and storage stability of PAA based on the variation of solution viscosity [5] have been reported. Sachdev et al. [6] has reported that the viscosity of PMDA

and BPDA based PAA can be stabilized by stoichiometry offset process. Hexamethyl disilazane was found to be an effective stabilizer for PAA solutions of PMDA [7]. In this work, we have synthesized and characterized two amic acid compounds and PAA namely poly(4,4$'$-oxydiphthalic anhydride-*co*-2,2$'$-dimethyl-4,4$'$-diaminobiphenyl) amic acid and its imide. Acid number change whether increase or decrease, during storage will highlight the degradation path of PAA. Therefore, we have monitored acid number as a function of storage temperature and time and determined rate constants at various temperatures for hydrolysis reaction using second order rate equation and activation energy using Arrhenius equation. This study will help to understand what type of reaction is taking place predominantly at what temperature of PAA.
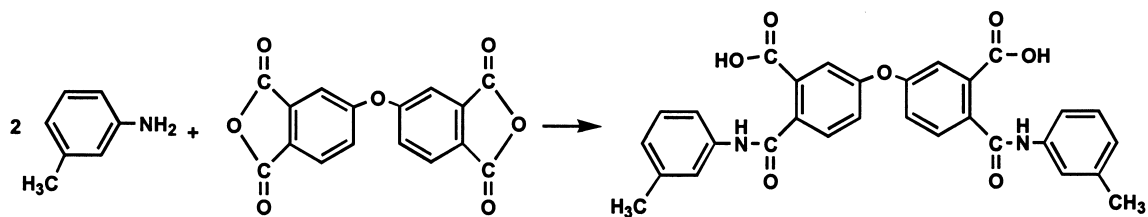
2. Experimental

2.1. Materials

Phthalic anhydride (PA) and 4,4$'$-oxydiphthalic anhydride (ODPA) were obtained from BDH Laboratory and Chriskev Co., respectively. *m*-Toluidine was purchased

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Scheme 1.

from Acros Organics Ltd. *N*-Methyl-2-pyrrolidone (NMP) was purchased from Lab-Scan. *m*-Tolidine (2,2'-dimethyl benzidine) was purchased from Wakayama Seika Kogyo Co., Ltd. Dichloromethane (DCM), tetrahydrofuran (THF), tetramethyl ammonium hydroxide (~25% in methanol) (TMAH) and potassium hydrogen phthalate were obtained from Aldrich Chemical Company.

ODPA was dried in an oven at 150 ± 2°C and *m*-tolidine at 55 ± 2°C overnight. PAA was powdered and dried in an air oven overnight at 110 ± 2°C. Other chemicals were used as such.

2.2. Synthesis of 4,4'-oxydiphthalamic acid of m-toluidine (amic acid 1)

ODPA (15.51 g (0.05 mol)) was taken in a 500 ml round-bottomed flask fitted with a calcium chloride guard tube. THF (250 ml) was added. It was stirred for about 10–20 min using a magnetic stirrer to dissolve the dianhydride. When the solution becomes homogeneous, 10.71 g (0.1 mol) of *m*-toluidine was added and the reaction was allowed to take place at room temperature overnight with continuos stirring. Solvent was removed from the reaction mixture using a Buchi-rotavapor. The concentrated solution was diluted with DCM and the product starts precipitating immediately. Then it was filtered and the solid was dried in vacuum at about 30°C. 23.42 g was obtained after drying (yield 89.4%) (Scheme 1).

2.3. Synthesis of bisphthalamic acid of 2,2'-dimethyl-4,4'-diaminobiphenyl (amic acid 2)

To a 500 ml single necked round-bottomed flask, 10 g of *m*-tolidine (47.17 mmol) and 400 ml of DCM were introduced. The contents were stirred until the diamine dissolves using a magnetic stirrer. PA (13.96 g, 94.34 mmol) was gradually added to the solution and the mixture was stirred

overnight. White precipitate was filtered off and left for air-drying. 22.12 g was obtained after drying (yield 92.3%) (Scheme 2).

2.4. Synthesis of PAA

In a 500 ml, three-necked round-bottomed flask fitted with a nitrogen inlet tube, mechanical stirrer and a thermometer; 21.23 g (0.1 mol) of dried *m*-tolidine was taken along with 135 g of NMP. It was mixed for 5–10 min to dissolve the diamine completely. Reaction mixture was cooled to around 20°C using ice. Dried ODPA powder (31.02 g (0.1 mol)) was added as such in about 10–15 min through a funnel taking care not to spill the powder. The remaining portion of NMP (74 g) was used to rinse the powder sticking to the walls of the funnel. The reaction was allowed to take place overnight with continuous stirring [8]. Next day the PAA (220 g) was filtered and packed in polypropylene bottle under argon environment (Scheme 3).

2.5. Thermal curing

PAA solution was spread on a glass plate using a Doctor's plate. The casted film was cured thermally in an air-circulating oven. Curing cycle used was 80°C (1 h), 100°C (1 h), 150°C (1 h), 200°C (1 h), 225°C (2 h) and 300°C (1 h). After heating, the film was allowed to cool down gradually to room temperature. The cured film was in golden yellow colour. It was taken off from the glass plate by dipping in warm water. The excess water was removed by wiping with a tissue paper. The thickness of cured film was found to be in the range of 25–30 μm (Scheme 4).

2.6. Characterization

FT-IR spectra were recorded on a Perkin–Elmer spectrometer 2000 with a NaCl disk. The scanning range was from 4000 to 400 cm^{-1}. ACF 300 MHz NMR spectrometer was
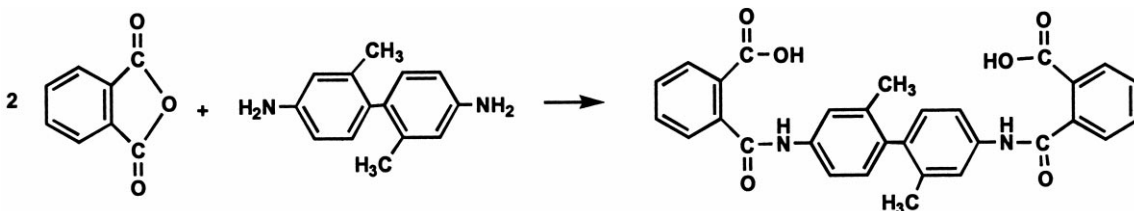
Scheme 2.
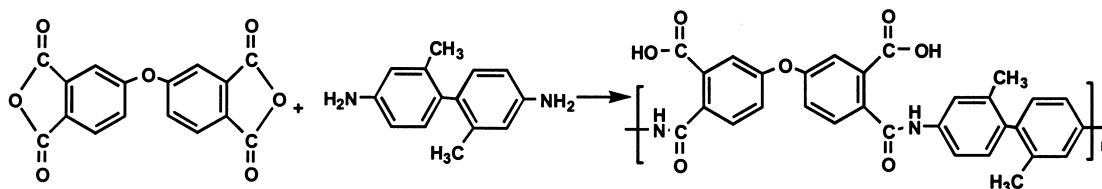
Scheme 3.

used for recording ^{1}H NMR spectra at room temperature using DMSO-d_6 as a solvent. Chemical shift (δ) is given in parts per million with tetramethylsilane (TMS) as an internal solvent. Mass spectrum was recorded using a Finnigan Mass spectrometer MAT 95 XL-T for fast atom bombardment (FAB) positive ionization mode and Micromass VG 7035 for electron impact (EI) ionization mode. Ionization potential used for EI mode was 70 eV and high voltage for FAB Cs-Gun Supply was 20 kV. For FAB mode, 3-nitrobenzyl alcohol was used as a matrix and Cesium ion for bombardment. Thermal behaviour of amic acid compounds was measured by differential scanning calorimetry (DSC) (TA Instruments DSC 2920) from 30 to 200°C, equipped with a refrigerated cooling system. A heating rate of 3°C/min, an oscillation amplitude of ±1°C for every 30 s were employed. Sample size used was 3.2 ± 0.2 mg and pan used was aluminium hermetic. Temperature and heat flow were calibrated by using indium as standard. Thermogravimetric data was obtained for amic acid compounds in the temperature range of 50–200°C using a Perkin–Elmer TGA 7 at a heating rate of 3°C/min in nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) measurement of compressed disks of average thickness 1 mm of amic acid compounds (1 and 2) and PAA were carried out on an X-ray diffractor unit (Phillips X'Pert-MPD) fitted with Cu-Kα radiation (45 kV, 40 mA) with wavelength of 1.54Å. Spectral window ranged from $2\theta = 10°$ to $2\theta = 50°$ and scan speed used was 0.05°/s.

Acid number was determined by titrating with TMAH [9,10] using a TitroLine alpha (TZ 2055) (Schott-Gerate GmbH) automatic potentiometric titrator fitted with a magnetic stirrer (TM125) and electrode used was SA N 6480 (filled with LiCl glacial acetic acid). In this paper, acid number is reported as mg of TMAH/g of the solution. Yilmaz et al. [9] and Kim et al. [10] have utilized potentiometry for determining the degree of imidization in PAA using TMAH as a titrant.

Inherent viscosity was measured according to ASTM 2515/D446 using a Schott-Gerate AVS360, Viscometer: DIN Ubbelohde at 25°C. Bulk viscosity was measured using a Brookfield Viscometer Model DV-III at 25°C, using CP42 spindle at 5 rpm. Molecular weight was determined using a Waters GPC system containing Waters 2690 separation module and Waters 2487 UV detector. Polystyrene (Polysciences Corporation) was used as a calibration standard and mobile phase used was THF:DMF (1:1) containing 0.06 M LiBr and 0.06 M H$_3$PO$_4$. Three numbers of Gelpack GL-S300MDT-5 column of size 8 mm × 300 mm was used. Conditions used were: wave length 270 nm, flow rate 1 ml/min, injection volume 200 μl and sample concentration 1 mg/ml. Average coefficient of thermal expansion (CTE) of PI film between 100 and 250°C was determined using a TMA 2940 from TA Instruments at a heating rate of 5°C/min in nitrogen. β-relaxation and glass transition temperature of PI film were determined using a DMA 2980 from TA Instruments. Thermal stability of PI film was evaluated using a Perkin–Elmer TGA 7 at a heating rate of 10°C/min in static air and nitrogen atmosphere and a sample size of 10 ± 1 mg was used.

2.7. Kinetic study for hydrolysis reaction

2.7.1. Amic acid compounds

About 3.45 g of amic acid compound was weighed accurately in a 25 ml clean and dry round-bottomed flask. Then 15 g of NMP was added. Amic acid compound was dissolved in the above solvent for about 5–10 min using a magnetic stirrer after closing the flask with a rubber septum. Moisture content of the solution was determined using Karl Fisher reagent. Then appropriate amount of water was added using a disposable syringe to keep the molar concentration of water same as that of amic acid concentration. When the solution becomes homogeneous, the magnetic bead in the solution was removed using an iron rod. Flask
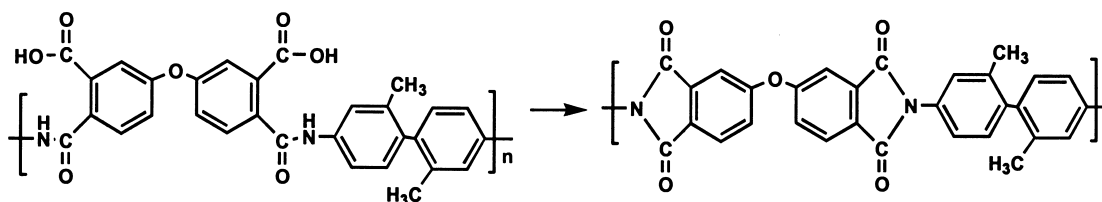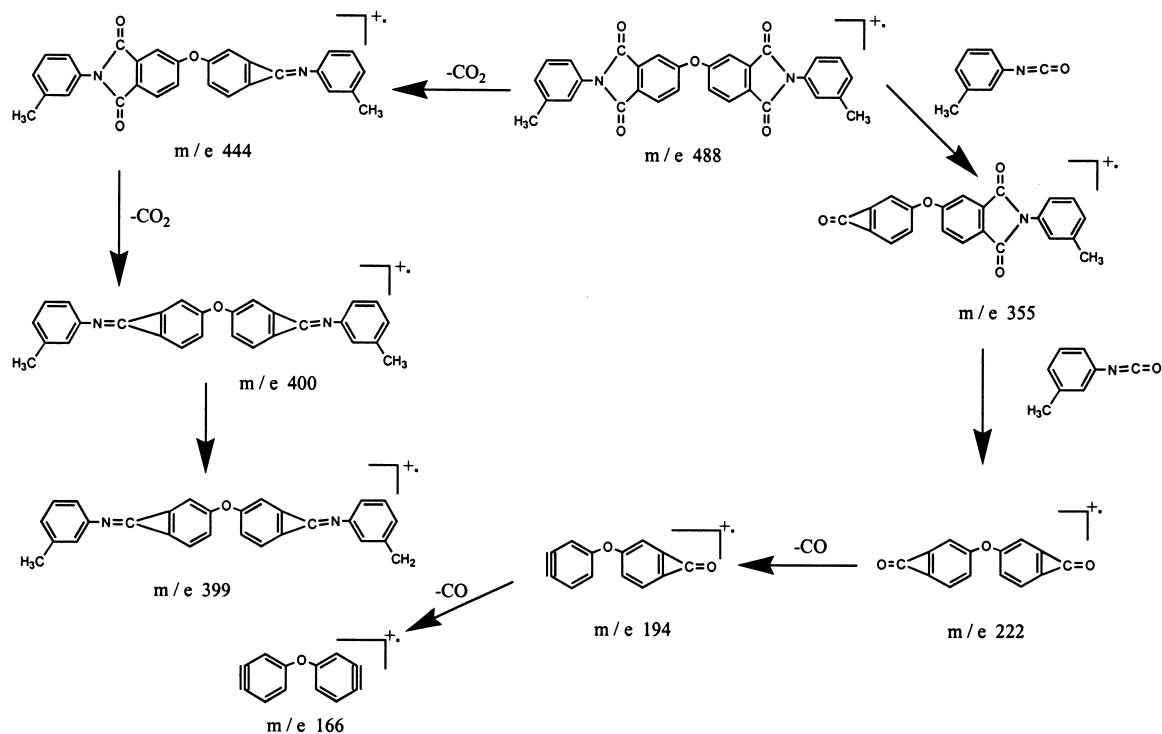

Scheme 4.

Fig. 1. Fragmentation schemes for amic acid 1 by EI mode.

was kept at constant temperature bath to an accuracy of ±1°C. Small aliquots were drawn at various intervals of time using a disposable syringe by piercing through the rubber septum. About 0.2 g of the drawn sample was weighed accurately in a clean and dry beaker followed by

the addition of 20 g of NMP. Then the solution was dissolved using a magnetic stirrer. After complete dissolution, potentiometric titration was carried out using a TMAH solution in methanol, which was previously standardized against potassium hydrogen phthalate. The end point was
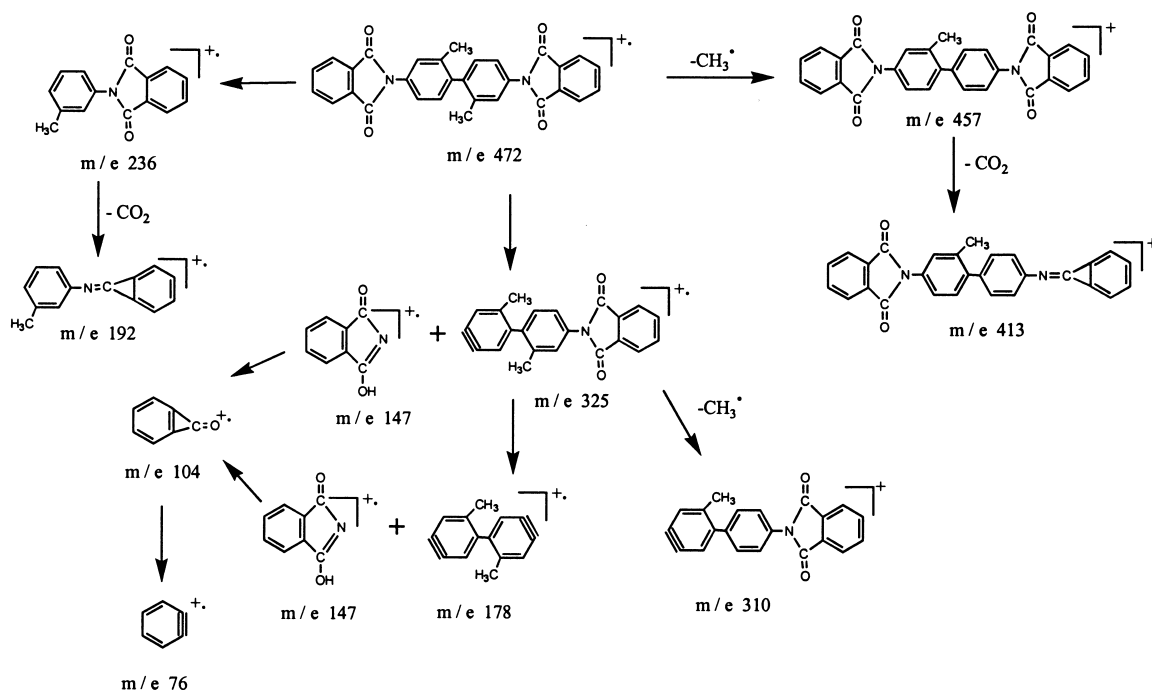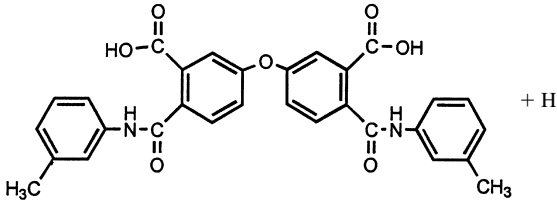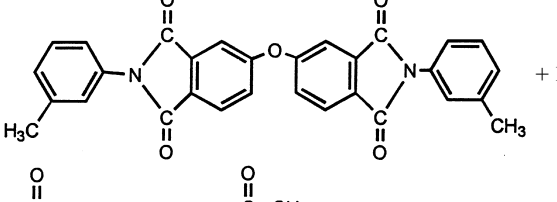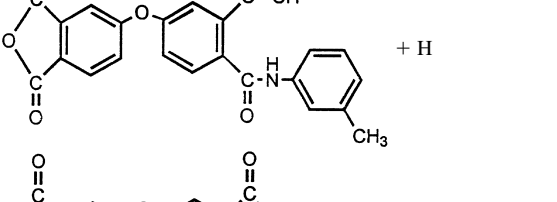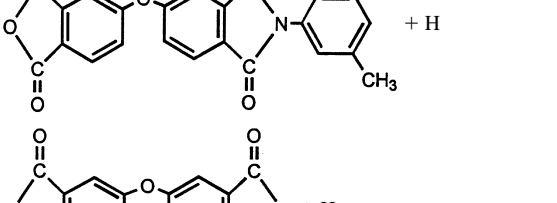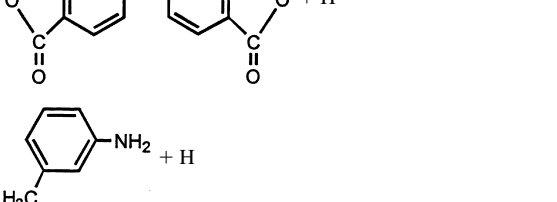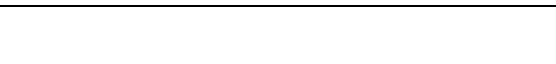

Fig. 2. Fragmentation scheme for amic acid 2 by EI mode.

Table 1
Fragment ions for various ion masses observed in FAB mode of amic acid 1

Mass	Fragment ion
525	
489	
418	
400	
311	
108	
79	
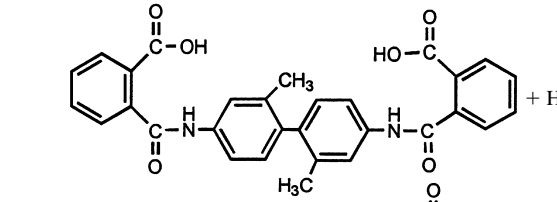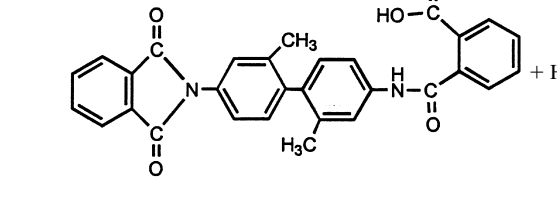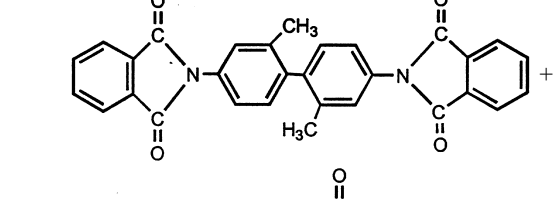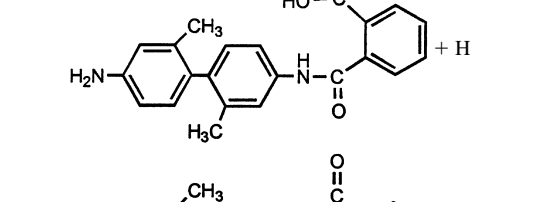
calculated as the peak point in the first derivative graph of potential vs. volume of the titrant plot.

2.7.2. PAA

Twenty grams of PAA solution was taken in 50 ml round bottomed flask fitted with a mechanical stirrer whose moisture content was determined using Karl Fisher reagent earlier. Then appropriate amount of water was added slowly to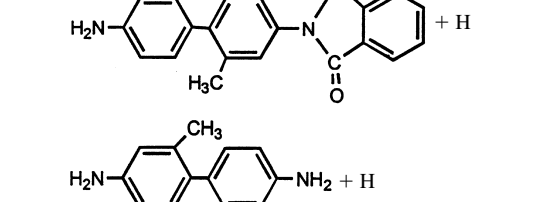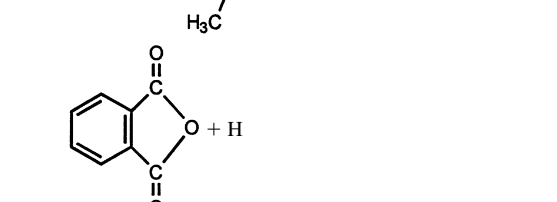 the PAA solutions using a disposable syringe to keep the molar concentration of water same as that of amic acid concentration and mixed well for about 15 min. Then PAA solutions were poured into various small bottles of 2 ml capacity and were closed with airtight caps. Then

these bottles were suspended into an oil bath maintained at certain temperature with an accuracy of ±1°C. At various intervals of time, one bottle was taken out for titration. About 0.2 g of the sample from the bottle was weighed accurately in a clean and dry beaker. Then 20 g of NMP was added and potentiometric titration was carried out using a TMAH solution in methanol.

Table 2
Fragment ions for various ion masses observed in FAB mode of amic acid 2

Mass	Fragment ion
509	
491	
473	
361	
343	
213	
149	
79	
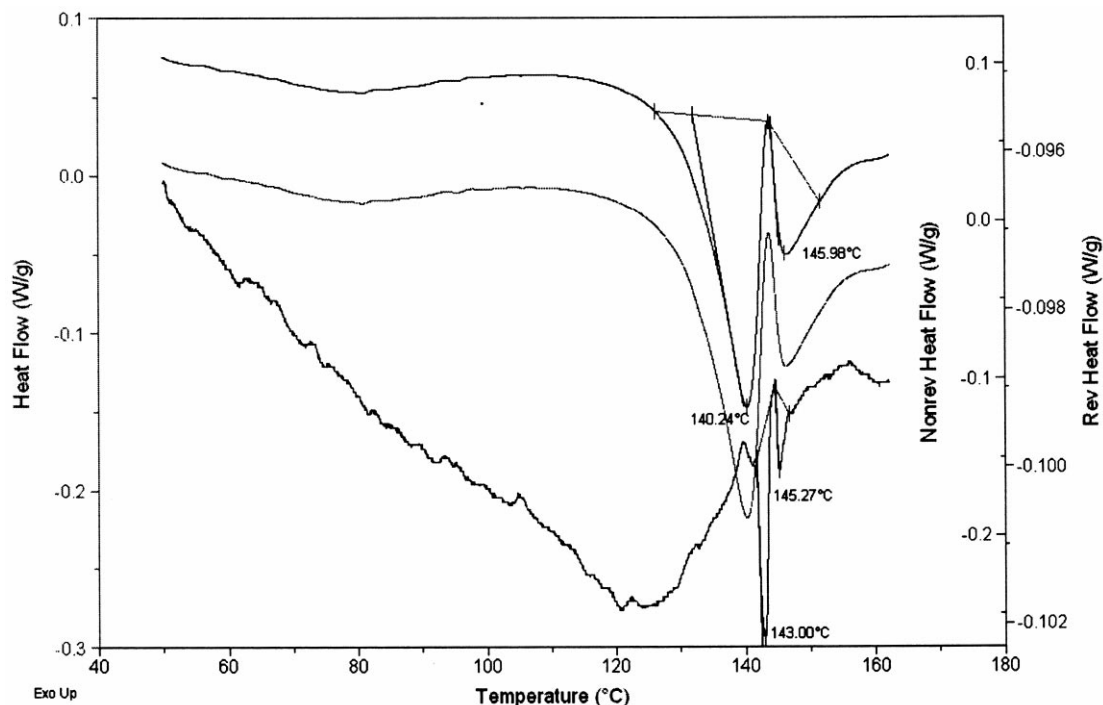
Fig. 3. Modulated DSC thermogram of amic acid 1.

2.8. Effect of water on imidization reaction of amic acid 2 at 80°C

Amic acid 2 (Bisphthalamic acid of 2,2′-dimethyl-4,4′-diaminobiphenyl) (1.84 g (3.622 mmol)) was taken in a 25 ml single necked round-bottomed flask; to which

6.16 g of NMP was added and dissolved completely using a magnetic stirrer. Then 0.1304 g (7.244 mmol) of distilled water was weighed in a disposable syringe and added to the above solution. The flask was closed with a rubber septum and stirred for about 5 min. Then stirring was stopped and the flask was kept in an oil bath at 80 ± 2°C. About 0.2 g of

Fig. 4. Modulated DSC thermogram of acid acid 2.

Fig. 5. Possible amic acid reactions during storage.

the solution was drawn at various intervals of time and acid number was determined as per the above procedure.
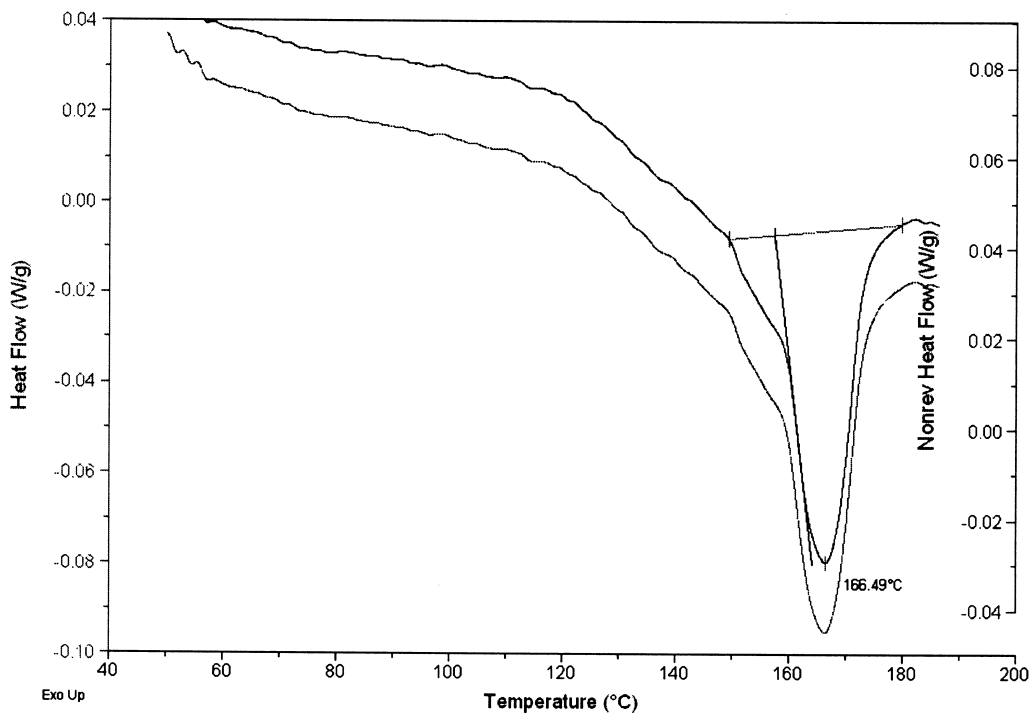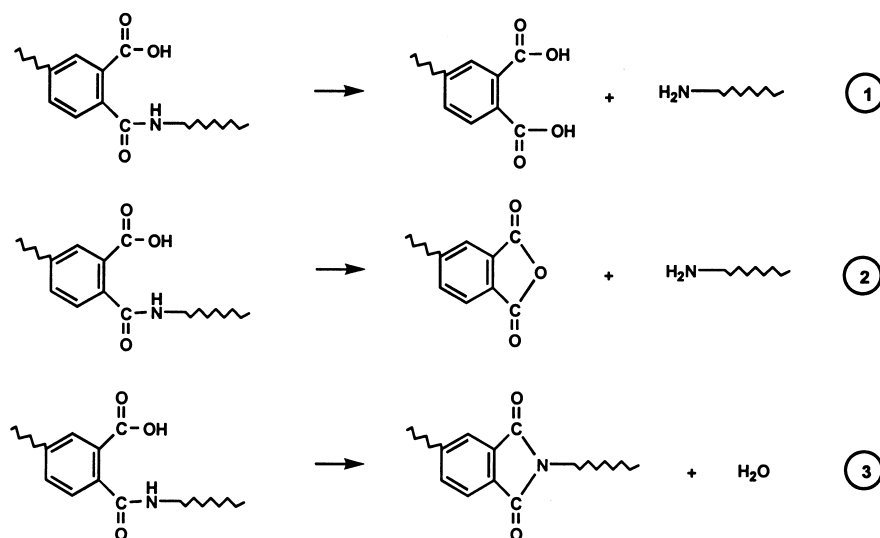
The same procedure was followed but without water.

3. Results and discussion

3.1. Amic acid compounds

Both compounds are white powders. Amic acid compounds are soluble in all common solvents except chloroform and *para* cymene. XRD study shows that both amic acid compounds were crystalline.

Peaks in the FT-IR spectra of amic acid compounds were assigned as follows:

Amic acid 1: ν_{NH}, ν_{OH} = 3287 cm^{-1}; ν_{CH} = 2979 cm^{-1}; ν_{CO} = 1714 cm^{-1} (COOH); ν_{CO} = 1659 cm^{-1} (amide); $\delta\nu_{NH}$ = 1557 cm^{-1}; ν_{C-O} = 1268 cm^{-1} (aryl ether).
Amic acid 2: ν_{NH}, ν_{OH} = 3436 cm^{-1} (broad overlap of OH and NH stretch);
ν_{CH} = 2979 cm^{-1}; ν_{CO} = 1726 cm^{-1} (COOH); ν_{CO} = 1630 cm^{-1} (amide); $\delta\nu_{NH}$ = 1591 cm^{-1}.

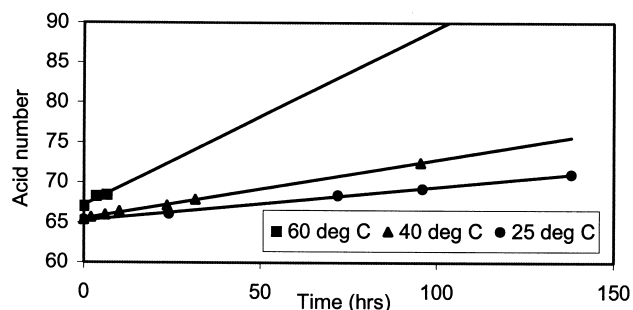Fig. 6. Plot of acid number of amic acid 2 vs. time at different temperature.

In ^{1}H NMR spectra of amic acid 1 and 2, methyl group in the aromatic ring of amine moiety (Ar(CH$_3$)) was observed at 2.2 ppm. Aromatic protons were observed in the region of 7.5–7.9 ppm. Amide proton (–NH–) was observed at 10.4 ppm [10]. Carboxylic proton (–COOH) was not observed in both the spectra. This was due to fast exchange of carboxylic proton with the water present in DMSO-d$_6$ [11].

In EI mode, molecular ion peak of amic acid 1 and 2 was not observed at 524 and 508, respectively. But a peak was observed at 488 and 472 for amic acid 1 and 2, respectively, which corresponds to its imide. Amic acid compound has imidized during ionization by EI. Mass fragmentation of amic acid compound 1 and 2 are given in Figs. 1 and 2, respectively.

In FAB positive ionization mode, the peak at 525 corresponds to quasi-molecular ion of amic acid 1. Quasi-molecular ion peak of amic acid 2 was observed at 509. The reactions of amic acid compound with matrix produce background ions at nearly every mass value [12]. Tables 1 and 2 show the assigned molecular ions to the peaks observed by FAB mode in the mass spectra of amic acid 1 and amic acid 2, respectively.

Fig. 3 shows MDSC thermogram of amic acid 1. Thermogram of amic acid 1 contains two non-reversible endotherm peaks at 140.2 and 146.0°C and two reversible endotherm at 143.0 and 145.3°C. Generally non-reversing heat flow provides information such as enthalpy relaxation, crystallization, thermal decomposition, thermal curing, evaporation of the solvent etc. [13]. In this case, it involved dehydration with cyclization i.e. imidization reaction as evidenced by infra red and thermogravimetry. FT-IR was run for DSC scanned sample up to first and second non-reversible endotherm. Characteristic imide peak at 1775 cm^{-1} was observed in both the samples. This shows that imidization has already taken place during the first
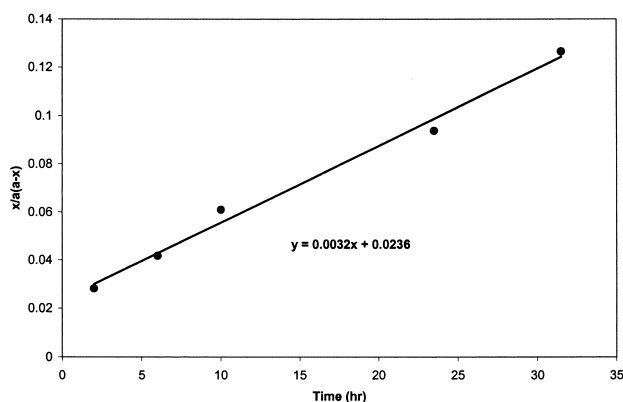
Fig. 7. Plot of $x/a(a - x)$ vs. time of amic acid 2 at 40°C.

non-reversible endotherm itself. The reversing endotherms could be due to melting. TGA curve of amic acid 1 shows a weight loss in the range of 120–180°C (at 3°C/min). This further confirms imidization reaction.

In amic acid 2, a non-reversible endotherm was observed at 166.5°C (Fig. 4). IR spectrum of DSC scanned sample shows a peak at 1775 cm^{-1}, which confirms that this endotherm was also due to imidization reaction. No reversible endotherm was observed. TGA curve of amic acid 2 shows a weight loss in the range of 150–200°C (at 3°C/min.) which further confirms the imide formation.

3.2. PAA

It was found to be soluble in all common solvents except acetone, chloroform and para cymene. Characteristic amic acid peaks at 3447 and 1669 cm^{-1} were observed in the FT-IR spectrum of PAA. Bulk viscosity and inherent viscosity were found to be >50,000 cPs and 0.82 at 0.5 g/dl, respectively, at 25°C. $\bar{M}_n$ and $\bar{M}_w$ and molecular weight distribution were found to be 44977, 73932 and 1.64, respectively. X-ray diffractogram of PAA shows only a broad amorphous halo.

3.3. PI

The characteristic imide peak at 1779 cm^{-1} was observed in FT-IR spectrum. It was found to be insoluble in all the common solvents. From DMTA study, glass transition (T_g) and β relaxation were found to be 317 and 131°C, respectively. T_g determined from DSC study was 306.4°C during second heating cycle. CTE was found to be

Table 3
Kinetic values of amic acids and polymic acid

Code	k at (kg/mol s)			E_a (kcal/mol)
	25°C	40°C	60°C	
Amic acid 1	4.99×10^{-7}	8.57×10^{-7}	3.05×10^{-6}	10.28
Amic acid 2	5.57×10^{-7}	8.92×10^{-7}	2.42×10^{-6}	8.32
PAA	1.11×10^{-7}	1.19×10^{-6}	1.72×10^{-6}	15.05

38.4 ± 0.1 μm/m °C. 5% weight loss in air and nitrogen atmosphere was found to be 513 and 529°C, respectively. Char yield at 800°C in nitrogen atmosphere was found to be 65%.

3.4. Kinetic study

According to reported literature [2], the possible amic acid reactions (Fig. 5) are:

1. amic acid undergoing hydrolysis to form dicarboxylic acid and diamine;
2. amic acid undergoing cyclization with elimination of amine and formation of anhydride ring;
3. amic acid undergoing cyclization with the elimination of water and formation of imide ring.

Out of all the above three reactions, only in reaction 1, the acid number can increase because two acid groups are produced from one group (amic acid). At 25, 40 and 60°C, the acid number was found to increase in amic acid compounds and in PAA. This shows that the reaction 1 was taking place at these temperatures. From the extent of increase in acid number, the extent of decrease in amic acid concentration was calculated. From the acid number increase, we have calculated the decrease in the concentration of amic acid as a function of time at a particular temperature.

For amic acid hydrolysis, the rate equation is

$$\frac{-d[\text{amic acid}]}{dt} = \frac{-d[\text{water}]}{dt} = k[\text{amic acid}][\text{water}] \quad (1)$$

If a and b represent the initial molar amounts of amic acid and water, respectively, and x the amount of each that has reacted after time the concentrations of amic acid and water will be $(a - x)$ and $(b - x)$, respectively, then the above equation becomes

$$\frac{-d[a]}{dt} = k(a - x)(b - x) \quad (2)$$

If a and b are present in equimolar amounts, i.e. $a = b$, then equation reduces to

$$\frac{-d[a]}{dt} = k(a - x)^2 \quad (3)$$

Upon rearranging and integrating Eq. (3)

$$k t = \frac{x}{a(a - x)} \quad (4)$$

$(x/a(a - x))$ vs. t was plotted where a the initial concentration of amic acid and x the amount of amic acid that has reacted at time t. The slope of this plot is equal to rate constant k. Unit for second order rate constant is (mol/kg)$^{-1}$ s^{-1}. A typical plot of acid number vs. time and $(x/a(a - x))$ vs. t for amic acid 2 are given in Figs. 6 and 7. The rate constants of amic acid compounds and PAA are given in Table 3. FT-IR spectra recorded for the aliquots drawn at various time intervals does not show an imide peak
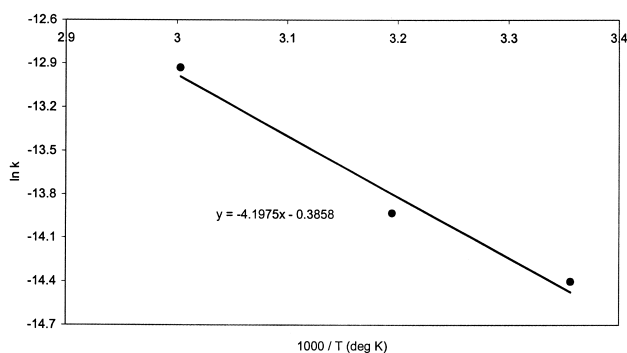
Fig. 8. Plot of ln k vs. 1000/T of amic acid 2.

Fig. 9. Plot of acid number of amic acid 2 vs. reaction time at 80°C in the presence and absence of water.

at 725 cm^{-1} when it was recorded after 22 h in the case of 60°C, five days at 40°C and seven days at 25°C for the amic acids. This also confirmed that imidization reaction has not taken place at 60, 40 and 25°C. Activation energy (E_a) in the temperature range of 25–60°C was determined using Arrehenius equation by plotting ln k vs. 1000/$_T$ and from the slope activation energy was calculated by multiplying with the universal gas constant R and it is reported in Table 3. Plot of ln k vs. 1000/T of amic acid 2 is given in Fig. 8. Activation energy of PAA hydrolysis reaction was found to be comparable to that of reported for PMDA/ODA and BPDA/PPD [3].

However, at 80°C, the acid number of amic acid and PAA was found to decrease. This suggests that the reaction 2 or 3 is taking place, i.e. cyclization reaction. Reaction 2 is ruled out because the moisture present in the reaction mixture will not allow the anhydride to remain as it is. Further the presence of imide peaks at 1775 and 725 cm^{-1} in the FT-IR spectra confirm the formation of imide at these temperatures. Therefore, we have not taken into consideration of the temperature for the activation energy of the hydrolysis reaction.

3.5. Effect of water on imidization reaction of amic acid 2 at 80°C

Plot of acid number of amic acid 2 vs. time at 80°C in the presence of water and absence of water are given in Fig. 9. In the presence of water, the slope of acid number vs. time plot is smaller when compared with that of in the absence of water. This shows that the reaction rate was affected by the presence of water in the amic acid 2. Imidization reaction will lead to the decrease in acid number but the hydrolysis reaction will lead to the increase in acid number. If both reactions are taking place at the same rate then the net result will be no change in the acid number. On the contrary, if hydrolysis is taking place at a much faster rate, then there will be increase in the acid number. But in our case the acid number decreases with increase in the reaction time. This suggests that the imidization reaction is taking place at a much faster rate than the hydrolysis reaction. FT-IR study confirms imidization has taken place and NMR confirms
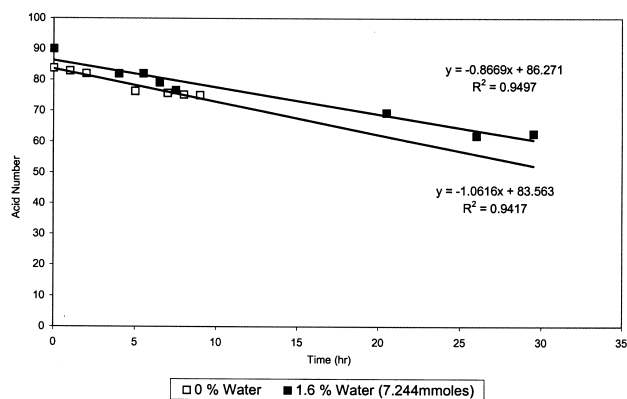
that hydrolysis has also taken place. How ever, in the presence of water, in addition to imidization reaction, hydrolysis reaction is also possible.

Buncick et al. [14] found out that PAA derived from PMDA and ODA is less cured at 85°C/dry environment than at 85°C/85% RH environment. They proposed three mechanisms for the water–PAA interaction namely water acting as a catalyst, plasticizer and water forming hydrogen bond to the carbonyl functionality and induce imidization by changing the charge structure to enhance ring closure. In our study, the presence of water reduces the extent of imidization. This suggests that water is not acting as a catalyst and hydrogen bonded water is not inducing imidization. The reason for getting higher percentage of imidization in their study needs further study.

4. Conclusions

Amic acid compounds and PAA have been synthesized. FT-IR, NMR and Mass fragmentation study confirmed the formation of amic acid compounds. Non reversible endotherm observed in the DSC scans of amic acid compounds is due to imidization. This was further confirmed by FT-IR and thermogravimetry. FT-IR study confirmed the formation of PAA and conversion to PI upon thermal curing. Based on the acid number change and FT-IR study, it was found to be hydrolysis reaction predominant below 60°C and imidization reaction at 80°C. Presence of water was found to affect the imidization reaction at 80°C in amic acid compounds. Activation energy of the hydrolysis of PAA derived from ODPA/m-tolidine is comparable to that of those from PMDA/ODA and BDA/PPD.

Acknowledgements

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