Controlled Molecular Weight Polyimides from Poly(amic acid) Salt Precursors

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ABSTRACT: Controlled molecular weight, thermoplastic polyimides have been prepared via poly(amic acid) salt precursors. 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride and *m*-phenylenediamine (the Ultem monomers), together with calculated amounts of phthalic anhydride were reacted in *N*-methylpyrrolidinone as well as in tetrahydrofuran to form poly(amic acid)s with controlled molecular weights. Poly(amic acid) salts were prepared in heterogeneous reactions of the poly(amic acid)s with quaternary ammonium bases or triethylamine dissolved in methanol or water, to yield soluble salts. The poly(amic acid) salts were then melt imidized in air at 250 or 300 °C for 30 min. Results suggest that the poly(amic acid) salt counterion controls the mechanism by which the salt imidizes, which in turn controls the properties of the final polyimide. The triethylammonium poly(amic acid) salts yielded linear, thermoplastic, molecular weight controlled polyimides upon melt imidization. The polyimides prepared from the poly(amic acid) salts containing the triethylammonium, tetraethylammonium, and tetrapropylammonium counterions showed dynamic weight loss profiles comparable to the polyimide produced directly from the control poly(amic acid).

Introduction

Thermoplastic polyimides such as General Electric's Ultem (Figure 1) have an excellent combination of thermal stabilities, mechanical properties, and processability.[1,2] Polyimides are typically formed either in organic solvents or from the melt from poly(amic acid) intermediates. Processing polyimides via water-soluble poly(amic acid) salt precursors presents an environmentally friendly method for processing polyimides which is not possible using traditional methods. The general approach is as follows: first the poly(amic acid) is synthesized from dianhydride and diamine monomers, next the poly(amic acid) salt is formed by reaction of the poly(amic acid) with a stoichiometric (or slight excess) amount of base, and finally the poly(amic acid) salt is thermally imidized (Figure 2). Several examples have been reported utilizing this general methodology.[3−8] Water solubility is enhanced by neutralizing the poly(amic acid)'s carboxylic acid groups with a suitable base. We are particularly interested in exploring these aspects for composite applications. Aqueous solutions of poly(amic acid) salts may make excellent fiber sizing media. The salts could subsequently be imidized to yield tough, relatively water insensitive, fiber−matrix interphase layers. Aqueous-based polyimide precursors might also be advantageous components of waterborne polymeric resins as curing or toughening reagents for thermoset matrices.

There may also be technical advantages other than water solubility in preparing polyimides from the salt form, as opposed to the more conventional process directly from the poly(amic acid). The hydrolytic stability of poly(amic acid) salts may be increased relative to the poly(amic acid) since the acid-catalyzed back reaction to amine and hydrolytically unstable anhydride is prevented.[7] Another possible advantage in forming polyimides from poly(amic acid) salts is found in enhanced imidization rates of tertiary ammonium poly(amic acid) salts relative to the imidization rates of free carboxylic acids. Sroog and co-workers found that tertiary ammonium salts of poly(amic acid)s had initial cyclization rates 4−10 times faster than those of the free poly(amic acid)s.[8] This should limit depolymerization during imidization, which can result in reduced polyimide molecular weight, especially in the presence of water.[9−11]

The focus of this paper is on effects of various cations (1) on water solubility and (2) on the properties of the

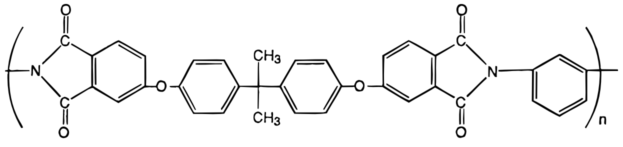

Figure 1. Ultem type polyimide.

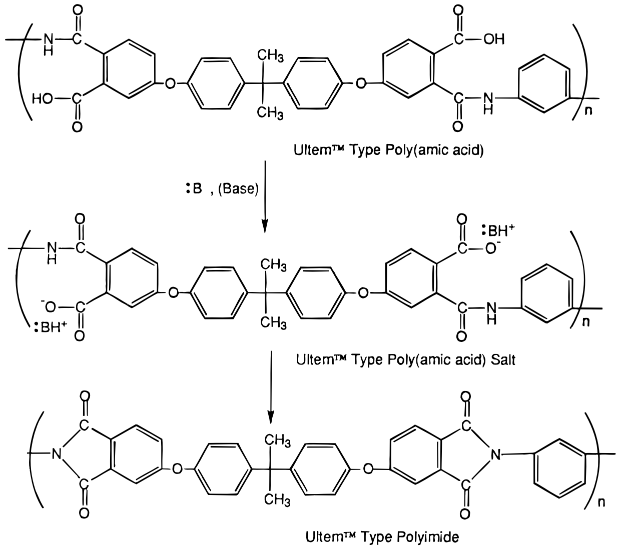

Figure 2. Preparation of Ultem type polyimides from poly(amic acid) salts.

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polyimides imidized in the melt from the salt precursors. Control of polyimide molecular weight under these conditions and avoiding cross-linking reactions are key issues since mechanical properties are a function of both factors. Some emphasis is also placed on reaction conditions for forming poly(amic acid)s since rapid attainment of desired molecular weights is of practical importance.

Poly(amic acid) salts have been made and imidized previously, but absolute molecular weights of the precursor poly(amic acid)s and resultant polyimides were not available.[6,7] In some cases, the conditions used to prepare the poly(amic acid) salts were also suspected to have caused hydrolysis of the poly(amic acid)s.[5,12] Studies have shown that controlled molecular weight polyimides may be realized from poly(amic acid)s,[13,14] but controlled molecular weight polyimides have not been reported via imidization of poly(amic acid) salt precursors. The molecular weight of a thermoplastic engineering polymer is critical to achieving the desired mechanical properties and processability.

During the synthesis of a poly(amic acid) from dianhydride and diamine monomers, the rate of polyamidization can be influenced by the solvent. Ether solvents such as tetrahydrofuran have been used to produce high molecular weight poly(amic acid)s.[15] However, lower critical solution temperature behavior has been observed for some poly(amic acid)/ether solutions, resulting in precipitation during polymerization when the polymerization temperature was too high.[16]

Experimental Section

Materials and Apparatus. Purified, monomer grade 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride) (Bisphenol A dianhydride) was kindly donated by the General Electric Co. It was vacuum dried overnight at approximately 140 °C to ensure complete anhydride cyclization prior to use. Tetrahydrofuran (EM Sciences) was refluxed over sodium metal with a small amount of benzophenone (which formed the purple sodium benzophenone ketyl) and was distilled immediately prior to use. *m*-Phenylenediamine (Aldrich) was sublimed twice under reduced pressure using an 80 °C bath and stored under argon in the dark prior to use. Phthalic anhydride (Aldrich, 99% ACS Reagent Grade) was also sublimed under reduced pressure using an 80 °C bath. *N*-Methylpyrrolidinone (Fisher Purified Grade) was vacuum distilled after stirring over P_2O_5 in an argon atmosphere and stored under argon prior to use. Tetramethylammonium hydroxide (TMAH, 25 wt % in MeOH) was purchased from Kodak. Tetramethylammonium hydroxide (TMAH, 25 wt % in H_2O) was purchased from Aldrich. Tetraethylammonium hydroxide (TEAH, 25 wt % in MeOH) was purchased from Acros. Tetrapropylammonium hydroxide (TPAH, 1.0 M in water) was purchased from Aldrich. Reagent grade triethylamine (TEA, neat) was purchased from Fisher. Tetrabutylammonium hydroxide (TBAH, 25 wt % in MeOH) was purchased from Fluka.

Poly(amic acid) Synthesis in *N*-Methylpyrrolidinone by a Homogeneous Method. 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (Bisphenol A dianhydride) (6.4889 g, 0.012467 mol) was weighed into a clean, dry, 250 mL round bottom flask equipped with a magnetic stir bar and sealed with a septum. The flask was twice evacuated and purged with argon. NMP (about 80 mL) was added to this flask by cannula with stirring, and the Bisphenol A dianhydride dissolved. *m*-Phenylenediamine (1.3913 g, 0.012865 mol) and phthalic anhydride (0.1198 g, 8.089×10^{-4} mol) was weighed into a second clean, dry, 100 mL round-bottom flask equipped with a magnetic stir bar. Then the flask was sealed with a septum and purged with argon. By cannula, 25 mL of NMP was added. The *m*-phenylenediamine and phthalic anhydride dissolved and were allowed to react for 20 min with stirring. Next, the contents of the 100 mL flask were added by cannula to the 250 mL flask with stirring (time = 0 min in Figure 4). The 100 mL flask was rinsed twice with 10 mL of NMP, and this was added to the 250 mL flask by cannula. Aliquots were removed periodically using a clean, dry syringe. The samples were 4–5 mL in volume and were precipitated into 250 mL of deionized water stirring rapidly inside a Waring blender. The samples were collected using an aspirated Büchner funnel. The samples were washed with deionized water and were further dried in vacuo at 20 °C for 48 h. The exposure time of the poly(amic acid) samples to water was greatest in the case of the first two samples (the 15 min sample and the 45 min sample in Figure 4) as the fine nature of the precipitates required a longer time for filtration. After the reaction had proceeded for 2 h, the viscosity had increased significantly. The samples were analyzed for solvent content by gravimetric imidization and then analyzed using size exclusion chromatography to determine the absolute molecular weights and distributions.

Poly(amic acid) Synthesis in Tetrahydrofuran by a Homogeneous Method. 2,2-Bis[4-(3,4-dicarboxyphenoxy)-phenyl]propane dianhydride (Bisphenol A dianhydride) (58.4002 g, 0.112201 mol) was charged to a clean, dry, 2 L round-bottom flask equipped with a magnetic stir bar. The flask was sealed with a rubber septum, evacuated, and purged with argon twice. Freshly distilled THF (about 1 L) was added by cannula, and with stirring, the Bisphenol A dianhydride dissolved. *m*-Phenylenediamine (12.5211 g, 0.115783 mol) and phthalic anhydride (1.0783 g, 0.0072802 mol) were weighed into a clean, dry 250 mL flask equipped with a magnetic stir bar. The flask was sealed with a rubber septum and purged for 5 min with argon. About 100 mL of THF was added by cannula, and stirring was commenced for ≈15 min to allow the phthalic anhydride and the *m*-phenylenediamine time to dissolve and react. Next the solution in the 250 mL flask was added to the solution in the 2 L flask by cannula with stirring (time = 0 min in Figure 4). The 250 mL flask was rinsed twice with 15 mL of THF, which was added to the 2L flask using a cannula. The solution became viscous almost immediately. Samples of about 2–3 mL were removed periodically from the reactor for size exclusion chromatographic analysis using a clean, dry syringe and were transferred to small Teflon containers. Each sample was immediately placed in a vacuum oven at 20 °C to rapidly remove most of the solvent. After 21 h, the poly(amic acid) solution was poured into a shallow Teflon dish and placed inside a covered glass container equipped with a nitrogen sweep and was exposed to a brisk nitrogen flow at room temperature for several days to evaporate most of the solvent. The poly(amic acid) was dried further for 48 h under high vacuum at 20 °C. A tough clear amber glass resulted, weighing 97.1 g, corresponding to 25.8 wt % THF remaining in the material. The samples were analyzed by ^{1}H NMR and by gravimetric imidization for solvent content and then analyzed by size exclusion chromatography to determine the absolute molecular weights and molecular weight distributions.

Determination of Weight Percent Solvent in Poly(amic acid). It was important that the wt % solvent remaining in the poly(amic acid) samples was accurately known to calculate stoichiometries correctly while preparing the poly(amic acid) salts and also to obtain accurate molecular weight data by SEC using dual viscosity and refractive index detectors. Three methods were used to determine this data. The determination of residual THF in a poly(amic acid) is discussed as an example. A value of 25.8 wt % THF remaining was calculated by comparing the weight of poly(amic acid) obtained as compared to the theoretical yield. Another sample was imidized in an air convection oven by heating from 30 to 330 °C at 3 °C/min, followed by holding the temperature for 30 min at 330 °C. Upon cooling and comparing the weight to the initial weight, a value of 26.0 wt % THF was calculated, assuming quantitative imidization with loss of water, plus solvent loss (gravimetric imidization method). A third method utilized ^{1}H NMR on a Varian 400 MHz instrument. The peak area due to the four THF protons at 3.6 ppm was compared to the peak area resulting from the two amide protons per poly-

Table 1. Poly(amic acid) Salt Preparation

base (solvent for base)	PAAS[a] solvent (mL)	g of PAA[b]	base/COOH
tetramethylammonium hydroxide (H_2O)	water (30)	1.4	1.10
tetramethylammonium hydroxide (MeOH)	methanol (30)	1.4	1.10
tetraethylammonium hydroxide (MeOH)	water (30)	1.4	1.10
tetraethylammonium hydroxide (MeOH)	methanol (30)	1.4	1.10
tetrapropylammonium hydroxide (H_2O)	water (30)	1.4	1.10
tetrabutylammonium hydroxide (MeOH)	methanol (30)	1.4	1.10
triethylamine (neat)	methanol (30)	1.4	1.02
control (no base)	none	1.4	none

[a] Poly(amic acid) salt. [b] Poly(amic acid).

(amic acid) repeat unit at 10.4 ppm to calculate a value of 25.6 wt % THF in the poly(amic acid). One or more of these methods were used to determine the weight percent % solvent in all poly(amic acid)s to be analyzed by SEC, so that the actual weight of poly(amic acid) could be used to calculate absolute molecular weight distributions and so that accurate stoichiometries could be measured when preparing the poly(amic acid) salts. All of the methods were found to be accurate, but the gravimetric imidization method was the most convenient method for most samples.

Preparation of Poly(amic acid) Salts. A poly(amic acid) synthesized in THF was ground to increase the surface area to volume ratio and to further reduce the THF content by using a 50 g capacity mill with the aid of liquid nitrogen to decrease the toughness and prevent heating (and the resultant imidization) of the poly(amic acid). Grinding was conducted in a nitrogen atmosphere to prevent moisture condensation on the cold poly(amic acid). Following grinding, the poly(amic acid) was again dried at 20 °C in a vacuum oven for 48 h. After this process, the poly(amic acid) was determined to contain 18.7 wt % THF by the gravimetric imidization method.

All of the bases used to prepare poly(amic acid) salts were titrated prior to salt preparation with 0.025 N HCl that was standardized against Na_2CO_3. The poly(amic acid) salts were prepared as follows: Thirty milliliters of solvent, methanol, or water was charged into a 100 mL round-bottom flask equipped with a magnetic stir bar. The volume of base needed to supply a 10% molar excess relative to the carboxylic acid groups was added (4.900×10^{-3} mol) using a volumetric pipet. Next 1.400 g (2.227×10^{-3} mol of repeat units) of powdered poly(amic acid) was added to the flask, and the flask was sealed with a rubber septum. The mixture was stirred, and as the poly(amic acid) salt formed, a clear, homogeneous solution resulted. The methanolic salts typically formed in 1 h or less, while the aqueous salts required stirring overnight. The quantities used are summarized in Table 1. Once the poly(amic acid) salts had formed homogeneous solutions, the solvents were evaporated under a nitrogen flow, and the poly(amic acid) salts were further dried in vacuo at 20 °C for 48 h. The poly(amic acid) salts formed transparent films upon drying. The yields corresponded to the expected theoretical yields plus 0−10 wt % residual solvent. The poly(amic acid) salts were analyzed by thermal gravimetry.

Thermal Imidization of Poly(amic acid) Salts. The poly(amic acid) salts were imidized using a Fisher Scientific Isotemp Model 838F programmable oven, with air convection. Two heating programs were used for each material, 250 °C for 30 min and 300 °C for 30 min. Weight losses during imidization were determined and compared to theoretical values. The polyimides were analyzed by SEC, potentiometric titration for aromatic amine, and DSC.

Determination of the Byproducts from Melt Imidization of Poly(amic acid) Salts. Each of five poly(amic acid) salts were analyzed using gas chromatography−mass spectrometry of the effluents from the imidization: (1) tetramethylammonium poly(amic acid) salt, (2) tetraethylammonium poly(amic acid) salt, (3) tetrapropylammonium poly(amic acid) salt, (4) tetrabutylammonium poly(amic acid) salt, and (5) triethylammonium poly(amic acid) salt. All of these salts had been originally prepared in methanol with the exception of the tetrapropylammonium salt, which had been prepared in water. An exemplary procedure for these analyses follows.

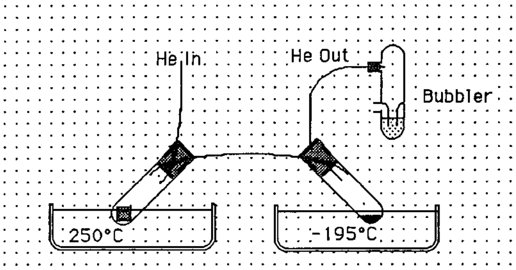

Figure 3. Apparatus for collection of poly(amic acid) salt imidization volatiles.

A poly(amic acid) salt sample (60−100 mg) was placed in a 10 mL test tube and sealed with a rubber septum. One end of a double-ended, 12 in., 20 gauge cannula was pierced through the rubber septum. The other end of the cannula was directed through a second rubber septum into a second 10 mL test tube placed in a bath of liquid nitrogen (cold trap) (Figure 3). A slow helium purge was introduced into the test tube containing the sample which flowed from the sample container, through the cannula, and out through the cold trap via a mineral oil bubbler. Helium was chosen as the purge gas since it would not condense in the liquid nitrogen cold trap. No condensate was collected without a gas purge. The low liquid nitrogen temperature, −195 °C, was deemed necessary to trap the low-boiling byproducts of the imidization. After cooling the cold trap in the liquid nitrogen bath, the test tube containing the sample was placed in a 250 °C poly(phenylmethylsiloxane) oil bath for 10 min. During the 10 min heating period, condensates were observed dripping into the cold trap. Imidization was judged to be complete in the 10 min period due to the cessation of condensate. The cannula was removed, and the sample was removed from the cold trap and warmed to room temperature.

Characterization. Analysis of Imidization Byproducts by Gas Chromatography−Mass Spectrometry. A Fisons GC 8060 coupled with a Fisons VG QUATTRO mass spectrometer was used to analyze the samples. The DB-5MS column, 15 m long, 0.25 mm i.d., with a 0.25 μm film was purchased from J&W Scientific. The gas chromatograph column temperature was 35 °C. Helium was used as the mobile phase at a flow rate of 1 mL/min. The pressure at the column head was 5 psi. For the tetramethylammonium, tetraethylammonium, and triethylammonium poly(amic acid) salts, all of the collected volatiles vaporized in the sealed sample container when warmed to room temperature. For the tetrapropylammonium and tetrabutylammonium poly(amic acid) salts, a condensed phase was visible at room temperature, which vaporized upon heating to 80 °C. Utilizing a 1 mL syringe, 0.2 mL of the vapor head space of the samples was injected directly into the gas chromatograph.

Size Exclusion Chromatography. SEC was conducted on a Waters GPC/ALC 150-C chromatograph equipped with the differential refractometer detector (RI) connected in parallel to a differential viscometric detector (DV) Viscotek Model 100. The injector and column compartment, connecting line, and DV detector were individually controlled to the same temperature (60 °C). The signals from the RI and DV detectors permitted calculation of intrinsic viscosity and intrinsic viscosity distribution for universal calibration purposes by using Viscotek software Unical 4.04 assuming that the polymer concentration at the outlet of the SEC columns approaches infinite dilution due to separation and column dispersion. *N*-Methylpyrrolidinone (Sigma-Aldrich HPLC grade) stirred over P_2O_5 was prepared according to Cotts and coworkers.[17,18] The concentration of P_2O_5 was 0.02 M.

Thermal Gravimetry. Thermal stabilities of the control poly(amic acid) and the poly(amic acid) salts were determined dynamically in air by measuring weight loss while heating at a rate of 10 °C/min. The instrument used was a Dupont Instruments 951 thermogravimetric analyzer and was calibrated against indium. Approximately 4 mg samples were used because the samples tended to foam upon heating, resulting in mechanical interference during analysis of larger samples.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was conducted using a Seiko 220C instrument under a nitrogen purge, which was calibrated with indium, tin, and zinc. Samples were scanned from 100 to 250 °C and then cooled quickly and scanned a second time from 100 to 250 °C. All scanning rates were 10 °C/min. No melting endotherms were observed. The glass transition temperatures measured from the first scan and the second scan were all within ±1 °C.

Potentiometric Titration of Polyimides for Residual Amine. Potentiometric titrations were used to quantify any residual aromatic amine in the polyimides prepared from the poly(amic acid) salts. Titrations were performed using an MCI GT-05 (COSA Instruments Corp.) automatic potentiometric titrator. Between 0.25 and 0.3 g of polyimide was dissolved in 50 mL of chloroform (EM Science HPLC Grade) with stirring. After the samples were completely dissolved, 18–25 mL of glacial acetic acid (Fisher Scientific ACS Plus) was added. Note that smaller amounts of acetic acid were used when this was necessary to avoid phase separation of the solution. The samples were potentiometrically titrated with a solution of HBr in AcOH (0.0137 N) standardized against potassium hydrogen phthalate. The end points of the titration were calculated by the autotitrator as the inflection point in the potential vs volume of titrant plot. Duplicate titrations were conducted for each polyimide sample and the results were averaged. The moles of imide functionality per mol of amine were calculated as explained by the following example.

$$\frac{\text{moles of imide}}{\text{moles of amine}} = \frac{0.2790 \text{ g of imide} \div (1 \text{ mol}/298.31 \text{ g})}{0.0137 \text{ N HBr} \times (2.599 \times 10^{-3} \text{ L})} = 26$$

Results and Discussion

Reactions to form poly(amic acid)s were compared in THF versus NMP at a concentration of 0.1 mol/L of the dianhydride monomer, and the molecular weights over time were analyzed. Both reactions were conducted using phthalic anhydride as a monofunctional end-capping reagent with targeted number-average molecular weights ($\langle M_n \rangle$) of 20 000. The Carothers equation[19] was employed to determine the amount of phthalic anhydride needed. Homogeneous reaction conditions were used in order to monitor the progress of molecular weight growth without any complications from initially skewed molecular weight distributions which might result from interfacial type heterogeneous reactions (when one of the monomers is added to the reaction mixture in the solid form).[14,20,21] The molecular weight distributions of the poly(amic acid)s obtained over time were analyzed by universal calibration SEC techniques developed recently utilizing an NMP mobile phase which had been stirred over P_2O_5 and polystyrene standards.[14,17,18,22,23] Results for the formation of the poly(amic acid)s in NMP and THF are shown in Figure 4. The data demonstrate that the weight-average molecular weight of the poly(amic acid)s prepared in THF reached a high value quite near the targeted value quickly, in less than 20 min, while the poly(amic acid) synthesized in NMP required about 15 h to reach a plateau for the weight-average molecular weight. Since both polymerizations were conducted at the same molar concentrations, this indicates that the rate of amidization in dry THF was rapid in comparison to the rate of amidization in dry NMP.

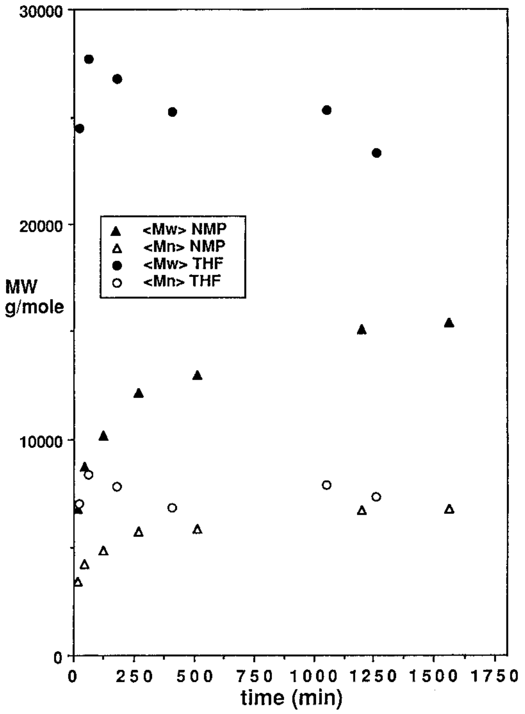

Figure 4. Molecular weights of Ultem poly(amic acid)s monitoring progress of the reactions over time (0.1 M dianhydride concentration).

The target $\langle M_n \rangle$ in both reactions was 20 000. Figure 4 shows attainment of a number-average molecular weight of only 7000. SEC traces of poly(amic acid)s synthesized in both solvents showed a small low molecular weight peak consisting of about 1–5 wt % of the total sample. This small peak is suspected to be due to low molecular weight cyclic oligomers formed as a result of the relatively low concentration of monomers used for the polymerizations (6.5 w/v). The presence of a small weight percentage of such a species reduces the calculated $\langle M_n \rangle$ greatly. In the case of the poly(amic acid) synthesized in THF, the molecular weight averages were recalculated, neglecting the small weight percentage of the low molecular weight species (Figure 5). The number-average molecular weight was calculated to be about 15 000 by neglecting the low molecular weight peak. For the final poly(amic acid) product, from which the solvent was evaporated more slowly, the molecular weight had increased further, reaching a number-average molecular weight of about 16 500. This might be attributed to (1) the equilibration of cyclic to linear species forming more linear species with increase in concentration or (2) a reequilibration of low molecular weight oligomeric species resulting in an increase in molecular weight.

When determining the weight percentage of THF remaining in the poly(amic acid)s synthesized in THF, it was found that regardless of how long the poly(amic acid) was dried at 20 °C under vacuum, approximately 19 wt % residual THF remained. The amount of THF in the poly(amic acid) calculated by considering 1 THF

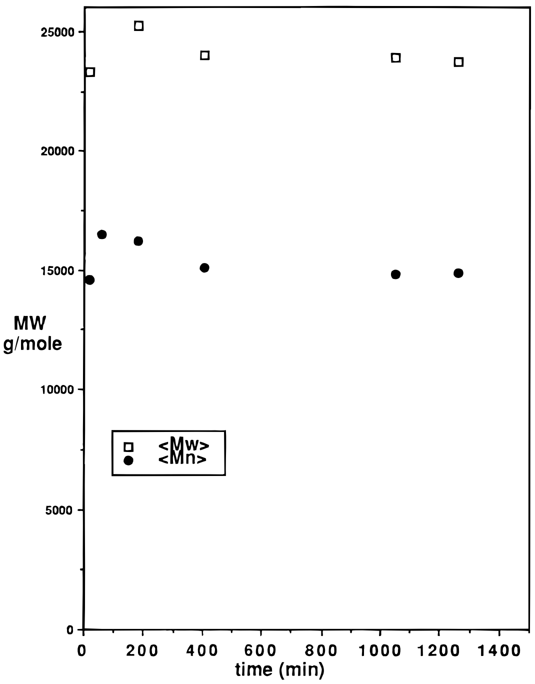

Figure 5. SEC results for the number- and weight-average molecular weights of Ultem type poly(amic acid)s (0.1 mol/L dianhydride concentration) in THF without including the low molecular weight peak in the calculations.

Table 2. Solubilities of Poly(amic acid) Salts

	concn = 0.15 M [COO$^-$]		concn = 0.15 M [COO$^-$]	
poly(amic acid) salt (preparation solvent)	sol MeOH	sol H_2O	sol MeOH	sol H_2O
tetramethylammonium (MeOH)	yes	no	yes	no
tetraethylammonium (H_2O)	yes	yes	yes	yes
tetraethylammonium (MeOH	yes	yes	yes	yes
tetrapropylammonium (H_2O)	yes	yes	yes	yes
tetrabutylammonium (MeOH)	yes	no	yes	no
triethylammonium (MeOH)	yes	no	yes	yes
$\langle M_n \rangle$ of poly(amic acid)	16 000		8800	

per 1 COOH group is 18.7 wt %. Similar stoichiometric association complexes are known to form between poly(amic acid)s and amide solvents such DMAc or NMP.[8,24] Complexes like these may help to drive the equilibrium amidization reaction to completion, thus offering an explanation for the rapid rate of amidization for Bisphenol A dianhydride with *m*-phenylenediamine in THF.

Poly(amic acid) salts with systematically varied cations were prepared from a 16 000 g/mol $\langle M_n \rangle$ poly(amic acid) in methanol or water and dried, and their solubilities in water and methanol were compared at a concentration of 4.7% w/v of poly(amic acid) in solvent (0.15 M based on [COO$^-$]). All of the poly(amic acid) salts were soluble in methanol. Water solubility is considered an important processing advantage since this would allow the salts to be applied as fiber sizings from aqueous solutions or to be incorporated into waterborne resins as thermoplastic toughening agents for thermosets. A 10 mol % excess of base was used (with the exception of the triethylamine case) because previous studies have suggested that small excesses of base should yield poly(amic acid) salt solutions where the polyelectrolytes are more hydrolytically stable.[7] Results from the solubility study are presented in Table 2. Interestingly, the solubilities of the salts followed a trend consistent with polyelectrolyte theory.[25] As the tetralkylammonium counterion size was increased from tetramethyl- to tetraethyl- to tetrapropylammonium, the salts became soluble in water (produced clear aqueous solutions). This is probably because the carboxylate charges are increasingly less shielded with the larger cations, and, hence, the polyelectrolyte becomes more soluble. However, a hydrophobic effect apparently overwhelms the deshielding effect for tetrabutylammonium cations, and water solubility again decreases. Although it is difficult to directly compare the shielding effect for the triethylammonium poly(amic acid) salts, it is important to note that although this material swelled appreciably, it was essentially water insoluble. However, an analogous triethylammonium salt was prepared using an 8,800 g/mol $\langle M_n \rangle$ poly(amic acid), and this lower molecular weight polymer did completely dissolve in water. This suggests that molecular weight may play a significant role in poly(amic acid) salt solubility. It is suggested that this point warrants further investigation at a later time.

Melt imidization conditions for the poly(amic acid) salts were investigated by conducting reactions at two temperatures, 250 and 300 °C, each for 30 min. To achieve quantitatively imidized polymers within a reasonable time, it is necessary to reach temperatures at least 20−30 °C above the glass transition temperature (T_g of Ultem polyimide $\sim$ 220 °C). It should be noted that cross-linking of the polyimide might also occur at imidization temperatures of 300 °C and higher. The percentage of weight loss which occurred during these imidization reactions and the glass transition temperatures of the polyimides were compared (Table 3). The experimental weight losses were corrected for the small amounts of solvent which were retained in the poly(amic acid) salts (and in the poly(amic acid) control). For all cases, the weight losses closely matched the expected values, indicating that the counterion byproducts quantitatively volatilized during the melt imidization processes. The appearance of the polyimides prepared at 250 °C differed from those formed at 300 °C. The 250 °C samples formed foams with varying densities, suggesting that the melt viscosities at 250 °C were sufficiently high to inhibit efficient flow during the process. The foam formed from the triethylammonium poly(amic acid) salt was qualitatively the least dense, yet appeared to have the best mechanical properties. The polyimides formed at 300 °C did not retain any foamed structure and exhibited significant viscous flow during the process. It is clear that the rheology of these melts, with respect to the particular imidization conditions, also warrants further investigation.

It is well known that T_g's increase with $\langle M_n \rangle$ for linear polyimides with molecular weights in the 5000−20 000 g/mol $\langle M_n \rangle$ range. The glass transition temperatures of the polyimides prepared from the poly(amic acid) salts were compared with the “control” material imidized directly from the poly(amic acid). It was reasoned that this data, in conjunction with SEC results, would provide an indication of whether the molecular weight of the original poly(amic acid) could be retained in the polyimides following salt formation in water (or methanol), subsequent drying, then imidization from the salts. No crystalline melting endotherms were observed by differential scanning calorimetry. In general, T_g's of the polyimides prepared at 300 °C were about 6 °C higher than of those imidized at 250 °C. The polyimides exhibiting the highest glass transition temperatures

Table 3. Weight Loss on Imidization and Thermal Properties of Polyimides from Poly(amic acid) Salts

poly(amic acid) salt	5% wt loss (°C)[a]	T (°C)[b] 30 min	% wt loss[c]	theor % wt loss	T_g (°C)[d]
poly(amic acid) salt	522	250	7.8	5.7	207
		300	6.6	5.7	213
tetramethylammonium (MeOH)	395	250	22.9	23.5	193
		300	24.4	23.5	190
tetraethylamminium (H_2O)	506	250	33.9	33.2	199
		300	33.8	33.2	204
tetraethylammonium (MeOH)	495	250	34.2	33.2	203
		300	34.4	33.2	211
tetrapropylammonium (H_2O)	503	250	41.1	40.7	198
		300	41.1	40.7	198
tetrabutylammonium (MeOH	444	250	47.1	46.7	189
		300	47.7	46.7	200
triethylammonium (MeOH)	519	250	30.4	28.7	213
		300	30.8	28.7	218

[a] 5% wt loss from polyimide plateau, air atmosphere, 10 °C/min. [b] Conditions for imidization. [c] Percent weight loss on imidization (corrected for residual solvent weight). [d] T_g determined by DSC, 10 °C/min.

Table 4. Molecular Weights of Polyimides from Poly(amic acid) Salts[a]

poly(amic acid) salt	T (°C) 30 min	$\langle M_n \rangle$	$\langle M_w \rangle$	$\langle M_w \rangle / \langle M_n \rangle$	
poly(amic acid) control	250	10400	19800	1.9	
	300	13200	28600	2.2	
tetramethylammonium (MeOH)	250	8990	16200	1.8	
	300	7500	20000	2.7	slight gel
tetraethylammonium (H_2O)	250	8970	17300	1.9	
	300	11500	73400	6.4	slight gel
tetraethylammonium (MeOH)	250	9500	21300	2.2	
	300	gel	gel	gel	gel
tetrapropylammonium (H_2O)	250	8910	15800	1.8	
	300	9840	19400	2.0	
tetrabutylammonium (MeOH)	250	8490	14700	1.7	
	300	10100	21900	2.2	slight gel
triethylammonium (MeOH)	250	15000	28800	1.9	
	300	16300	32600	2.0	

[a] Molecular weights determined by SEC (values not including small low molecular weight peak).

were the materials imidized from the poly(amic acid) at 300 °C, from the triethylammonium salts at both temperatures, and from the tetraethylammonium salt prepared in methanol and imidized at 300 °C. Of these higher T_g polyimides, the control material and both polyimides prepared from the triethylammonium salts were soluble in NMP and chloroform, whereas, by contrast, the polyimide prepared from the tetraethylammonium salt was no longer soluble. The thermal analyses, combined with the SEC results, suggest that the polyimides prepared from the triethylammonium salts under these melt conditions retained their original molecular weights and that cross-linking did not occur. In contrast, none of the polyimides prepared from the tetralkylammonium salts had these characteristics.

The weight-average and number-average molecular weights of the polyimides (Table 4) support these same observations. It should be noted that the average molecular weights reported in Table 4 were calculated neglecting the small low molecular weight peak in the SEC chromatograms. The highest polyimide number-average molecular weights of 16 300 and 15 000 g/mol corresponded to the triethylammonium salts prepared in methanol and then imidized at 300 and 250 °C, respectively. Partially insoluble gel's were observed for some of the polyimide samples by analyzing the polyimides' solubilities in chloroform. The polydispersities ($\langle M_w \rangle / \langle M_n \rangle$) rose above the most probable distribution value of 2.0 as cross-linking began to occur in the polyimides imidized at 300 °C.

According to free-volume theory, free volume around the polymer chain ends is greater than along the polymer chain, due to the poorer packing ability of the chain ends. It follows that $T_g = T_g^{\infty} - c/\langle M_n \rangle$.[26] This relationship was shown empirically by Fox and Flory.[27] The glass transition temperatures of the polyimides formed from the poly(amic acid) salts are plotted versus the polyimide $1/\langle M_n \rangle$ values (Figure 6). The number-average molecular weights were not corrected in this case for the small low molecular weight component, as this low molecular weight component might contribute significantly to the glass transition temperature value. T_g^{∞} is the value of the glass transition temperature for a linear polymer with infinitely few chain ends or infinitely high $\langle M_n \rangle$. By extrapolating the plot of T_g versus $1/\langle M_n \rangle$ to infinite molecular weight, the T_g^{∞} value for the Ultem type poly(ether imide) was determined to be 237 °C.

Each of the polyimides was potentiometrically titrated with hydrobromic acid in glacial acetic acid to detect residual aromatic amine end groups which may have resulted from hydrolysis or methanolysis during salt formation or imidization (Table 5). Theoretically, for a molecular weight controlled polyimide with nonreactive end groups, there should be no aromatic amine present in the form of end groups. However, if chain scission had taken place through a hydrolysis mechanism, aromatic amine endgroups would be expected. The results are given in terms of number of imide moieties per aromatic amine, with 2 imide moieties per polymer repeat unit. For a perfectly nonfunctional end-capped polyimide, this number will be infinite. With the detection limits in the titration experiment, values of up to 115 imide groups per amine group could be calculated. The polyimides formed from the poly(amic acid) and from the triethylammonium poly(amic acid) salts had low aromatic amine content (undetectable) when imidized at either imidization temperature (250

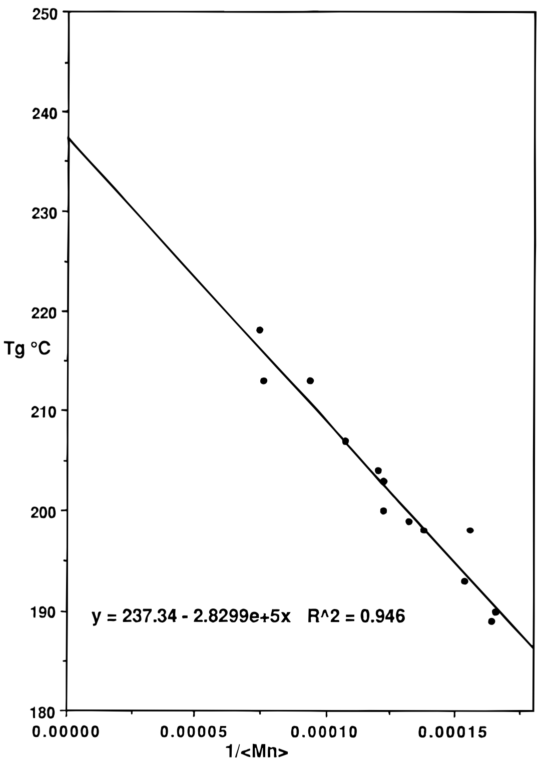

Figure 6. T_g vs $1/\langle M_n \rangle$.

Table 5. Potentiometric Titration of Imidized Poly(amic acid) Salts with HBr for Aromatic NH_2

poly(amic acid) salt	T (°C)[a] 30 min	$\langle M_n \rangle$[b]	imide/ NH_2[c]	
poly(amic acid) control	250	9300	>115	
	300	10700	>115	
tetramethylammonium (MeOH)	250	6510	19	
	300	6040	14	slight gel
tetraethylammonium (H_2O)	250	7550	56	
	300	8270	>115	slight gel
tetraethylammonium (MeOH)	250	8150	112	
	300	gel	>115	gel
tetrapropylammonium (H_2O)	250	6420	69	
	300	7240	79	
tetrabutylammonium (MeOH)	250	6110	25	
	300	8150	30	slight gel
triethylammonium (MeOH)	250	13200	>115	
	300	13400	>115	

[a] Conditions for imidization. [b] $\langle M_n \rangle$ values for polyimide samples imidized from poly(amic acid) salts were determined by SEC (includes the small low molecular weight "tail peak"). [c] Moles of imide moieties per mole of amine moieties. The limit of detection for the determination was 115 mol of imide per mol of amine.

and 300 °C). The polyimides formed from the tetraethylammonium poly(amic acid) salts also had low levels of aromatic amine, but these samples had cross-linked upon imidization at 300 °C. The polyimides from the tetramethylammonium poly(amic acid) salts and the tetrabutylammonium poly(amic acid) salts showed high levels of aromatic amine by titration. Quantitative correlation was not found between the titrations and the $\langle M_n \rangle$ results obtained by size exclusion chromatography. Not surprisingly, however, there was a good correlation between thermal stabilities measured by TGA and the absence of amine functional end groups.

Poly(amic acid)s are known to be hydrolytically unstable. Even if water is not present during the inital poly(amic acid) formation stage, when the poly(amic acid) is thermally imidized, the water byproduct of the imidization may react with amides (and with any anhydride groups which might have formed) to result in chain scission. The products of the hydrolysis reaction are a dicarboxylic acid and an aromatic amine. With sufficient thermal energy and chain mobility at elevated imidization temperatures, anhydride formation and amidization can reoccur followed by imidization. Therefore, even if chain scission of a poly(amic acid) occurs during processing to a polyimide, chain rehealing can occur, resulting in high or controlled molecular weight polyimides. For a poly(amic acid) salt, if hydrolysis occurs during preparation of the salt by reaction of the base with the poly(amic acid), or after the poly(amic acid) salt is prepared, chain rehealing can take place during thermal treatment to imidize the poly(amic acid) salt. This may be critical to achieving high molecular weight or controlled molecular weight polyimides. Chain healing was observed for poly(amic acid) salts imidized at 300 °C for 30 min (Table 6). Imidization of two slightly hydrolyzed poly(amic acid)s was investigated, one synthesized in THF (and containing residual quantities of THF) and the other synthesized in NMP. The original $\langle M_n \rangle$ for both poly(amic acid)s was ≈15 000. The poly(amic acid)s were slightly hydrolyzed during storage at room temperature with occasional exposure to laboratory air. Salts were prepared with a stoichiometric amount of triethylamine relative to carboxylic acid. The poly(amic acid)s and the poly(amic acid) salts were imidized at 300 °C for 30 min and then analyzed by SEC utilizing universal calibration techniques.

Table 6. Chain Rehealing during Imidization of Poly(amic acid) Salts

	PAA THF[a]	PAA 300 °C 30 min[b]	1/1 TEA/PAAS 300 °C 30 min[b]	PAA NMP[a]	PAA 300 °C 30 min[b]	1/1 TEA/PAAS 300 °C 30 min[b]
$\langle M_n \rangle$	8840	12400	15800	9620	20200	13000
$\langle M_w \rangle$	14400	24600	32500	19000	47000	30300
$\langle M_z \rangle$	20700	41200	53100	36100	82800	64700

[a] Preparation solvent. [b] Conditions for imidization.

The poly(amic acid) salts imidize by different mechanisms, depending on which counterion is present. It is reasonable to suggest that a poly(amic acid) salt does not imidize directly from the salt form due to the inherent low reactivity of the carboxylate toward nucleophilic acyl substitution. In one plausible route, imidization could be preceded by a Hoffman elimination reaction involving abstraction of the proton β to the nitrogen by the carboxylate anion to form the acid, ethylene, and a trialkylamine (Figure 7, eq 1A). After the poly(amic acid) forms, it might imidize with loss of water, or it might reprotonate the trialkylamine product after which further Hoffman elimination reactions would be possible. A second possibility involves an S_N2 type nucleophilic substitution reaction where the carboxylate anion would displace an alkyl group from a tetraalkylammonium cation to form the ester of the poly(amic acid) and a trialkylamine (Figure 7, eq 1B). The poly(amic ester) would subsequently imidize with loss of alcohol. The Hoffman elimination route is not possible for the tetramethylammonium poly(amic acid) salt since no proton β to nitrogen is present. Only S_N2 substitution could occur, with the carboxylate anion displacing a methyl group from the tetramethylammonium cation, resulting in trimethylamine and the methyl amic acid ester. Alkyl amic acid esters have been shown to imidize readily, though at higher temperatures than the corresponding poly(amic acid)s.[28-32] In the case of the triethylammonium poly(amic acid) salt, an equilibrium route exists where the carboxylate anion

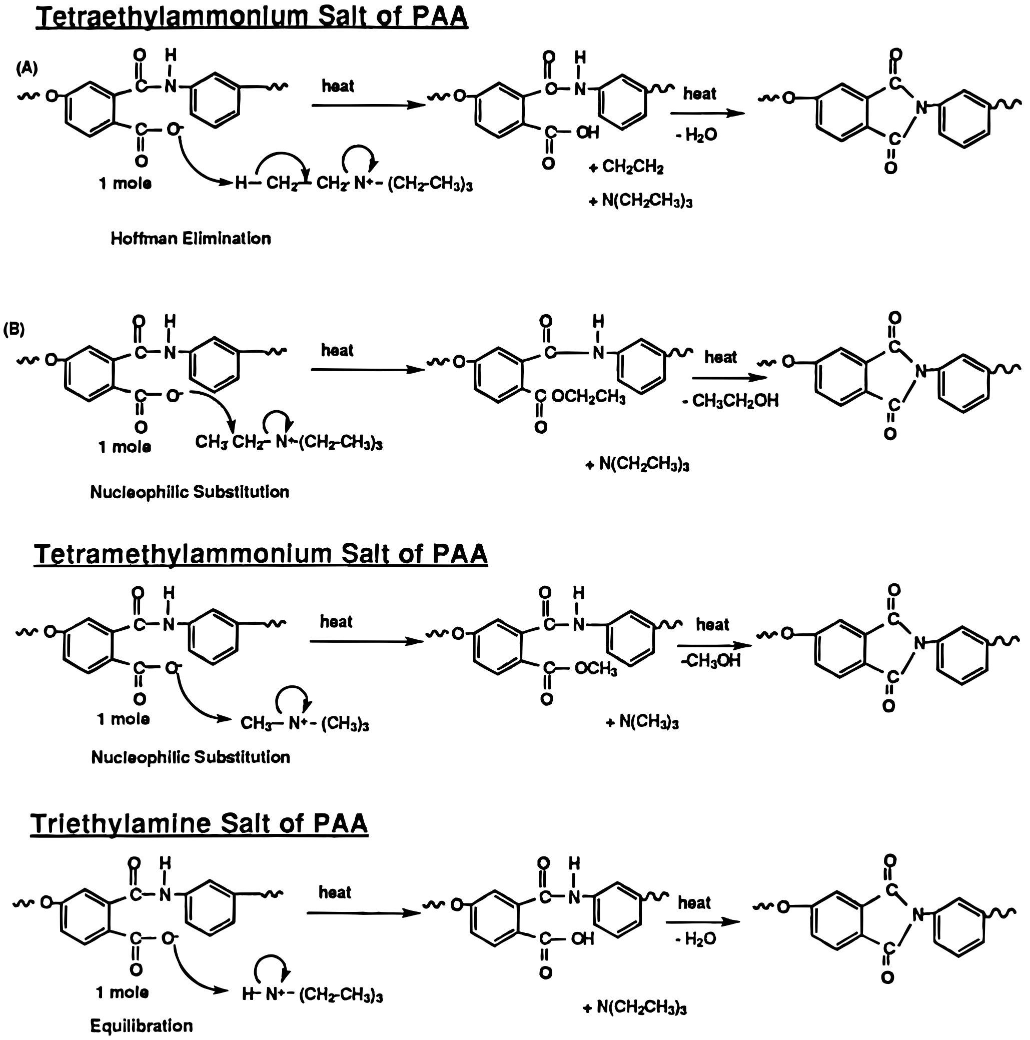

Figure 7. Imidization mechanisms for poly(amic acid) salts.

Table 7. Species Detected by GC−MS Analysis of Imidization Products

poly(amic acid) salt	species detected
tetramethylammonium	trimethylamine, methanol
tetraethylammonium	triethylamine, ethanol
tetrapropylammonium	propanol
tetrabutylammonium	butanol
triethylammonium	triethylamine

could simply abstract the proton associated with the protonated triethylamine, to result in the poly(amic acid) and triethylamine. The trialkylamines formed during the conversion to acid may act in situ to facilitate the imidization, by acting in a dual fashion as plasticizing agents in a similar fashion to NMP[33] and also as rate-increasing catalysts for imidization.[8]

Chemical species detected using mass spectrometry to analyze the effluents resulting from imidization of the poly(amic acid) salts are provided in Table 7. The GC−MS analyses suggest that the nucleophilic substitution route to form the poly(amic ester) and then the polyimide is the predominant route of imidization for all of the quaternary ammonium poly(amic acid) salts studied. The alkene byproducts of Hoffman type elimination reactions were not observed. Apparently, the carboxylate anion is not a strong enough base to participate in the proton abstraction step in an E2 type elimination, but is an efficient nucleophile (at 250−300 °C) for dealkylation of the quaternary ammonium ion. Similar dealkylation reactions by carboxylate ions have been reported previously. In a British study, dealkylation of quaternary ammonium salts by the acetate anion was shown to proceed at 60−140 °C in solvents with low dielectric constants.[34] The GC−MS experiments confirmed the simple proton transfer mechanism for the triethylammonium poly(amic acid) salt to form the poly(amic acid) and then the polyimide, since triethylamine was the only effluent detected.

Dynamic thermal behavior of the poly(amic acid) salts was determined in air by measuring weight losses while heating at 10 °C/min (Figure 8). The first weight losses were observed at about 200 °C corresponding to imidization of the poly(amic acid) salts. Quantitative weight losses were not determined using the DuPont TG instrument as the small sample sizes (3 mg) would have resulted in low precision. However, quantitative mass losses upon imidization were determined by using larger samples and imidizing in an oven isothermally at 250 or 300 °C for 30 min. After correcting the values for the weight percent solvent contained in the poly(amic acid) salts, the experimental values, were in all cases within 1% of the theoretical values indicating that quantitative imidization had occurred (Table 3). The higher temperature weight losses observed for all of the poly(amic acid) salts were due to degradation of the polyimides. The 5% weight loss from the polyimide plateau was calculated for all of the poly(amic acid) salts (Table 3). This value is representative of the dynamic thermal stabilities of the polyimides resulting from

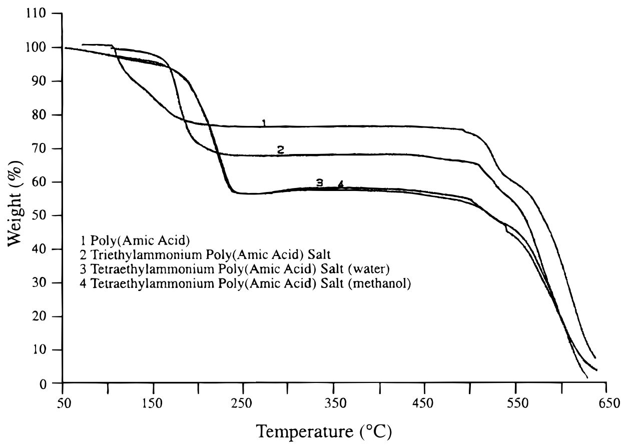

Figure 8. Mass loss during imidization and thermal stabilities of polyimides prepared from poly(amic acid) salts.

heating the precursor poly(amic acid) salts in air. The polyimides formed from the poly(amic acid) and the triethylammonium poly(amic acid) salt showed the best stabilities, with 5% wt loss values of about 520 °C. The polyimides from the tetraethylammonium and tetrapropylammonium poly(amic acid) salts displayed 5% wt loss values of about 500 °C. The materials imidized from the tetrabutylammonium and tetramethylammonium salts showed less stability, with 5% wt loss values of 444 and 395 °C respectively.

Conclusions

Controlled molecular weight polyimides were synthesized via triethylammonium poly(amic acid) salts. The mechanism of imidization and the properties of polyimides derived from poly(amic acid) salt precursors are dependent on the identity of the counterion. Synthesis of UIltem type poly(amic acid) precursors in tetrahydrofuran appears to proceed more rapidly than in *N*-methylpyrrolidinone. The tetrahydrofuran forms a stoichiometric complex with the carboxylic acid groups of the poly(amic acid) resulting in a residual 18.7 wt % THF in the poly(amic acid) upon drying.

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