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A Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry Study of the Imidization of Vapor-Deposited ODA–PMDA Poly(amic acid)

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ABSTRACT: Polyimides synthesized by vapor deposition have potential uses as gas barriers, dielectric coatings, and fusion laser targets. Efforts to further refine the process dictated an extensive understanding of the imidization of ODA–PMDA poly(amic acid) to ODA–PMDA polyimide. To aid in understanding this process, we have utilized MALDI–TOF MS to identify the products formed at various thermal intervals. The spectra obtained in this study identify critical temperatures of imidization (130–160 °C), average molecular mass growth, and previously unreported end group changes from a predominance of ODA in the uncured poly(amic acid) to a predominance of PMDA end groups in the fully cured polyimide. The gases evolved during curing were identified by GC/MS as monomer which was trapped in the solid poly(amic acid) during vapor deposition.

Introduction

Polyimides constitute an important class of polymers due to their excellent thermal stability, wear resistance, outstanding electric properties, radiation resistance, inertness to solvents, good adhesion properties, long-term stability, and superior mechanical properties.[1] Their exceptional merits have far outweighed the high costs and processing difficulties of these aromatic polyimides and have encouraged the development of new compositions and new processing methods aimed at value-added niche markets in high technology applications such as the space industry, microelectronics, optoelectronics, and composite fiber optics.[2]

The most popular polyimides are synthesized from the reaction of 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) to form poly(4,4′-oxydiphenylene pyromellitimide) (ODA–PMDA polyimide).[3] The common problem of insolubility generally associated with these high-temperature polymers is coped with by synthesizing the soluble ODA–PMDA poly(amic acid) precursor and thermally curing it to the final insoluble ODA–PMDA polyimide.[4,5] This elegant process made it possible for DuPont to bring the first significant commercial polyimide, Kapton, into the market, and it is still the method of choice in the majority of applications.[6]

The solution-based synthesis of ODA–PMDA polyimide suffers from several drawbacks in processing, e.g., residual solvent, microporosity induced by solvent evaporation, and difficulties in controlling film thickness and uniformity, because of the rheological properties of the polymer solution.[3] In contrast, vapor phase deposition (VPD) is a dry process in which the diamine and the dianhydride are coevaporated onto a substrate where they react to form a polyimide precursor, which converts to polyimide upon thermal curing.[7] This dry process was introduced by Iijima et al.[8] in Japan and by Salem et al.[7] in the United States in 1985 and 1986, respectively. Because of the low pressures used in the VPD process, usually below 10^{-3} Pa, chemical reactions in the gas phase can be neglected, and reactions are assumed to occur only in the condensed phase.[9]

The imidization of vapor-deposited ODA–PMDA poly(amic acid) has been analyzed in the past through spectroscopic methods such as XPS,[7,10–16] IR spectroscopy,[7,12,16–19] Raman spectroscopy,[20,21] UV photoelectron spectroscopy (UPS),[22,23] and near-edge X-ray absorption fine structure spectroscopy (NEXAFS).[15,24] Although multilayer polyimide films have been profiled by secondary ion mass spectrometry,[25] the imidization process has never been followed by the direct use of mass spectrometry. We present for the first time the use of MALDI–TOF MS for the direct analysis of the conversion of ODA–PMDA poly(amic acid) to ODA–PMDA polyimide. This analysis employs a unique method called the evaporation–grinding method (E–G method) that was developed[26] and optimized[27] in our laboratory specifically for the characterization of poorly soluble/insoluble polymeric samples. Results of this analysis have identified critical temperatures of imidization, molecular mass growth, and previously unreported end group changes during the thermal curing process of these vapor-deposited oligomers.

Experimental Section

Vapor Deposition Polymerization of Poly(amic acid) Films. Poly(amic acid) films were fabricated using vapor deposition polymerization. Pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) were placed in separate Knudsen cell evaporator chambers. The evaporator temperatures were controlled within 0.2 °C of 174 °C for PMDA and 163 °C for ODA. During deposition, diffusion pumps maintained a base pressure of 5×10^{-6} Torr. The source-to-substrate distance was 70 mm. Final film thickness was in the range 150–280 μm, and deposition rates were in the range 20 μm/h. Additional details regarding the experimental setup and equipment are provided elsewhere.[28–30]

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10.1021/ma035911i CCC: $27.50

Scheme 1. ODA−PMDA Poly(amic acid) Synthesis and Conversion to ODA−PMDA Polyimide

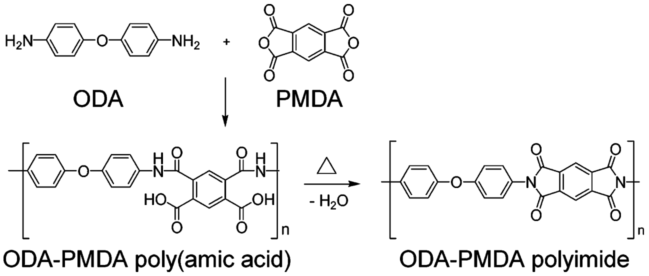


Table 1. Mass Assignments of the Peaks Displayed in the MALDI−TOF Mass Spectrum Reported in Figure 1

	M (Da)	
species	H^+	K^+
2−1	620 (n = 1)...2292 (n = 5)	657 (n = 1)...2329 (n = 5)
2−3		513 (n = 0)...1350 (n = 2)
2−7	1508 (n = 1)...1929 (n = 2)	1127 (n = 0)...2384 (n = 3)
2−9	1216 (n = 2)...2471 (n = 5)	1256 (n = 2)...2510 (n = 5)
2−10	1760 (n = 3)...2598 (n = 5)	1799 (n = 3)...2218 (n = 4)
2−11	1178 (n = 0)	1216 (n = 0)...2471 (n = 3)
3−1		639 (n = 1)...1475 (n = 3)
3−2		623 (n = 1)...3548 (n = 8)
3−3		1021 (n = 0)...3945 (n = 7)
3−4		1422 (n = 1)...3094 (n = 5)
4−1	585 (n = 1)...3260 (n = 8)	624 (n = 1)...2531 (n = 6)
4−2	403 (n = 0)...3458 (n = 8)	442 (n = 0)...2351 (n = 5)
4−3	804 (n = 1)...2330 (n = 5)	839 (n = 1)...3133 (n = 7)
4−4	930 (n = 0)...3602 (n = 7)	966 (n = 0)...3260 (n = 6)
4−5	1057 (n = 1)...2965 (n = 6)	712 (n = 0)...3768 (n = 8)
4−6	601 (n = 1)...4040 (n = 10)	639 (n = 1)...3699 (n = 9)
4−7	727 (n = 1)...3404 (n = 8)	765 (n = 1)...3060 (n = 7)
4−8	857 (n = 1)...3146 (n = 7)	894 (n = 1)...3566 (n = 8)
4−9	872 (n = 1)...2401 (n = 5)	909 (n = 1)...3202 (n = 7)
4−10	1017 (n = 1)...2544 (n = 5)	1057 (n = 1)...2965 (n = 6)
4−11	1526 (n = 2)...3053 (n = 6)	799 (n = 0)...3473 (n = 7)
4−12	782 (n = −1)...3455 (n = 6)	819 (n = −1)...3491 (n = 6)

MALDI−TOF MS Measurements. All poly(amic acid) and polyimide samples were analyzed using a Voyager Elite MALDI−TOF MS (Applied Biosystems, Framingham, MA) equipped with a 337 nm N_2 laser. All the spectra were obtained in the positive ion mode using an accelerating voltage of 20 kV and a laser intensity of ∼10% greater than threshold. The grid voltage, guide wire voltage, delay time, and reflectron mode were optimized for each spectrum to achieve the best signal-to-noise ratio. Mass calibration was performed using protein standards from a Sequazyme Peptide Mass Standard Kit (Applied Biosystems) and a two-point calibration method using Angiotension I (m = 1297) and Insulin B chain (m = 3497). The instrument was calibrated just after the measurements to keep the experimental conditions constant. All poly(amic acid) and polyimide samples were run in 3-aminoquinoline (3AQ, Aldrich) doped with potassium trifluoroacetate (KTFA, Aldrich) salt. The samples were prepared using the evaporation−grinding method (E−G method) which has been detailed in a previous publication.[26] For this work all samples were run using mole ratios of 25:1:1 (3AQ:polymer:KTFA). Moles of polymer were estimated by determining a number-averaged molecular mass (M_n) of the polymer (1450 g/mol) with software supplied by the manufacturer of our MALDI−TOF MS.

Evolved Gas Analysis/Gas Chromatography/Mass Spectrometry (EGA/GC/MS) Measurements. Poly(amic acid) samples were analyzed using a Frontier Labs double-shot pyrolyzer (Frontier Labs, Japan) interfaced to a Hewlett-Packard 5890 II gas chromatograph and a Hewlett-Packard 5970 mass selective detector. Platinum sample cups were used to ensure homogeneous heating of the sample. Evolved gas analysis was performed using the following protocol: 50 mg of poly(amic acid) was placed into a platinum sample cup and was allowed to purge under a 100 mL/min flow of 99.999% pure (grade 5) helium for 3 min inside of the pyrolyzer. The pyrolyzer was then heated to 100 °C, and a GC/MS was taken of the evolved gases. After the completion of the GC/MS the sample was briefly removed from the pyrolyzer furnace, and the furnace temperature was raised 10 °C. This procedure was repeated until a temperature of 300 °C was completed by the GC/MS. The GC/MS used a heating program starting at 50 °C for 2 min and ramping at 12.5 °C/min for 20 min before finally holding at 300 °C for 8 min, for a total GC/MS heating cycle of 30 min. A 99/1 split of the carrier gas was used to ensure that the gases were introduced as a “plug” and not to corrupt the mass spectrometer.

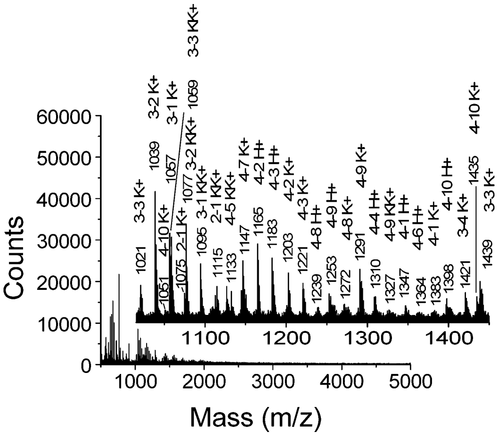


Figure 1. MALDI−TOF mass spectrum of ODA−PMDA poly(amic acid) cationized with KTFA prepared by the E−G method in 3AQ and KTFA after heating at 150 °C for 45 min.

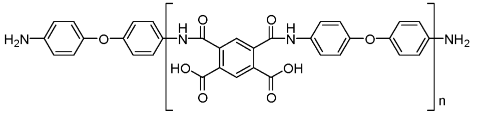
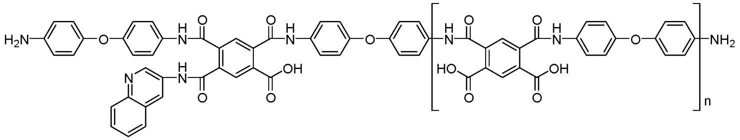
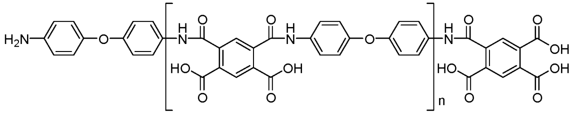
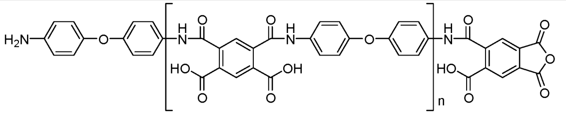
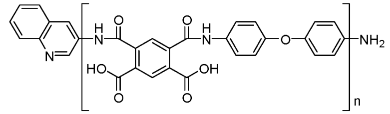
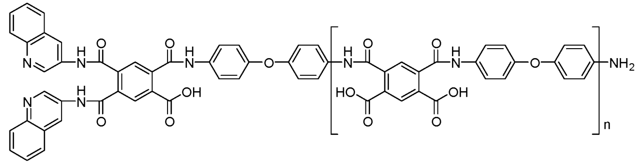
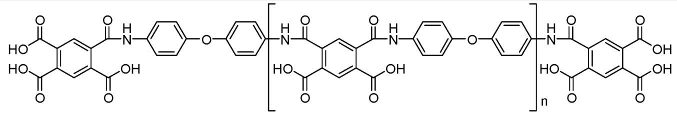
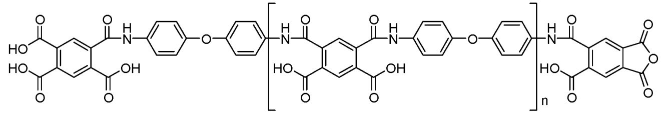
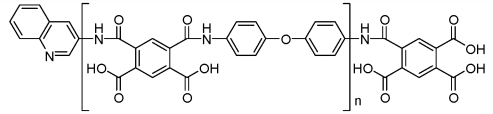
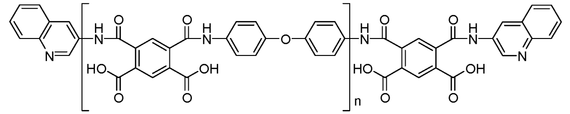
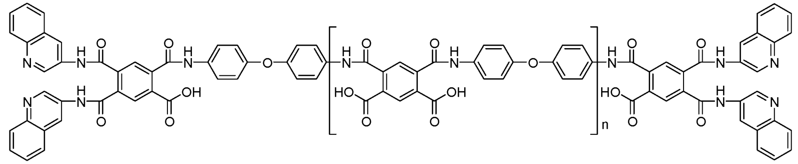
The pyrolyzer was also used to imidize the poly(amic acid) samples for MALDI−TOF MS analysis. 50 mg of poly(amic acid) was placed in a platinum sample cup and allowed to purge under a 100 mL/min stream of grade 5 helium gas. The sample cup was introduced into the furnace at a temperature of 100 °C and maintained at that temperature for 45 min. After this time interval had expired the platinum sample cup was removed from the pyrolyzer, and a 2 mg sample of polymer was analyzed by MALDI−TOF MS. The platinum cup was then suspended in a sealed chamber above the furnace in a 100 mL/min stream of grade 5 helium for 3 min before being introduced into the furnace that was set at 10 °C higher than the last heating temperature and reheated for 45 min. This procedure was repeated until a 300 °C heating interval was completed.

Results and Discussion

The usual method for conversion of a poly(amic acid) to a polyimide is by heating the poly(amic acid) at a given temperature until imidization is complete. The chemical reaction that takes place involves the nucleophilic attack of an amide nitrogen on a carboxylic acid with the production of water and results in the attachment of two acyl groups to the now imide nitrogen. The complete conversion of the amide in an oligomeric species involves numerous such reactions. The polymerization and imidization reactions are pictured in Scheme 1.

To follow the imidization of the poly(amic acid), it was necessary to identify species in the MALDI−TOF mass spectra which were characteristic of (1) the pure poly(amic acid), (2) an incompletely imidized poly(amic acid), and (3) a completely imidized species. To this end representative species were identified in the uncured poly(amic acid), partially cured poly(amic acid) and completely cured poly(amic acid). Figure 1 contains a spectrum of an incompletely imidized sample which contains peaks found in the pure, incompletely imidized, and completely imidized form. Table 1 identifies the

Table 2. Structural Assignments of the Peaks Displayed in the MALDI−TOF Mass Spectrum Reported in Figure 1

Species	Structure (M)
2-1	
2-2	
2-3	
2-4	
2-5	
2-6	
2-7	
2-8	
2-9	
2-10	
2-11	

masses of these peaks. (In this figure the peaks are labeled in the *x*−*y* format (*x* = table number, *y* = structure number) followed by the atom and/or ion which has been added to the oligomer during the MALDI process. For instance, a peak labeled 3−2 KK+ would arise from a structure found in Table 3, structure 3−2, which added a potassium atom and a potassium ion during the MALDI process.) It should be noted that small amounts of poly(amic acid) species larger than dimers or trimers were found, but it appears that the dimers and trimers are the main species as first proposed by Dimitrakopoulos and coauthors.[31] Tables 2−4 contain structures associated with species listed in Table 1. Heating studies were carried out with a poly(amic acid) sample that was heated at temperatures ranging from 100 to 300 °C in 10 deg increments in a pyrolysis furnace. At the end of each 45 min heating period a portion of the sample was removed and analyzed by MALDI−TOF MS, and the remainder returned to the furnace for additional heating at the next temperature level. Spectra were obtained at temperatures of 25, 150, 160, and 300 °C. Peaks were then

Table 3. Structural Assignments of the Peaks Displayed in the MALDI−TOF Mass Spectrum Reported in Figure 1

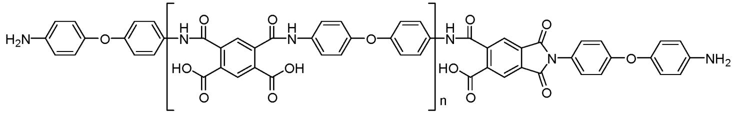
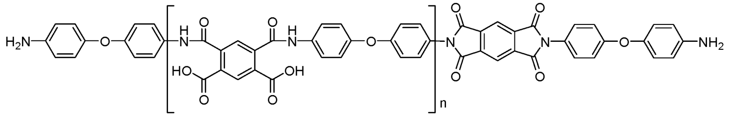
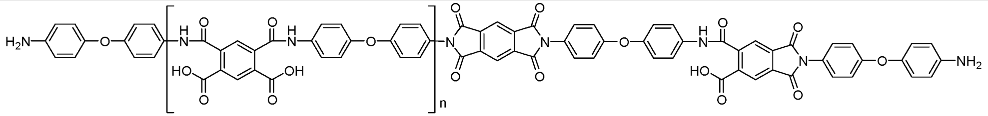
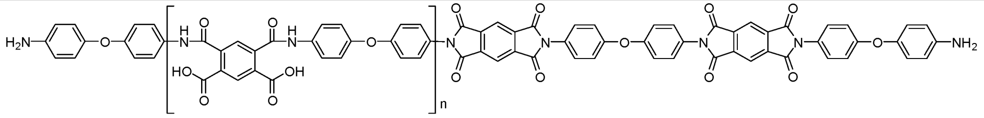
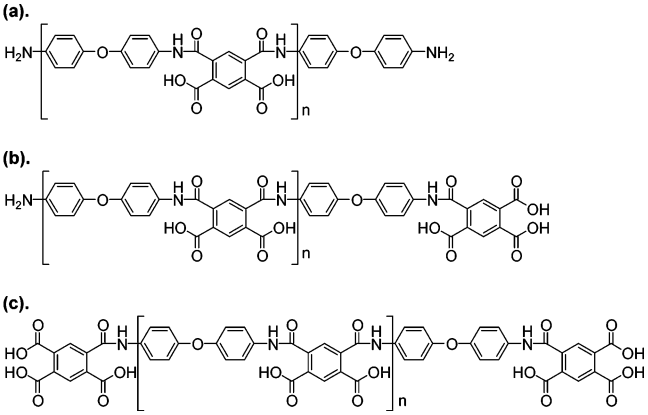
Species	Structure (M)
3-1	
3-2	
3-3	
3-4	

Chart 1. ODA−PMDA Poly(amic acid) End Group Combinations (a) ODA−ODA, (b) ODA−PMDA, and (c) PMDA−PMDA



identified as arising from poly(amic acid), partially imidized poly(amic acid), and fully imidized poly(amic acid). It was evident from the distribution of peaks in these spectra that the imidization has well begun at 150 °C (110 °C as a threshold value) with the imidization virtually complete at 160 °C. Spectra between these two values contained peaks representing pure poly(amic acids), pure polyimides, and partially imidized poly(amic acids). For example, the spectrum obtained at 25 °C contained a total of 146 identifiable peaks, all of which represented the pure poly(amic acid). The spectrum obtained at 150 °C contained a total of 149 identifiable peaks—16 of them represented the pure poly(amic acid), 34 represented partially poly(amic acid), and 99 of them represented fully imidized poly(amic acid). Finally, the spectrum obtained at 300 °C contained a total of 169 identifiable peaks, virtually all of which represented fully imidized polymer.

The spectra discussed above were then subjected to end group analysis and peaks identified containing the three possible end group combinations shown in Chart 1. At temperatures below 120 °C there is a mixture of all three possible combinations of end groups with a slightly greater abundance of ODA−ODA followed by ODA−PMDA and a lesser amount of PMDA−PMDA. As the temperature increases, however, a shift is observed toward more PMDA−PMDA end groups with a clear predominance observable by 160 °C. For example, the spectrum obtained at 25 °C contained a total of 146 identifiable peaks—62 of them represented ODA−ODA end groups, 61 represented ODA−PMDA end groups, and 23 of them represented PMDA−PMDA end groups. The spectrum obtained at 150 °C contained a total of 149 identifiable peaks—54 of them represented ODA−ODA end groups, 33 represented ODA−PMDA end groups, and 62 of them represented PMDA−PMDA end groups. Finally, the spectrum obtained at 300 °C contained a total of 169 identifiable peaks—24 of them represented ODA−ODA end groups, 29 represented ODA−PMDA end groups, and 116 of them represented PMDA−PMDA end groups.

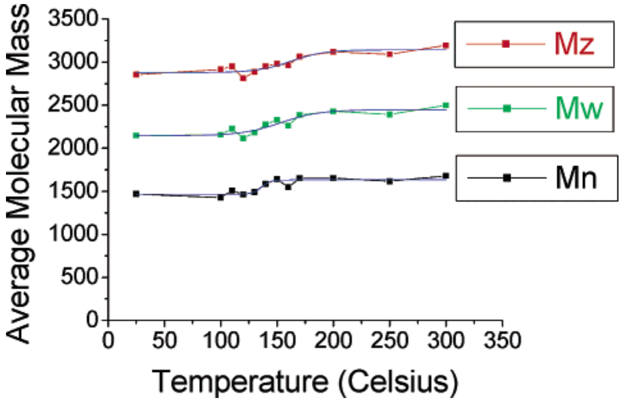
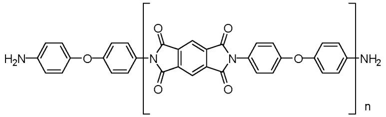
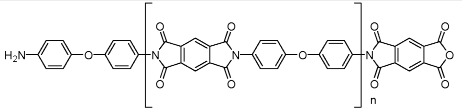
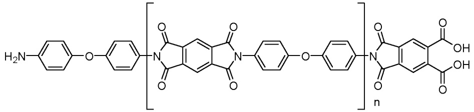
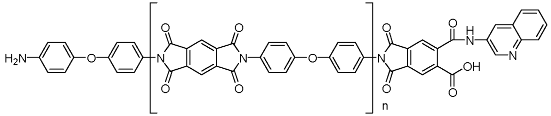
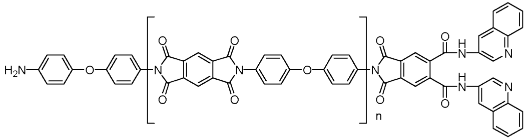
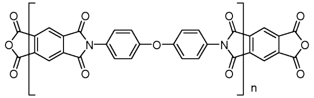
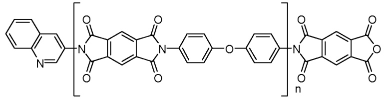
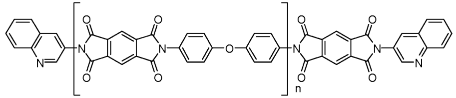
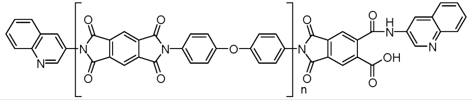
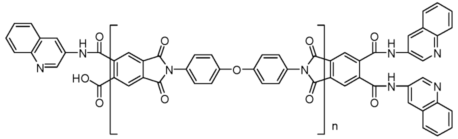
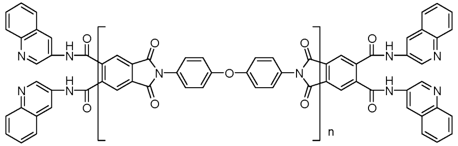
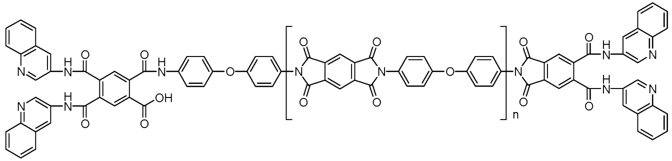


Figure 2. MALDI−TOF MS average molecular masses of ODA−PMDA poly(amic acid) when heated at various temperatures (°C).

Figure 2 exhibits a graph of a plot of average molecular mass of each of the spectra discussed above vs temperature. These data were obtained by using software provided by Applied Biosystems. Only the peaks listed in Table 1 were used in this calculation. These data indicate that the number-averaged, weight-averaged, and *z*-averaged molecular masses increase slightly in the 130−160 °C range.

Figure 3 exhibits two graphs of PMDA and ODA monomer ion current as a function of temperature. These data was obtained by pyrolyzing the poly(amic acid) in a furnace which was interfaced with a GC/MS.

Table 4. Structural Assignments of the Peaks Displayed in the MALDI−TOF Mass Spectrum Reported in Figure 1

Species	Structure (M)
4-1	
4-2	
4-3	
4-4	
4-5	
4-6	
4-7	
4-8	
4-9	
4-10	
4-11	
4-12	

From these data it is apparent that a small amount of PMDA relative to ODA is evolved beginning at 140 °C and reaches a maximum at 160 °C. No PMDA evolution was observed above 170 °C. A similar experiment for ODA monomer shows the beginning of evolution at 180 °C with a maximum at 270 °C with some evolution observed up to the maximum temperature in the experiment. Identical experiments with solution-cast ODA−PMDA poly(amic acid) demonstrated no evolution of either monomer, leading to the conclusion that the monomer gases evolved were from unreacted monomer trapped in the vapor deposited film and not from oligomer breakdown.

The change in the distribution of end groups and molecular weight increase we believe can be explained by the evolution of trapped PMDA monomer during the curing process. The vaporization of the trapped PMDA monomer allows it to diffuse throughout the sample and

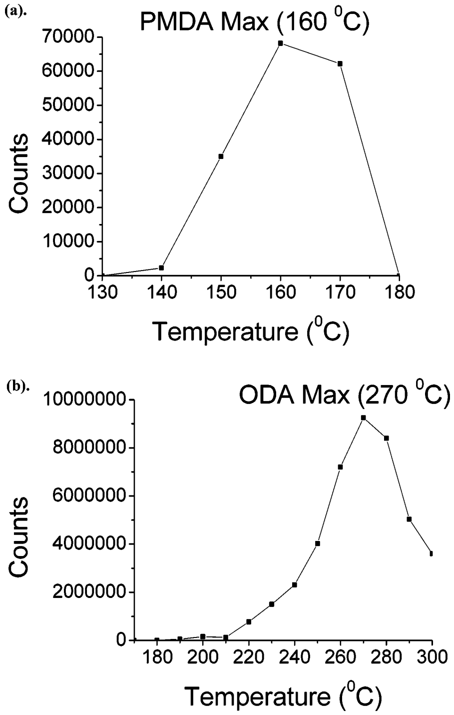


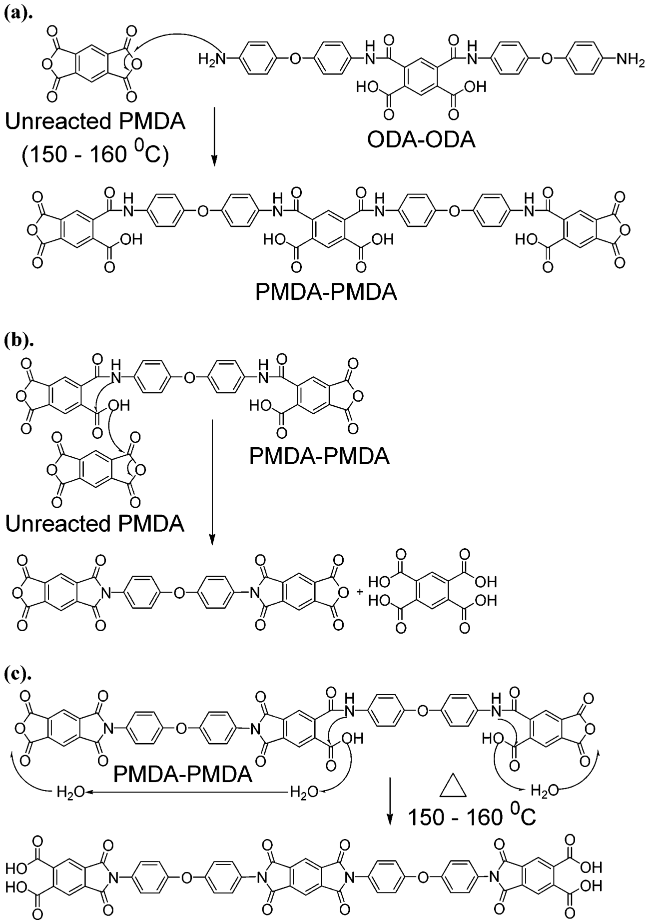
Figure 3. EGA/GC/MS plot of (a) PMDA evolution and (b) ODA evolution temperatures (°C) vs ion counts.

react with any encountered ODA end group adding one more PMDA unit to the end of the oligomeric chain (thus increasing its molecular mass) and creating an additional PMDA end group. This reaction is shown in Scheme 2a. PMDA evolution has also been shown to aid the imidization process by dehydrating the poly(amic acid), as shown in Scheme 2b.[2] Since ODA is evolved from 180 to 300 °C, one might expect the ODA to further react with the PMDA groups formed at lower temperatures to again even out the distribution of end groups. The heating/end group studies discussed above suggest that this does not occur. We believe that this can be explained by the fact that, at the temperature at which the ODA begins its vaporization, the water evolved by the imidization has already reacted with the anhydridic PMDA end group moieties converting them to carboxylic acids, thus inhibiting their ability to react with the evolved ODA monomer. This hypothesis is impossible to prove, however, by our MALDI−TOF mass spectra since the 3AQ used as matrix reacts with PMDA end groups and might be expected to react with these end groups in either their anhydridic or carboxylic form. Further evidence, however, for this hypothesis resides in IR data recently acquired by Anthamatten and coworkers[32] that has identified the presence of carboxylate species in the polyimide after curing. Assuming that the imidization process has taken place completely, these carboxylate species must then be assumed to arise from the hydrolysis of the anhydridic PMDA end groups.

Conclusions

The imidization of ODA−PMDA poly(amic acid) formed in the vapor deposition process is accompanied by evolution of both PMDA and ODA monomer, increase in molecular mass, and a shift from an ODA dominated distribution of end groups to a overwhelming predominance of PMDA end groups. We hypothesize that the molecular mass increase and shift to PMDA end groups can be explained by the vaporization of PMDA monomer which was trapped in the sample during the vapor deposition of the poly(amic acid) which reacted with the ODA end groups, causing an increase in the molecular mass of the oligomer and formation of additional PMDA end groups.

Scheme 2. PMDA Monomer Reactions with ODA−PMDA Poly(amic acid) Resulting in (a) Chain Growth with End Group Changes, (b) Increased Rate of Imidization, and (c) Hydrolysis of Anhydride End Groups



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