Time-of-Flight Static SIMS Study of Imidization in Pyromellitic Dianhydride–4,4′-Oxydianiline Polyimide Films

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ABSTRACT: In this study the positive and negative static secondary ion mass spectrometry (SSIMS) spectra of pyromellitic dianhydride–4,4′-oxydianiline (PMDA–ODA) polyimide before and after imidization were analyzed. Isotopically labeled materials were used to deduce the structure and source of secondary ions produced by this material. A signature for imidization of the surface layer is given by disappearance of fragment ions attributed to ODA and PMDA end groups from the positive SSIMS spectrum. In addition to confirming our speculations as to the source of secondary ions, we found that addition of free ODA dramatically increases the amount of ODA end groups after curing. This, in concert with observations that include invariance of the ^{14}N to ^{15}N ratio with film depth, appearance of a new high-temperature weight loss region in the thermogravimetric analysis (TGA) of films containing excess ODA, and overall molecular weight reduction for cured films, leads us to propose a cascading mechanism of excess amine incorporation and equilibration throughout the film.

I. Introduction

The mechanical and electrical integrity of polyimides over a large temperature range has made them the material of choice for many integrated circuit and interconnect applications.[1] The use of these materials in applications where tightly controlled final properties must be obtained upon curing implies that the physical and chemical changes taking place during the conversion of the poly(amic acid) precursor to the polyimide are of considerable interest. The sampling depth for static secondary ion mass spectrometry (SSIMS) is quite shallow. Ions are typically extracted from a depth of 10 Å or less. The established sensitivity of SSIMS spectra to aspects of polymer structure[2-5] holds out the possibility of observing structural changes as they take place in the near-surface region of a bulk polyimide film. The surface properties of the cured polymer will have a strong influence on the success or failure of subsequent process steps, especially those involving various interface interactions. In this study, the positive and negative SSIMS spectra for pyromellitic dianhydride–4,4′-oxydianiline (PMDA–ODA) were examined before and after in vacuo imidization of the poly(amic acid) precursor. Addition of an excess of isotopically labeled free aromatic amine (ODA) allowed a determination of the source of observed secondary ions from within the polymer. SSIMS measurements of these mixtures after curing provide an interesting picture of the chemistry of free aromatic amines in the presence of the poly(amic acid) at the surface of the polymer film. Time-of-flight SSIMS (TOF SSIMS) measurements were complemented by dynamic SIMS depth profiling, thermogravimetric analysis (TGA), and transmission Fourier transform infrared (FTIR) spectroscopy results to form a continuous picture of the chemical changes taking place from the surface into the bulk of the films under study.

II. Experimental Section

(a) Static and Dynamic SIMS. The apparatus used for these experiments was a reflectron type time-of-flight mass spectrometer fitted with SIMS extraction optics. A rapid sample introduction system allowed introduction of prepared samples into the working chamber held under ultrahigh-vacuum conditions in ~20 min. Complete design details have been published elsewhere;[6] however, relevant details are repeated here for clarity. The primary ion beam species is $^{40}Ar^+$ supplied at an energy of 10 keV. The primary ion beam current is 10 nA dc, but the beam is pulsed at a pulse width of 6 ns. This leads to an estimated number of $^{40}Ar^+$ ions per primary ion beam pulse of $\sim 10^3$. The integrated ion dose into any sample was held at less than 1×10^{12} ions/cm^2. No sign of degradation or change in the SSIMS spectra with ion dose was observed. The spectrometer mass resolution is 1350 at $m/e = 500$. The area subject to the primary ion beam is 1 mm × 1.2 mm. The TOF chamber working pressure with the primary ion beam off is 1.5×10^{-10} Torr. Neutralization of sample charging was not possible with this apparatus. In some cases sample charging was found to be a problem, leading to distortion of the observed mass spectrum and some loss of both signal and mass resolution. Nevertheless, useful spectra and results were obtained from all samples studied. Dynamic SIMS depth profiles of cured films were obtained with a Cameca IMS 4F secondary ion microscope.

The monomer units used to form PMDA–ODA polyimide are shown in Figure 1a. The repeat unit of the poly(amic acid) formed by the addition reaction of the monomer units is shown in Figure 1b. The polyimide formed by imidization of the poly(amic acid) is shown in Figure 1c. Two different PMDA–ODA formulations were used for this study. Sample I: PMDA–ODA poly(amic acid) (PAA) was synthesized with equimolar amounts of recrystallized (twice from methyl ethyl ketone) 1,2,4,5-benzenetetracarboxylic acid dianhydride (PMDA) and zone-refined (Aldrich) 4-aminophenyl ether (oxydianiline, ODA) in 1-methyl-2-pyrrolidinone (NMP) under nitrogen atmosphere. The solution was used without further purification. The solution viscosity of the final 15 wt % NMP solution was consistent with a polymer molecular weight on the order of 35 000–40 000.[7] Sample II: 99% ^{15}N-labeled PMDA–ODA PAA was obtained from Merck.[8] The material had a quoted average molecular weight of 10 000. The obtained NMP solution contained 15 wt % solids. For all the samples studied, 1–2 μm-thick films were prepared by spinning the above solutions at 2000–3000 rpm onto 0.6-in.-diameter n-type Si ⟨100⟩ wafers with a bulk resistivity of 10 Ω cm. The samples were then dried on a hot plate for 5 min at 90 °C prior to introduction into the vacuum system. A heating stage in the sample holder was used to imidize the samples in situ. The samples were fully cured by heating to 400 °C for 1–3 h until a steady-state condition for the SSIMS spectra was achieved.

(b) TGA and Transmission FTIR. TGA data were recorded on a Perkin-Elmer TGS-2 thermogravimetric analyzer. All runs were conducted under a nitrogen atmosphere at a constant heating rate of 10 °C/min from room temperature to a maximum of 430 °C. The polymer solution was applied to a glass slide. After baking for 10 min, at 90 °C, films were delaminated and cut into small pieces for analysis. Fourier transform infrared spectra were acquired with a Nicolet 710 FTIR spectrometer equipped with a mercury cadmium teluride detector. Spectra were recorded at a resolution of 2 cm^{-1} over 500 scans. Samples were prepared for

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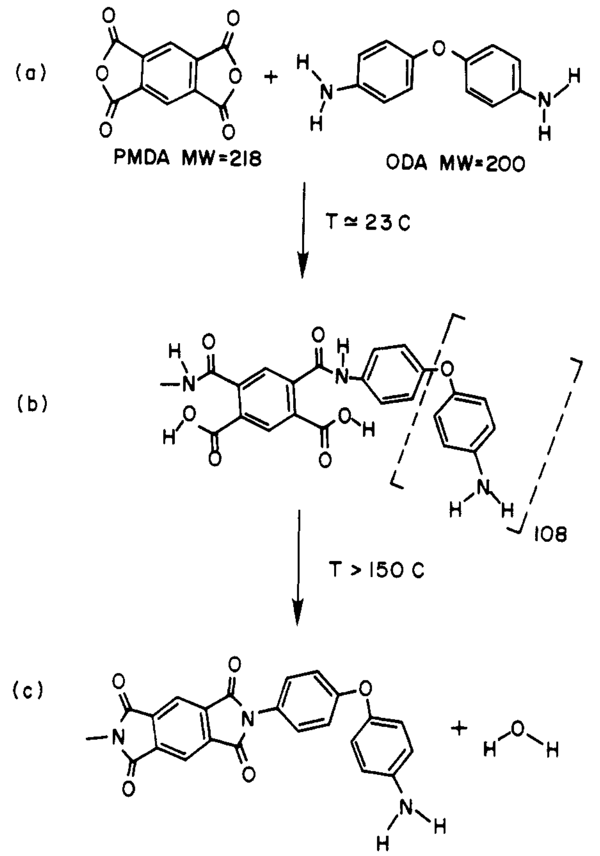

Figure 1. (a) Monomers for formation PMDA-ODA polyimide. (b) Poly(amic acid) formed by addition reaction of PMDA and ODA. The ODA is here shown as an end group for clarity in further discussions. (c) Polyimide formed by curing of (b).

FTIR analysis by spin casting polymer solutions onto polished KBr disks under conditions that gave film thicknesses on the order of 1.5 μm. Baking of the disk on a hot plate for 10 min at 90 °C preceded data acquisition. Film thickness variation for the various samples was within 10% and therefore no spectral normalization was required prior to plotting on the same scale.

III. Results and Discussion

(a) Static SIMS. A comparison of the positive SSIMS spectrum of I before and after imidization is shown in panels a and b of Figure 2. In all further discussions, the units for features in the mass spectra are mass to charge or m/z. Structural assignment of the peaks at 108 and 200 was assisted by comparison with the positive-ion spectrum of II, where, due to the ^{15}N isotope, these features were observed at 109 and 202, respectively. The feature at 108 is assigned to a fragment formed by cleavage of ODA to include the ether oxygen. This fragment is shown in Figure 1b. The peak at 200 is due to $(ODA)^+$. The feature at 219 is assigned to $(PMDA + H)^+$ since it was not shifted in the positive SSIMS spectrum of II. No large fragments attributable to ions formed from combinations of monomers or their fragments were observed for either I or II.

The most noticeable change in the positive SSIMS spectrum upon imidization is loss of the feature at 200 attributed to $(ODA)^+$ and that at 219 attributed to $(PMDA + H)^+$. The feature at 100 attributed to $(NMP + H)^+$ also disappears upon sample heating. While NMP appears in the spectrum shown, it was not observed for all of the samples tested. This is possibly due to vacuum pumping on the surface concentration of NMP. (The time spent under vacuum prior to acquisition of positive SSIMS spectra varied somewhat from sample to sample.) Systematic studies to confirm this hypothesis were not carried out. It is interesting to note that the peak at 108 of Figure 2a,b is not affected by imidization. We will return to this point later.

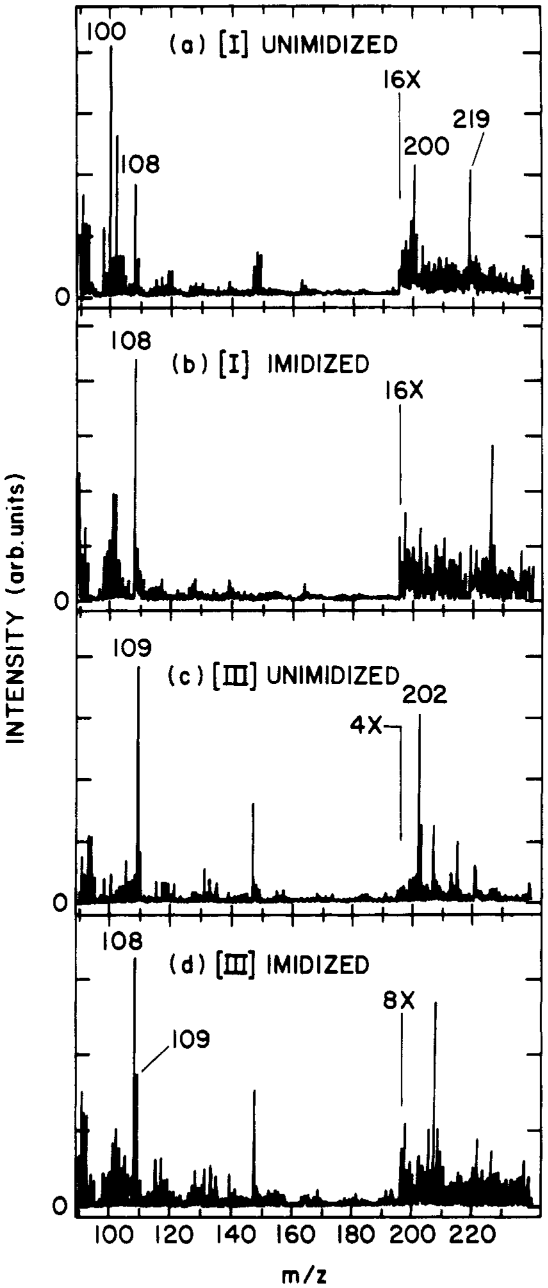

Figure 2. Positive SSIMS spectra for films studied: (a) unimidized PMDA-ODA (I); (b) PMDA-ODA (I) after imidization; (c) unimidized PMDA-ODA + 20 wt % of ODA* (III); (d) PMDA-ODA + 20 wt % of ODA* (III) after imidization. The structure of the peak at 108 is shown in Figure 1. The peak at 109 is structurally equivalent to that at 108 with substitution of ^{15}N for ^{14}N. Additional peaks at 147, 207, and 221 in (c) and (d) are due to small amounts of siloxanes present in this material as received.

The negative SSIMS spectrum of I before imidization is shown in Figure 3a. Assignment of the peaks, as labeled in the figure, was again assisted by comparison of the negative SSIMS spectrum of I with that of II in Figure 3b. Imidization of the polymer does not result in the elimination or creation of any peaks in the negative SSIMS spectrum. This is to be expected since formation of the relatively small fragments observed should not show a strong dependence on ring closure of the polyimide.

(b) Source of Structurally Significant Secondary Ions. The peaks in the positive SSIMS spectrum at 108

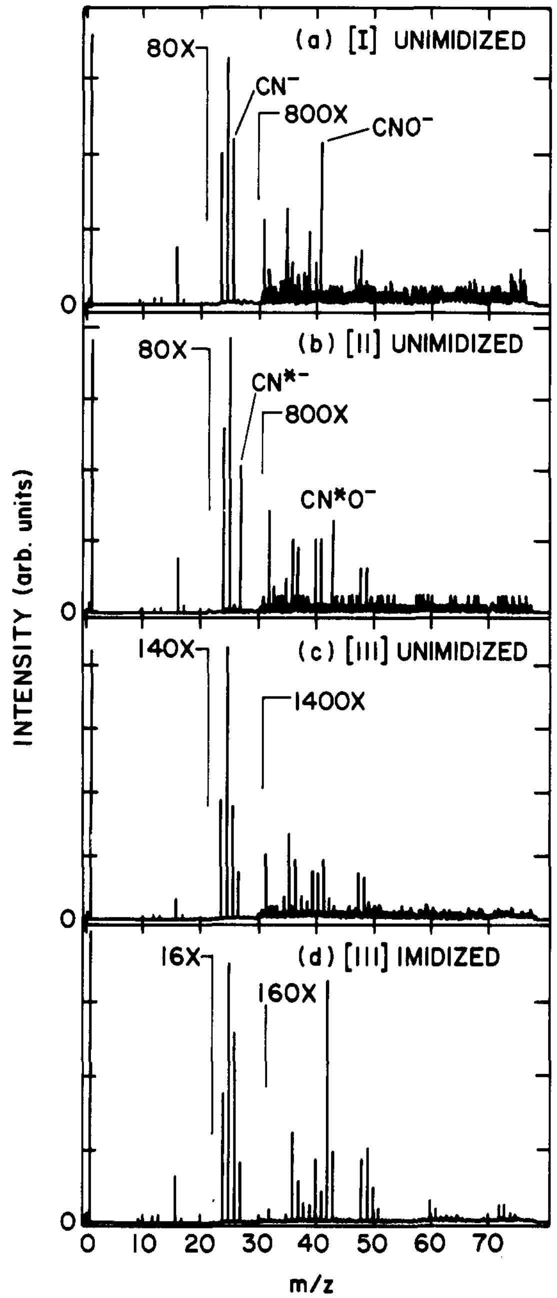

Figure 3. Negative SSIMS spectra for films studied: (a) unimidized PMDA-ODA (I); (b) unimidized PMDA-ODA* (II); (c) unimidized PMDA-ODA + 20 wt % of ODA* (III); (d) PMDA-ODA + 20 wt % of ODA* (III) after imidization.

and 200 of Figure 2a can be assigned to specific structural elements of the polymer, i.e., interchain units or end groups of the polymer chains. The stability of the peak at 108 before and after the imidization step suggests that it is associated with ODA end groups which are structurally unaffected by cycloimidization. To test this hypothesis we introduced 99% ^{15}N-labeled ODA (designated ODA*) into I in an amount of 20 wt % of the weight of solids in the original solution. This was done with the solution at room temperature. The solution was immediately spun onto the water, dried at 90 °C for 5 min, and introduced into the SSIMS vacuum system. We will refer to this mixture as III in subsequent discussions. This procedure, which will be discussed in further detail below, prevents incorporation of significant amounts of ODA* into the polymer through equilibration in solution. It does not, however, rule out other reactions leading to ODA incorporation. The stoichiometric ratio of ODA:ODA* in III is 1:0.42.

Table I
Ratios for Integrated Peak Intensities at 109/108 (A) and 27/26 (B) for the Curves of Figures 2c,d and 3c,d[a]

	109/108	27/26
III, unimidized	7.2 ± 2.5	0.43 ± 0.02
III, imidized	0.38 ± 0.03	0.31 ± 0.01

[a] The stability of the ratio B through the imidization step and the large change in the ratio A are discussed in the text.

Sample III was prepared because of the following observation: In the negative SSIMS spectrum of I (Figure 3a), the peak at 26 ($C^{14}N^-$) is not accompanied by a peak of significant intensity at 27 ($C^{15}N^-$). Likewise the negative SSIMS spectrum of II shown in Figure 3b shows no signal intensity of significance at 26 relative to the peak at 27. The ratio of the peak areas for the 27 and 26 peaks is therefore a measure of the ratio of $^{15}N/^{14}N$ at the surface of a polyimide film containing a mixture of the nitrogen isotopes.

Using the intensity of the peak at 26 as the normalization factor and the abundance of ^{15}N- and ^{14}N-containing fragments, given by the ratio 27/26, we may now establish the structural makeup of the polymer surface. The results of this experiment are shown in Figures 2c,d and 3c,d. Table I summarizes the result of integrating and taking the ratio of areas for the peaks at 109:108 and 27:26 for these spectra. From Table I, it is clear that addition of ODA* to I has skewed the ratio of 109:108 strongly to 109 for the unimidized film (Figure 2c), in a ratio far exceeding the expected stoichiometric ratio of ODA*:ODA. Figure 3c shows the negative SSIMS spectrum for III before imidization. Integration of the peaks at 27 and 26 reveals that in this case the ratio $^{15}N:^{14}N$ detected at the surface is very close to the expected stoichiometric ratio abundance of ODA*:ODA, indicating that the skewing of Figure 2c toward 109 is not due to excessive surface segregation of ODA* monomer. All this strongly supports the proposal given above that it is ODA end groups to the PMDA-ODA polymer as well as breakage at the ether bond of the unincorporated ODA* monomer that generate the signals at 108 and 109, respectively. Of course, most of the ODA is incorporated into the polymer backbone whereas most of the ODA* is either free or reacted on only one side. Therefore, even though the absolute ODA concentration is much higher than the ODA* concentration, the amount of the latter present in a configuration resembling that of end groups vastly outnumbers the former. This accounts for the large enhancement of 109 over 108. The sensitivity of these measurements to end groups of the polyimide is consistent with SSIMS measurements of other polymer systems where side chains and pendant groups are found to contribute characteristic features of the SSIMS spectra.[2-5]

Further information is provided by the impact of imidization on the SSIMS spectra of III. Figures 2d and 3d shows that imidization alters the observed $^{15}N:^{14}N$ ratio only slightly, while the ratio of 109:108 undergoes a complete reversal, with the result that the observed ratio is close to the starting isotopic abundance ratio. This shift indicates that the ratio of ODA*:ODA fragments produced from end groups is driven toward the stoichiometric ratio of ODA*:ODA. Efficient retention of ODA* at the surface at temperatures well above the volatilization temperature in vacuo suggests that reaction of the free ODA* amine with the polymer and not simple physical trapping during imidization is the mechanism for this observed retention

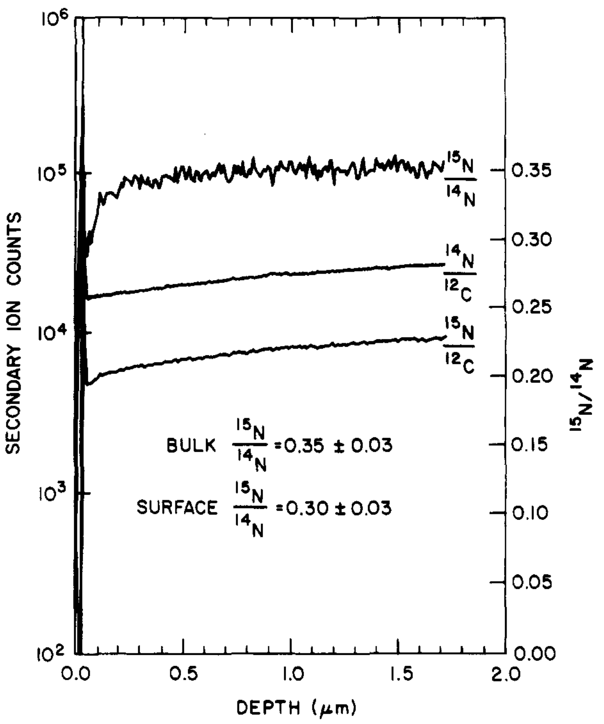

Figure 4. Dynamic SIMS depth profile of III after imidization. The ratio of ^{15}N to ^{14}N is invariant for depths greater than 0.2 μm. The profile shows depletion of ODA and ODA* toward the surface of the film in the form of a decreasing nitrogen to carbon ratio.

of ODA* in the cured film. The experiment described above was repeated with ^{15}N-labeled PMDA–ODA II and unlabeled ODA. The results were analogous to those described above, with approximate reversal of the ratios quoted, in accordance with the reversed roles now played by the labeled and unlabeled ODA groups present.

The above description of curing for PMDA–ODA polyimide films containing excess free amine based on SSIMS results is predictive of macroscopic changes within the cured films that should be observable with other analytical techniques. In parts IIIc and IIId we will show that other analytical methods yield results that are consistent with the above-presented picture.

(c) Dynamic SIMS. Figure 4 shows a SIMS sputter depth profile through the polyimide film III after imidization. The ratio of ^{15}N:^{14}N at the surface of the film is (0.30 ± 0.03:1). This is in excellent agreement with that of Figure 3d shown in Table I. The ratio of ^{15}N:^{14}N at a depth greater than 0.2 μm is essentially constant at (0.35 ± 0.03:1). This is an indication that trapping of ODA during imidization is continuous from the surface through the bulk of the film and that during imidization labeled and unlabeled ODA are behaving in a manner that is indistinguishable. The observed steady decrease in the nitrogen to carbon ratio toward the surface of the film as well as the slight decrease in the ratio of ^{15}N:^{14}N at the surface will be addressed below.

(d) TGA and FTIR. Delineation of the reaction pathway leading to such large-scale incorporation of excess ODA into the polymer, as indicated above, is of interest since it permits a more complete picture of the link between the highly surface-sensitive results provided by SSIMS and the more conventional bulk methods employed to characterize organic systems and reactions.

Figure 5 shows the changes occurring in the Fourier transform infrared (FTIR) spectra for PMDA–ODA having 0, 20, and 50 wt % excess ODA added followed by film casting on KBr disks and heating for 5 min at 90 °C on a hot plate. On a molar basis, addition of 20 and 50 wt % of free ODA corresponds to a ratio of carboxylic acid to amine groups of 7:1 and 3:1, respectively. Concomitant with a decrease in the carbonyl stretch at 1720 cm^{-1}, compared to the unadulterated polymer, is an increase in the peak at 1659 cm^{-1}. Similar behavior is observed when a monofunctional amine such as 4PA is used instead of ODA.

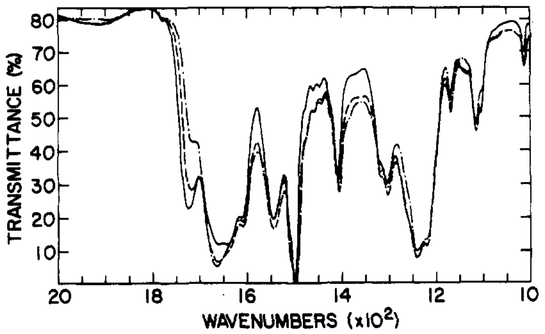

Figure 5. FTIR spectra of PMDA–ODA PAA containing 0 wt % (—), 20 wt % (- - -), and 50 wt % (-·-) of excess ODA after heating for 5 min at 90 °C.

The observed shift of the carbonyl band may be due to polyamate formation (see also below). The carboxylate anion absorption was found by Lee and co-workers to be at 1608 cm^{-1} for PMDA–ODA polyimide that was ring opened by reaction with KOH.[9] Upon protonation using dilute HCl this peak shifts to 1727 cm^{-1}, characteristic of the carboxylic acid group in PAA which is devoid of complexing solvent.[10] In a PAA film cast from NMP and subsequently heated to 90 °C, there is still NMP remaining, which is complexed with the carboxylic acid group.[11-13] ODA as the stronger base should replace the NMP in the complex. The overall shift in the IR spectrum, presumably occurring upon this exchange, cannot be predicted.

The relationship between the degree of polyamate formation of PAA with ODA and shifts in the FTIR spectra in the carbonyl region has not been established. However, the direction of the shift to lower wavenumbers is consistent with some degree of hydrogen bonding occurring. Another possibility that would lead to similar shifts in the spectra is diamide formation occurring by nucleophilic attack of the excess amine on the acid moiety.

Figure 6 shows the TGA plot for PMDA–ODA films with and without added ODA. Films were prepared on glass slides and baked for 10 min on a hot plate, prior to film removal and analysis. PMDA–ODA itself shows loss of water and NMP which accompanies imidization, to be at its maximum rate of approximately 180 °C with dehydration virtually complete by 300 °C.[11,14,15] By contrast, samples with 20 wt % added ODA exhibit a second region of weight loss whose maximum rate occurs at 340 °C with continued slow weight loss out past 420 °C.

TGA analysis of ODA itself shows the onset of rapid weight loss at 190 °C with only a few percent of material remaining after 260 °C (Figure 6). This indicates that volatilization of unreacted ODA should occur at temperatures below 340 °C. However, the loss of free ODA might be impeded by the polymer matrix and thus might occur at temperatures greater than that of the neat compound. This possibility has been addressed by the addition of large amounts (1:1 molar ratio of H_2N:COOH groups) of ODA. In this case one observes a new region of rapid weight loss at a temperature almost identical with that of pure ODA, indicating that the polymer matrix does not substantially inhibit the loss of free ODA (Figure 6).

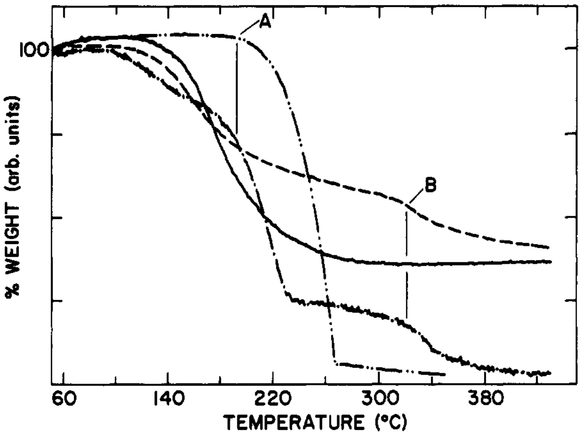

Figure 6. TGA trace of PMDA-ODA PAA containing 0 wt % (—), 20 wt % (- - -), and 100 wt % (- · -) of excess ODA. Also shown is the TGA data for bulk ODA (- · ·). Feature A, the onset of volatilization for bulk ODA, is also observed in the film containing 100 wt % excess of ODA. Feature B, presumably due to diamide curing and volatilization of ODA is visible in both the 20 and 100 wt % curves. Heating rate is 10 °C/min under nitrogen.

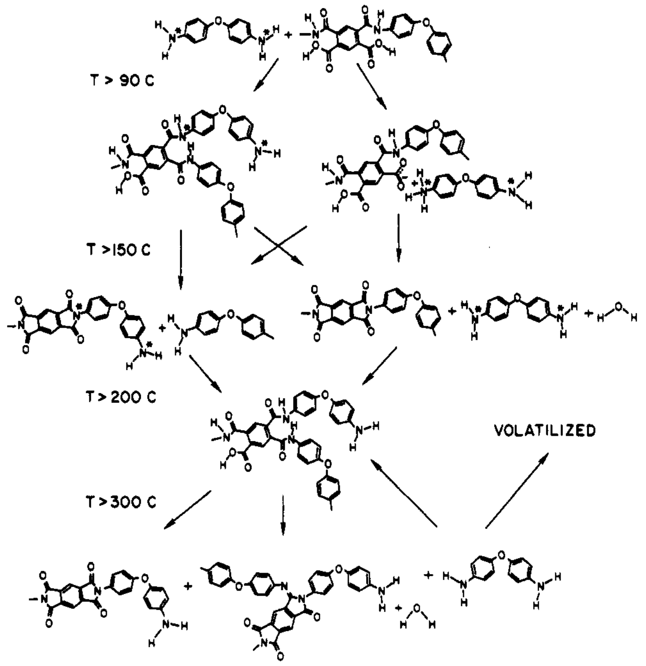

Figure 7. Reaction scheme for curing of PMDA-ODA films containing excess ODA. The configurations examined by SSIMS are those at $90 < T < 150$ °C and 300 °C $< T$. No attempt is made to distinguish between ^{14}N- and ^{15}N-labeled species for 200 °C $< T$ since scrambling renders them indistinguishable.

The second weight loss at about 320 °C exhibited by PMDA-ODA films containing free aromatic amine warrants an analysis of the possible reactions occurring during the curing step. As indicated above, the first and fastest reaction will be an acid-base reaction leading to complexation of the free acid. Since FTIR data admit of the possibility of diamide formation for films heated to 90 °C, both of these possibilities are shown in the reaction scheme of Figure 7. The next reaction is attack of the carboxylate or amide group by the excess amine and subsequent exchange of the amine participating in the original amic acid (Figure 7). The exact mechanism of this reaction is not known; however, it does not involve anhydride formation.[16] This reaction leads to chain cleavage, i.e., lowering of the molecular weight of the PAA. These reactions can be observed by following the viscosity of PAA solutions before and after addition of excess ODA.

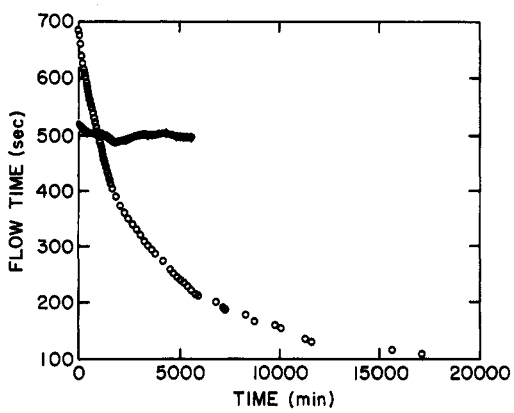

Figure 8. Solution viscosity data. The closed circles are for a solution containing 0 wt % of excess ODA, e.g., I. The open circles are for a solution containing 20 wt % of excess ODA added to the solution at $t = 0$, e.g., III. Both solutions were maintained at 30.5 ± 0.1 °C during the experiment.

The flow time change (which is directly proportional to the viscosity change) with time has been measured for a PAA solution without (closed circles) and with (open circles) excess ODA (Figure 8). The viscosity of the former stays essentially constant; the observed variations are due to temperature fluctuations of ±1 °C. The strong temperature dependence of the viscosity is due to the strong interaction between PAA and NMP.[12]

In the presence of excess ODA two effects are observed. Initially, the viscosity of the solution increases. This is caused by the acid-base interaction described above. This viscosity increase is due to coil expansion effected by the repulsion of the charged carboxylate groups.[17] Secondly, there is a drop in the viscosity over time at the fixed temperature of 30.5 °C. This effect is ascribed to chain scission, which leads to molecular weight lowering, chemical bonding of the attacking amine, and, thus, formation of new ODA end groups (two per chain scission). It must be noted that the time scale for ODA incorporation is such that this mechanism is not operative for sample III, where only 5 min elapsed between addition of excess ODA and film spinning and drying.

Upon heating a PAA system containing added ODA, the chain scission/ODA incorporation reaction rate increases.[10] The reaction proceeds even in dried films at temperatures as high as 145 °C.[18] Therefore, it is not surprising that excess ODA containing dried PAA (as well as cured polyimide) films become very brittle and crack easily in marked contrast to the usually obtained tough films.

Heating of PAA films containing excess ODA above 120 °C opens up a number of further reactions. At approximately 120 °C the NMP/PAA complex falls apart, and cycloimidization proceeds at an appreciable rate[12,19] above 150 °C. The decomplexation temperature of the ODA/PAA complex is not known but is expected to be higher. In any case the TGA data (Figure 6) show that the onset of imidization related weight loss occurs at approximately the same temperature (115–125 °C) at a heating rate of 10 °C/min (Figure 6) for both unadulterated PAA and PAA with 20 wt % of excess ODA. Cycloimidization is accompanied by formation of amine end groups and anhydride (reversal of the amic acid formation).[20,21] The anhydride reacts eventually either with amine end groups or in the presence of excess ODA with the latter. Ultimately, all amic acid groups are converted to imide groups. These, in turn, can react with amine groups at temperatures above 200 °C to form diamide compounds[22,23] (see Figure 7). At temperatures above 300 °C amine groups can react in yet another way with polyimides (Figure 7). At such temperatures Schiff bases can be formed between the amine groups and the imide carbonyl groups, leading to cross-linking of the polyimide.[24]

It is assumed that the appearance of a second region of weight loss in the TGA spectra at 340 °C (Figure 6b) is due to subsequent volatilization of ODA upon conversion of diamides to imide (Figure 7). At these high temperatures there would be sufficient energy for subsequent reactions available to free ODA of the types shown in Figure 7. This would lead to a scrambling of ^{15}N- and ^{14}N-labeled ODA groups. With the exception of the near-surface region, the ratio of ^{15}N to ^{14}N, as determined by dynamic SIMS and shown in Figure 4, is constant throughout the film, consistent with a scrambling mechanism. The SIMS depth profile of Figure 4 shows a steady decrease in the ratio of nitrogen to carbon as the surface of the film is approached, consistent with a mechanism involving loss of ODA via diffusion. The slight decrease in the ratio of ^{15}N to ^{14}N at the surface of the film is probably an artifact of more efficient diffusion loss of free ODA from the surface of the film at the start of imidization.

The reaction scheme detailed in Figure 7 should result in observable changes in the average molecular weight of cured films containing excess aromatic amines. It is well-known[25] that fully cured (300 and 400 °C cured) PMDA–ODA films dissolve ready in H_2SO_4, allowing the molecular weight to be analyzed via viscometry. For standard PMDA–ODA (e.g., I) molecular weights were found to be around 30 000. Excess ODA containing PMDA–ODA films cured to 300 °C also dissolved readily in H_2SO_4. These solutions, however, were very dark and turbid compared with the clear, amber standard PMDA–ODA/H_2SO_4 solutions. The viscosity of the former solution was very low, indicating, as expected, severe molecular weight degradation. Upon curing to 400 °C, however, excess ODA containing PMDA–ODA was not attacked by H_2SO_4 even at slightly elevated temperatures. The solvent remained colorless after several weeks. This behavior could be due to polymer cross-linking via Schiff base formation, as shown in Figure 7.

IV. Conclusions

In this study the positive and negative SSIMS spectra of PMDA–ODA before and after imidization were analyzed. Isotopically labeled materials were used to deduce the structure and source of secondary ions produced by this material. A signature for imidization of the surface layer is given by disappearance of fragment ions attributed to ODA and PMDA end groups from the positive SSIMS spectrum. In addition to confirming our speculations as to the source of secondary ions, we found that addition of free ODA dramatically increases the amount of ODA end groups after curing. This, in concert with observations that include invariance of the ^{14}N to ^{15}N ratio with film depth, appearance of a new high-temperature weight loss region in the TGA of films containing excess ODA, and an overall molecular weight reduction (as determined by viscosity analysis), lends credence to a cascading mechanism of excess amine incorporation and equilibration throughout the film. Details of this mechanism, such as favored pathways and rates of reactions, are the subjects of an ongoing study. Overall, a comprehensive surface and bulk picture of PAA curing in the presence of excess ODA has been proposed.

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Registry No. (ODA)(PMDA) (copolymer), 25038-81-7; (ODA)(PMDA) (SRU) polyimide, 25036-53-7; (ODA)(PMDA) (SRU) polyamic acid, 9043-05-4; ODA, 101-80-4.