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Curing studies of the *meta*, *para* and 50/50 mixed isomers of the ethyl ester of 4,4′-oxydianiline/pyromellitic dianhydride polyamic acid

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The cure behaviour of the ethyl ester derivatives of 4,4′-oxydianiline (ODA)/pyromellitic dianhydride (PMDA) poly(amic acid) to the corresponding imide was investigated using isothermal and dynamic mass spectroscopy, *FT*-Raman spectroscopy and density gradient column analysis. Both the rate of cure and per cent conversion were dependent on the isomer composition, occurring in the order *para* > *meta* > 50/50 mixed isomer at temperatures below 275°C. This order holds both for amorphous solid samples and samples cast from *N*-methylpyrrolidone (NMP) solution. With increasing isothermal temperatures or ramp speeds of the dynamic mass spectroscopy scans, the imidization rates and per cent conversions of all three isomers converged. The cure kinetics were also found to be dependent on the presence of solvent. The temperature of the maximum rate of cure in the dynamic mass spectroscopy data decreased with increasing solvent content and the temperature range over which imidization occurred narrowed by 300% for samples cast from NMP solution compared with solid samples precipitated from solution. The presence of NMP directly affected the cure by plasticizing the films. In addition, the narrowing of the imidization temperature range occurred even if there was complete removal of NMP before the onset of imidization, suggesting that the morphology of the films or the orientational alignment of the chains was changed by prior annealing in NMP, perhaps due to mesophase formation. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Aromatic polyimides are an important class of high temperature polymers useful as interlayer dielectrics in electronic packaging applications, as structural materials and in membranes. Since most polyimides are insoluble, they are often formed in a two step process involving the synthesis of a processable poly(amic acid) precursor[1], followed by an intramolecular ring closure reaction to form the polyimide (*Figure 1*). Increased hydrolytic stability and solubility are achieved when the alkyl ester derivatives instead of the poly(amic acids) are used[2–5]. The ethyl ester[6], tert-butyl ester[4] and other alkyl and alkylsilyl ester[7] derivatives of oxydianiline/pyromellitic dianhydride poly(amic acid), and several *para*-linked aromatic poly(amic ethyl esters)[8] have been prepared and investigated.

The kinetics of the imidization reaction for poly(amic acids) have been investigated in solution[9,10] and in the solid state[11]. In the solid state, the location of the glass transition temperatures, T_gs, of the parent poly(amic acids) as well as the increase in T_g with increasing conversion slowed down the imidization kinetics[12]. Solvent, which acts as a plasticizer to reduce T_g, increased the rates of imidization for the pyromellitic dianhydride/4,4′-oxydianiline (PMDA/ODA) based poly(amic acids)[13,14]. In the case of low molecular weight model compounds, the crystal structure influenced the cyclization rate[15,16]. Theoretical considerations have indicated that the imidization reaction should also depend on the stereoisomerism of the poly(amic acid), with complete conversion achieved only for the *para* isomer, decreasing to 91% for the 50/50 isomer and 82% for the pure *meta* isomer[17]. Supporting experimental evidence has been reported in the case of the poly(amic alkyl esters), which can be more easily synthesized as the pure *para*, pure *meta* or 50/50 mixed isomers[18].

The formation of a mesophase might also be expected to affect the imidization kinetics. However, not many poly(amic acids) or poly(amic esters) exhibit this behaviour at the concentrations at which they are soluble. In the case of PMDA/ODA poly(amic acid), poly(4,4′-oxydiphenylene pyromellitamic acid) did not exhibit lyotropic behaviour[19–21], although highly parallel alignment and nearly fully extended local conformations were observed in films containing 30 wt% solids in NMP[20]. The lack of liquid crystallinity in the PMDA/ODA system, which is a 50/50 mixed isomer, was attributed to the lack of isomeric purity.

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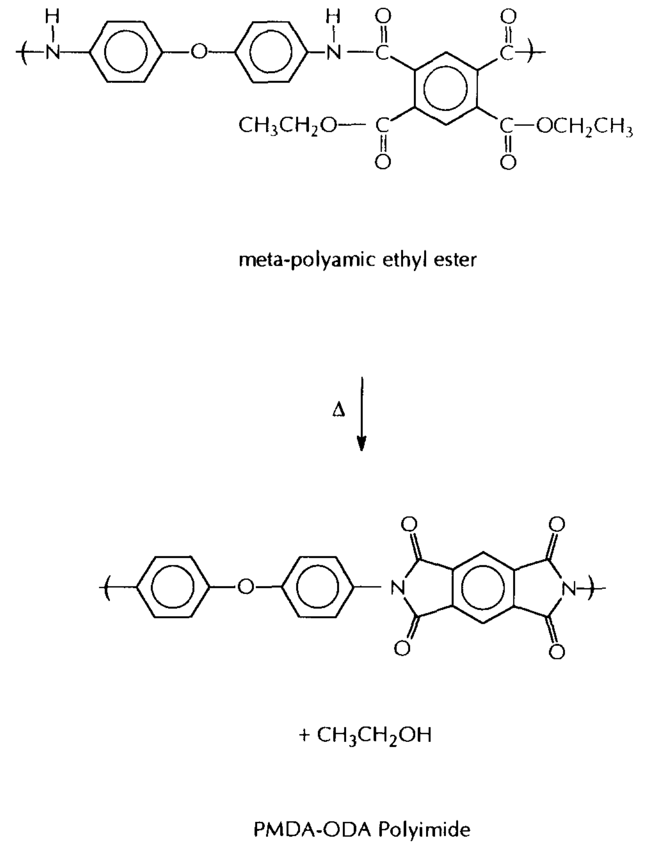

Figure 1 The structure of the *meta* poly(amic ethyl ester) and resultant polyimide

Here we investigate the curing reactions of the polymers formed from the *para*, *meta* and 50/50 mixed isomers of the ethyl diester of pyromellitic acid and 4,4'-oxydianiline (also called PMDA/ODA based poly(amic ethyl ester)), using mass spectroscopy, *FT*-Raman spectroscopy and density gradient column analysis. The precipitated powders, or these same samples spun or doctor-bladed from *N*-methylpyrrolidone (NMP) solution were investigated in order to elucidate the effects of solvent, thermal annealing in the presence of solvent, and stereoisomerism. Mass spectroscopy was used to monitor the elimination of volatiles, namely ethanol and solvent (NMP) in this case. *FT*-Raman spectroscopy data provided information directly on the formation of the polyimide.

EXPERIMENTAL

Synthesis

Samples of *meta*, *para* and 50/50 mixed isomers of the ethyl ester of oxydianiline/pyromellitic dianhydride polyamic acid were synthesized from diethyl dihydrogen pyromellitate or isomerically pure diethyl dihydrogen pyromellitate. The latter was prepared using a procedure similar to that reported by Bell and Jewell[22] with the following modification: After most of the *para* isomer had been selectively removed by slow concentration in excess ethanol, the remaining ethanol was stripped and the residue twice recrystallized from *n*-butyl acetate. The *meta* isomer was obtained in greater than 90% isomeric purity using this procedure. The corresponding diacyl chloride derivatives (of the isomerically pure diethyl dihydrogen pyromellitate or the 50/50 mixed isomer) were prepared by reaction of the diacid diester with oxaloyl chloride (a 1/1 weight ratio of oxaloyl chloride to diacid diester to ensure excess reagent) in ethyl acetate at about 50°C. Reaction was facilitated by addition of several drops of dimethyl formamide (DMF), which greatly accelerated the chlorination. Once gas evolution stopped the reaction was continued for another 3 h and the ethyl acetate stripped under vacuum. *meta*-Diethyl pyromellitate diacyl chloride and the 50/50 mixed isomer of diethyl pyromellitate diacyl chloride were recrystallized from hexane, whereas *para*-diethyl pyromellitate diacyl chloride was best recrystallized from cyclohexane.

The corresponding isomerically pure or 50/50 mixed isomer poly(amic ethyl ester) samples were then synthesized by low temperature solution polycondensation in freshly distilled *N*-methylpyrrolidone (NMP), utilizing sublimed ODA and equivalent amounts of pyridine (based on acyl chloride groups) to scavenge the liberated HCl. The polymerizations were conducted at a concentration of about 10 wt% with a stoichiometric imbalance, *r*, of 0.985 using the aromatic diamine in excess. The temperature was controlled via an external ice/water bath and the mixture was stirred for 12 h after acyl chloride addition was complete. Precipitation of the polymerization mixture in water and thorough washing with water followed by ethanol and ethyl acetate yielded a light yellow powder after vacuum drying at 50°C for 24 h.

Sample preparation

The samples were studied either (i) as directly obtained after precipitation and washing (henceforth called solid samples) or (ii) as films, cast or spun from NMP solution. The cast films were made by doctorblading concentrated solutions of the polymers in NMP onto glass slides. The concentrations (25–35% *meta*, 15–20% *para* and 25% 50/50 isomer) were approximately the maximum amount of polymer that would go into solution without heating. The viscosity of the *para* solution was greater than that of the *meta* or 50/50 mixed isomer solutions. The doctorblade was set at a 100 μm setting, producing films that were approximately 30 μm thick after imidization. Films were spun using a Headway Research photoresist spinner. The films for the density gradient studies were spun from concentrated solutions at 1000 rpm onto glass slides. The films for the mass spectroscopy studies were spun from 10% NMP solutions at speeds between 1000 and 6000 rpm; the films so produced were relatively thick (10–15 μm). Orientational effects were not expected under these conditions. Excess NMP was removed from the spun or cast films by vacuum drying at temperatures below 100°C, producing films below their glass transition temperatures.

Both the cast and spun films were cured off of the substrate in order to eliminate effects of substrate orientation. Previous studies of PMDA/ODA polyamic acids indicated that imidization of films in contact with a substrate produced substantial orientation of the PMDA/ODA molecules parallel to the surface[23,24], but films cured off of the substrate[25,26] did not exhibit orientation.

The *meta*, *para* and 50/50 mixed isomer solid samples for the *FT*-Raman studies and the spun films for the density gradient studies were cured in the mechanical convection oven of a gas chromatograph which had excellent thermal stability (±0.2°C). The oven was brought to temperatures of 152, 227, 235 and 247°C and the samples cured for various lengths of time ranging from 10 min to 70 h and then quenched in liquid nitrogen. The temperatures investigated were selected to minimize errors in cure time due to the time requirements of bringing the samples to the preset temperature. Insertion of the samples caused a slight drop in the oven temperature (due to opening the oven door), but temperature reequilibration to the preset temperature occurred after less than 30 s. One hour runs at temperatures up to 300°C were also obtained in an inert atmosphere.

Characterization

The solid samples were investigated using mass spectroscopy (m.s.) and *FT*-Raman spectroscopy, the cast samples by m.s. and the spun samples by m.s. and density gradient column analysis. Constant heating rate and isothermal m.s. data were obtained on a Hewlett-Packard Model 9133 Mass Spectrometer. The total ion chromatogram and that of a characteristic fragment of ethanol (45 amu) were monitored for all of the samples. A characteristic fragment of NMP (57 amu) was also monitored for the cast and spun films. The ethanol ion chromatograms were used to compare rates of imidization for the samples investigated, since for each ring closure reaction, one molecule of ethanol was given off. The dynamic ethanol ion chromatograms were characterized by the temperature at which the maximum evolution of ethanol occurred, $T_{\max}$, and the full width at half height, $\Delta T_{1/2}$.

The samples were dried or annealed below 120°C in the m.s. because above this temperature imidization was initiated. The samples were heated in the m.s. to a final temperature which was chosen to include as much of the ion chromatogram peaks as possible; the highest temperature measured was 320°C. Sample sizes varied and absolute count rates were not determined, so it was not possible to compare absolute percent conversions for the different isomers cured under identical thermal treatments.

Dynamic mass spectroscopy scans were run at speeds of 2, 5, 10, 20 and 25°C min^{-1}. A maximum temperature of 320°C was attained after holding the samples at temperatures between 90–120°C for 10–60 min in order to remove residual solvent. For the isothermal m.s. scans, the samples were heated at 100°C for 30 min, ramped to 10–15°C below the designated isothermal temperature at 60°C min^{-1} and then heated to the isothermal temperature at 10°C min^{-1}. This ramping sequence was employed in order to heat the sample quickly to the preset isothermal temperature while avoiding the temperature overshoot which occurred at the highest heating rate. Isothermal temperatures of 225, 235, 255, 275, 300° and 350°C were investigated; it took between 3.3 and 4.5 min to reach the isothermal temperatures from 100°C. The total run times of the chromatograms after the initial 30 min heat treatment were 1.5 h.

FT-Raman spectra were measured on an instrument described previously[27]. Spectra were acquired at 8 cm^{-1} resolution with 1.0 W of laser power (1.064 μm) at the sample. Scanning times of the order of 45 min were needed to obtain a spectra, so that *in situ* time resolved measurements were not possible. Curing times were chosen to permit spectral observation of the cure using *FT*-Raman spectroscopy.

A density gradient column was constructed following the procedure of Tung and Taylor[28].

RESULTS

Mass spectroscopy data

Solid samples. Figure 2 shows the ethanol ion chromatogram for the solid samples of *para*, *meta*, and 50/50 isomers of the diethyl ester of PMDA/ODA, heated at 2°C min^{-1}. The total ion chromatograms

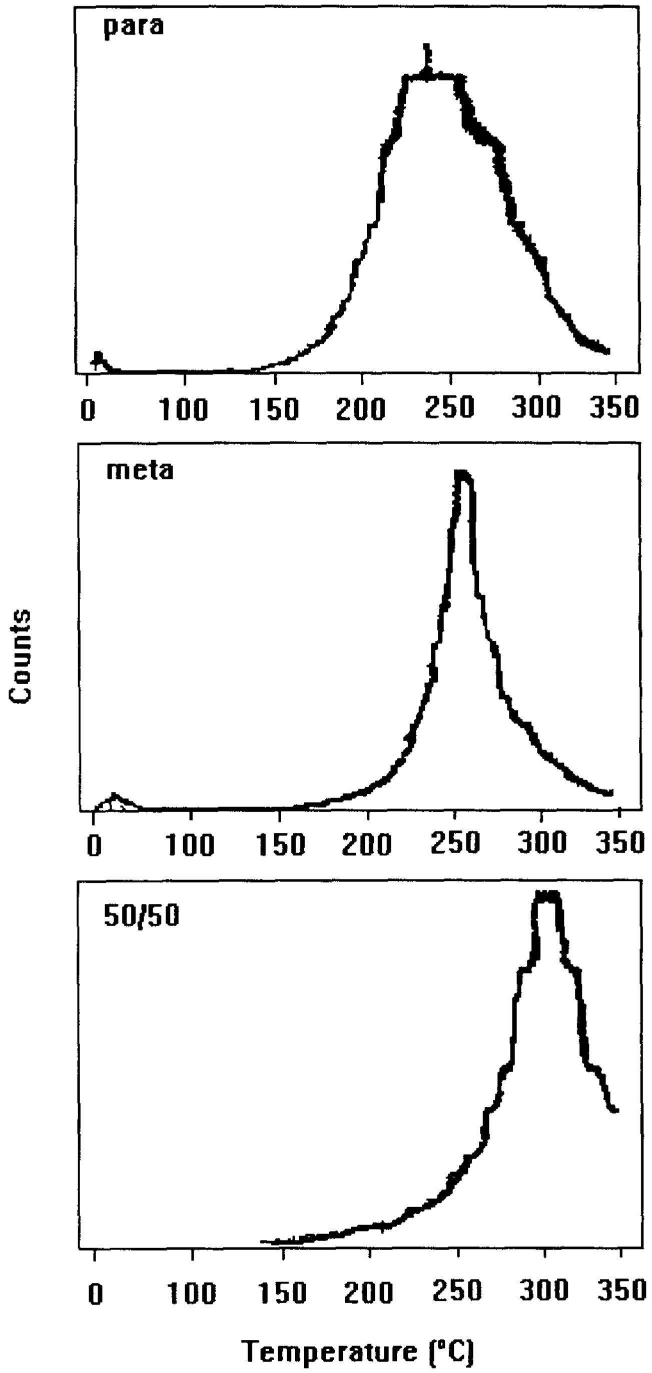

Figure 2 Ethanol ion chromatograms of the solid samples of *meta*, *para* and 50/50 mixed isomers of the diethyl ester of PMDA/ODA heated at 2°C min^{-1} in the mass spectrometer; samples were first heated at 100°C for 10 min in the mass spectrometer

Table 1(A) Mass spectroscopy of solid samples of PMDA/ODA PAAES

	Heating conditions in mass spec.			
Sample	Treatment	Rate ($^{\circ}C\,min^{-1}$)	T_{max} ($^{\circ}C$)	$\Delta T_{1/2}$ ($^{\circ}C$)
Para	10 min @ 100°C	5	285	65
Meta	10 min @ 100°C	5	295	30
50/50	10 min @ 100°C	5	300	55
Para	30 min @ 100°C	2	240	80
Meta	30 min @ 100°C	2	252	33
50/50	30 min @ 100°C	2	285	60

Table 1(B) Mass spectroscopy of solid samples of PMDA/ODA PAAES

Sample	Rate ($^{\circ}C\,min^{-1}$)	T_{max} ($^{\circ}C$)	$\Delta T_{1/2}$ ($^{\circ}C$)
Para	25	318	45
Meta	25	—	—
50/50	25	308	45
Para	20	294	44
Meta	20	298	27
50/50	20	310	48
Para	10	266	52
Meta	10	285	29
50/50	10	271	42
Para	5	245	63
Meta	5	262	24
50/50	5	276	50
Para	2	226	65
Meta	2	247	30
50/50	2	275	60

Samples were heated for 30 min at 100°C in the mass spectrometer prior to the temperature ramp. T_{max} and $\Delta T_{1/2}$ values reported here were collected under different vacuum conditions than the other m.s. data in this paper

(TIC) for the samples were identical in shape to the ion chromatograms for ethanol and analysis of the contributing mass spectra yielded no other components, except at very short times, where small amounts of residual solvent (water, ethyl acetate and ethanol) were eliminated. The chromatograms for the *para*, *meta*, and 50/50 mixed isomer solid samples were all roughly symmetric in shape but differed both in the values of the peak maxima, T_{max}, and halfwidth, $\Delta T_{1/2}$. The data for samples run at different scan rates is presented in *Tables 1A* and *B*. Note that the values reported in *Table 1B* were obtained under different mass spectrometer vacuum conditions to the other m.s. data in this paper. While these data cannot be compared with other data in this paper, trends within each table are valid. The trend in the location of the peak maxima for the elimination of ethanol from the *para*, *meta* and 50/50 mixed isomers was T_{max} (50/50) > $T_{max}(meta)$ > $T_{max}(para)$, and the halfwidths of the chromatograms occurred in the order $\Delta T_{1/2}(para) \geq \Delta T_{1/2}(50/50) > \Delta T_{1/2}(meta)$.

When the data for each isomer were compared as a function of heating rate, the value of T_{max} increased with increasing heating rate. Heating at the slower rates broadened the ethanol ion chromatograms slightly for the *para* isomer. The peak shapes, T_{max} and $\Delta T_{1/2}$ for the three isomers were clearly different for the $2^{\circ}C\,min^{-1}$ ramp, but converged to more similar values at the faster heating rates: T_{max} for the three isomers were spread over 49°C for the $2^{\circ}C\,min^{-1}$ ramp but were within 21°C for the $20^{\circ}C\,min^{-1}$ and $25^{\circ}C\,min^{-1}$ ramps.

Figure 3 (*A*, *B*) compares the ethanol ion chromatograms of the *meta*, *para* and 50/50 mixed isomers at two isothermal temperatures, 225 and 255°C, and data for all six temperatures are reported in *Table 2*. The time at which the isothermal temperatures were reached, t_{iso}, is marked by an arrow on the *meta* ion chromatogram in *Figure 3A*. As t approaches t_{iso}, there is a steep rise in the ethanol counts, reaching a maxima at a time, t_{max}. The values of $t_{max} - t_{iso}$, which are a measure of the steepness of this rise, are reported for the six isothermal runs in *Table 2*. These times were shortest for the *para* isomer, followed by the *meta* isomer, and longest for the 50/50 mixed isomer. With increasing temperature t_{max} approached t_{iso}. The chromatograms were also asymmetric, with the counts at $t > t_{max}$ falling off more slowly than the rise at $t < t_{max}$. The chromatograms were most asymmetric at low temperatures, with the ethanol counts dropping most steeply for the *para* isomer, followed by the *meta* isomer, and significantly more slowly for the 50/50 isomer. One measure of the decay rate of the ion chromatograms is the time it takes for the ethanol counts to reach one half of their maximum value, $t_{1/2}$. This time, compared to t_{max}, $(t_{1/2} - t_{max})$ is reported in *Table 2* for the six temperatures studied. The shortest times occurred for the *para* isomer, and were longest for the 50/50 mixed isomer. With increasing temperature, especially between 300 and 350°C, the data for all three isomers converged.

Effects of solvent

Cast films. Mass spectroscopy results obtained on cast films of the *meta* and *para* ethyl esters of PMDA/ODA are listed in *Table 2*. As was the case for the solid polymers, when samples were compared under identical annealing and heat treatment conditions, e.g. *Table 3*, #1 and #4, #2 and #5, #3 and #6, T_{max} for the ion chromatogram of ethanol occurred in the order: $T_{max}(meta) > T_{max}(para)$; and $\Delta T_{1/2}$ occurred in the order: $\Delta T_{1/2}(para) > \Delta T_{1/2}(meta)$.

All of the cast polymer films investigated after vacuum drying had residual NMP that could be observed in their TIC's and in the NMP ion chromatogram. Thermal annealing for longer times or higher temperatures in the mass spectrometer removed much of the NMP from the samples, but during the ramping sequence at constant rate in the mass spectrometer to 320°C a second NMP peak was often observed at the temperature of ethanol elimination. The occurrence of NMP after the thermal annealing treatment in both the vacuum oven and mass spectrometer, but before the onset of imidization is indicated in *Table 3*. The elimination of a small amount of NMP at the temperature of imidization is also noted.

Qualitatively, the NMP peak (relative to that of the ethanol peak) was larger for the *para* polymer than for the *meta* polymers. Removal of NMP required longer times or higher temperatures for the *para* isomer compared with the *meta* isomers. NMP could almost completely be removed from the *meta* sample by annealing under vacuum in the mass spectrometer at 100°C for 1 h. Under these conditions, it was not possible to remove all of the NMP from the *para* films. Complete removal of the NMP from the *para* films was affected only after heating for 1 h at 120°C, conditions which also resulted in slight imidization of the sample, as

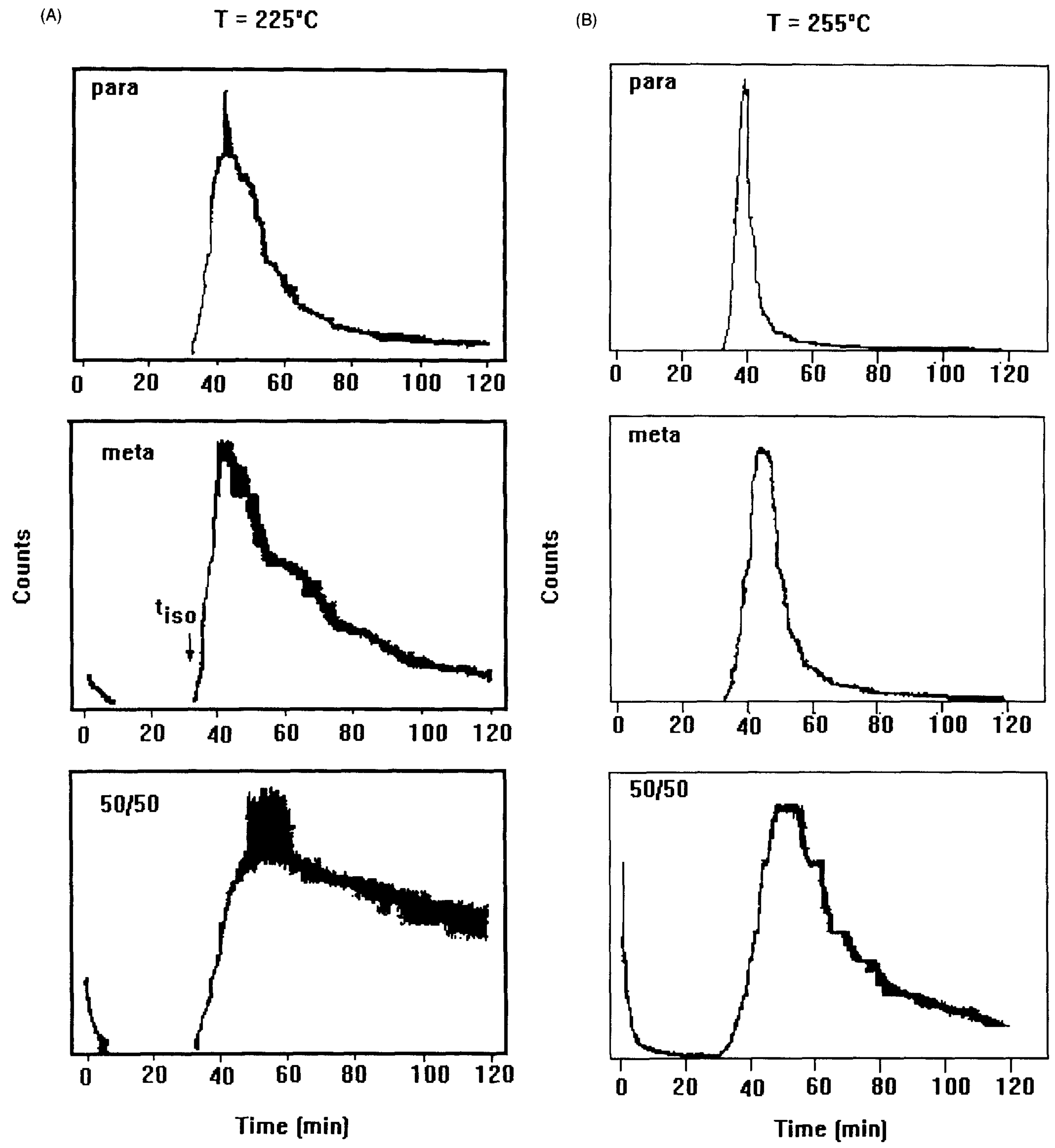

Figure 3 Isothermal ethanol ion chromatograms of the solid samples of *meta*, *para* and 50/50 mixed isomers of the diethyl ester of PMDA/ODA at (A) 225°C and (B) 255°C

detected by the appearance of ethanol fragments in the mass spectrum.

When NMP was present in the films, there was an asymmetry on the low temperature side of the ethanol ion chromatograms that was not observed for the solid samples. This asymmetry was directly correlated with the presence of NMP still in the samples, as indicated by a comparison of the ethanol and NMP ion chromatograms. Imidization, as evidenced by the evolution of ethanol, started sooner when NMP was present.

The most dramatic effects of the presence of NMP were the decrease in T_{max} and the narrowing of $\Delta T_{1/2}$ for

Table 2 $t_{1/2} - t_{max}$ and $t_{max} - t_{isothermal}$ for the isothermal ethanol ion chromatograms of solid samples of PMDA/ODA PAAES

Temperature (°C)	$t_{1/2} - t_{max}$ (min)			$t_{max} - t_{isothermal}$ (min)		
	Para	*Meta*	50/50	*Para*	*Meta*	50/50
225	12	23	70	9	10	21
235	9	17	35	7	14	19
255	3	6	19	4	11	16
275	3	4	9	6	10	12
300	3	3	3	6	9	8
350	2	2	2	—	—	—

Table 3 PMDA/ODA PAAES cast from NMP solution

Sample	Thermal annealing		Occurrence of NMP	T_{max} (°C)	$\Delta T_{1/2}$ (°C)
	Vacuum oven	Mass spec.			
#1 *meta*	1 h, 70°C	10 min, 100°C	yes	275	20
#2 *meta*	16 h, 90°C	10 min, 100°C	yes	260	12
#3 *meta*	16 h, 90°C	1 h, 100°C	no	275	16
#4 *para*	1 h, 70°C	10 min, 100°C	yes	255	25
#5 *para*	16 h, 90°C	10 min, 100°C	yes	247	20
#6 *para*	16 h, 90°C	1 h, 100°C	yes	235	20
#7 *para*	16 h, 90°C	100 min, 100°C	none @ 100°C yes @ $T > 100$°C	240	20
#8 *para*	16 h, 90°C	1 h, 100°C 30 min, 110°C	none @ 110°C yes @ $T > 110$°C	240	20
#9 *para*	16 h, 90°C	1 h, 120°C	no	245	20

Samples were heated in the mass spectrometer at 5°C min^{-1} to 300°C. *Meta*: cast from 25% NMP solution; *para*: cast from 20% NMP solution.

Table 4 Effect of heating rate and annealing time on spun films of *para* PMDA/ODA PAAES

Thermal treatment in mass spectrometer	Rate (°C min^{-1})	T_{max} (°C)	$\Delta T_{1/2}$ (°C)
20 min/100°C, then 10 min/110°C	5	255	50
20 min/110°C	2	230	45
30 min/110°C		220	50
60 min/110°C		215	40
20 min/110°C	1	225	52

Samples spun from 10% NMP solution; spun at 3000 rpm; dried in vacuum oven at 100°C for 45 min; no NMP was observed in scans after thermal annealing.

Table 5 T_{max} and $\Delta T_{1/2}$ for *meta*, *para* and 50/50 mixed isomers of the ethyl ester of oxydianiline/pyromelletic dianhydride polyamic acid spun from 10% NMP solutions

Sample	Spin speed	T_{max}	$\Delta T_{1/2}$	Minutes NMP observed
Para	1000	266	12	95
	2000	275	17	35
	3000	265	15	40
	5000	278	20	30
	6000	288	25	25
Meta	1000	285	12	23
	2000	295	27	14
	3000	278	25	16
	4000	303	45	16
	5000	312	60	18
	6000	312	50	12
50/50	1000	283	16	23
	2000	294	45	19
	3000	282	50	18
	4000	305	55	17
	5000	305	60	—
	6000	305	60	—

Samples were held at 110°C for 60 min and then heated at 5°C min^{-1}.

all of the solution cast isomers relative to the solid samples. (For samples compared under the same mass spectrometer vacuum conditions, i.e. *Tables 1A* and *3*.) The temperature drop in T_{max} was 20–35°C for the *meta* isomer and 30–50°C for the *para* isomer when samples were compared at identical heating rates. The width of the ethanol ion chromatogram, $\Delta T_{1/2}$, narrowed by a factor of 2 to 3, from 30 to 16°C for the *meta* isomer and from 65 to 20°C for the *para* isomer. The decrease in T_{max} and $\Delta T_{1/2}$ in the ethanol ion chromatogram for the solution cast samples occurred both when NMP was present throughout the cure and also when all of the NMP was removed. For example, for *meta* sample #3 and *para* sample #9 from *Table 3*, no NMP was observed at the end of the thermal annealing cycle nor during imidization. Nevertheless, $\Delta T_{1/2}$ was still narrow, 16 and 20°C, respectively, compared with 30 and 65°C for the solid samples.

Table 3 presents the data for the *meta* and *para* isomers in the order of increasing total annealing time. For *meta* (#1 and #2) and *para* (#4, #5, #6) isomers run under these conditions, T_{max} decreased and $\Delta T_{1/2}$ narrowed as the annealing time increased. However, with the complete removal of NMP from the *meta* sample (#3), T_{max} and $\Delta T_{1/2}$ increased. For the *para* sample, it was not possible to remove all of the NMP without reaching a temperature at which imidization began to a small extent, but for this isomer also, removal of the NMP increased T_{max} slightly, by 5°C, from a cure in which NMP was liberated during the imidization reaction (samples #7, #8, $T_{max} = 240$°C) to one in which all of the NMP had been removed (sample #9, $T_{max} = 245$°C). However, T_{max}(245°C) was still relatively low compared with the value for the solid samples (285°C). The small amount of NMP given off did not affect $\Delta T_{1/2}$. Comparison of *para* samples #5–#9 indicated that $\Delta T_{1/2}$ had the same value. The decreases in both T_{max} and $\Delta T_{1/2}$ were thus correlated with the thermal annealing cycle at low temperature (i.e. at 100–110°C) in the presence of NMP.

Spun samples. *Table 4* presents T_{max} and $\Delta T_{1/2}$ data for *para* samples spun at 3000 rpm as a function of heating rate and thermal annealing time in the mass spectrometer. As was the case for the solid samples, T_{max} decreased with decreasing heating rate, but $\Delta T_{1/2}$ remained the same. Annealing the polymers for increasing lengths of time prior to the onset of imidization also had the effect of decreasing T_{max}. The annealing occurred in the presence of NMP, which was still in the samples, as evidenced by its subsequent evolution in the m.s. scans.

Table 5 presents data for the *meta*, *para* and 50/50 mixed isomers as a function of spin speed. The amount of time that NMP was observed in the chromatogram, from

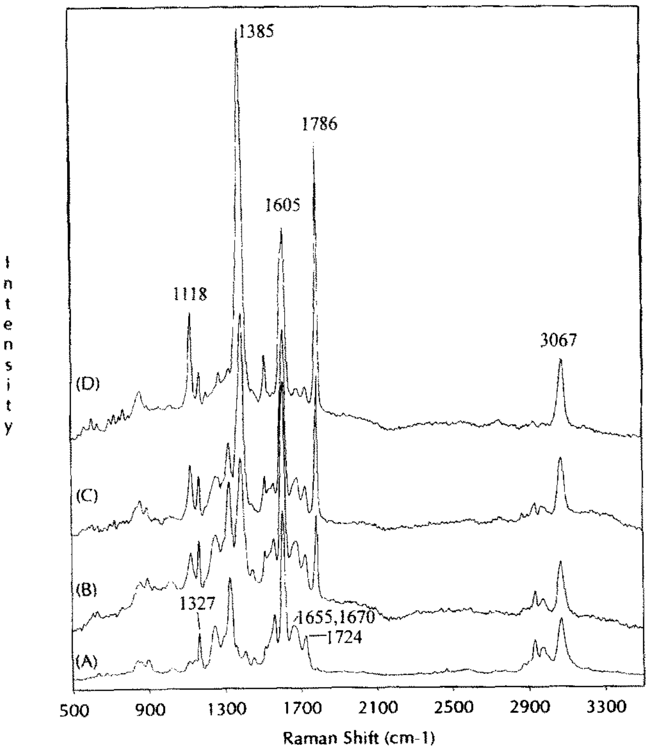

Figure 4 *FT*-Raman spectra of the *para* isomer of the ethyl diester PMDA/ODA polyamic acids: (A) uncured solid sample; (B) 225°C for 15 min; (C) 225°C for 30 min; and (D) 225°C for 20 h

the time the sample reached 110°C is reported in the last column. Several trends are apparent from the data: (i) for each isomer, T_{max} increased with spin speed, reaching values close to the solid state values; the 3000 rpm data appears anomalous for all the isomers; (ii) T_{max} was lowest for the *para* isomer at all spin speeds, but the values of T_{max} were comparable for the *meta* and 50/50 isomers; (iii) $\Delta T_{1/2}$ increased with spin speed; (iv) the amount of NMP observed at a particular spin speed was greatest for the *para* isomer, and comparable for the *meta* and 50/50 isomers; and (v) for all samples except that of the *para* spun at 1000 rpm, NMP was removed from the samples in less than 60 min, which was before the beginning of the 5°C min^{-1} constant heating rate ramping sequence.

Values of T_{max} and $\Delta T_{1/2}$ for the *meta* and *para* isomers spun from solution were closer to the values for the solid samples at high spin speeds which were shown to contain less solvent, and closer to the cast samples at low spin speeds which were shown to contain more solvent. At the lowest spin speed, when most of the solvent was retained in the films, $\Delta T_{1/2}$ was actually lower than the values for the cast samples, and T_{max} was in between the values for the case and solid samples. With increasing spin speed, more solvent was removed during the spinning process, and T_{max} for the *meta*, *para* and 50/50 mixed isomers approached or exceeded slightly the value of T_{max} for the solid samples. In the case of the *para* isomer, $\Delta T_{1/2}$ remained close to that of the cast film, but for the *meta* and 50/50 isomers, $\Delta T_{1/2}$ approached and then exceeded the value of $\Delta T_{1/2}$ for the solid samples. The films spun at higher speeds were thinner, and this may also affect the rate of diffusion of ethanol from the films.

FT-*Raman spectroscopy*

Figure 4A shows the *FT*-Raman spectra of the uncured solid sample of the *para* isomer of the ethyl diester PMDA/ODA polyamic acids. The spectra of the *meta*, *para*, and 50/50 mixed isomers were identical except for slight intensity variations for some of the modes. The frequencies and band assignments are listed in *Table 6*. The characteristic functional group modes of the aliphatic CH_2CH_3 are observed at 2932, 2982 (CH_2 and CH_3 stretches) and 1450 cm^{-1} (CH_2 bend). Shoulders observed at (1300) and (1275) are also due to the aliphatic moiety. The strongest vibrations in the spectra arise from the C–O vibration at 1327 cm^{-1}, the aromatic ring stretching mode at 1605 cm^{-1}, and the carbonyl vibrations of the amide (1655, 1670 cm^{-1}) and the ester (1724 cm^{-1}). The aromatic CH stretch is observed at 3067 cm^{-1}. No evidence was found for imide formation in the beam under these conditions, as evidenced by the lack of the characteristic imide I mode at 1786 cm^{-1}.

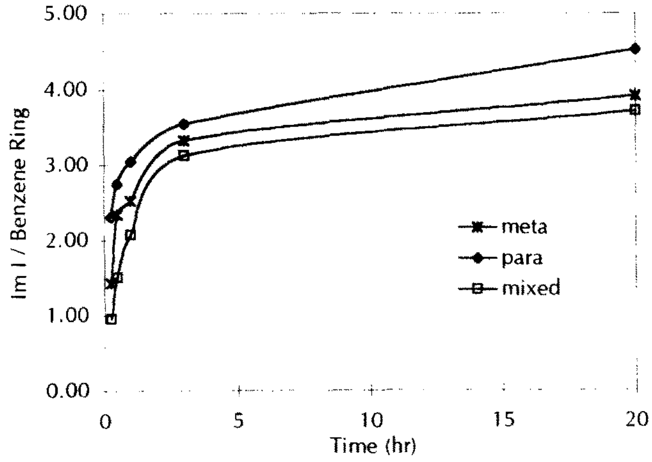

Figure 5 Plots of the imide I mode ratioed to the 1600 cm^{-1} ring vibration for the *para*, *meta* and 50/50 mixed isomers, respectively as a function of time at 225°C

The evolution of the *FT*-Raman spectra for the 225°C run is shown in *Figure 4(B–D)* for the *para* isomer at times of 15, 30 min, and 20 h. Frequencies and band assignments for the polyimide formed, presented in *Table 6*, are identical to those previously assigned for PMDA/ODA polyamic acid[12] or Kapton[a], since the polymer formed from the ester diacid of PMDA/ODA is the same as that of the acid. The ring closure reaction to form the polyimide can be monitored by the losses of the ethyl group at 2932, 2982 cm^{-1}, the ester carbonyl at 1724 cm^{-1}, the amide carbonyl at 1655, 1670 cm^{-1}, and the C–O stretch at 1327 cm^{-1}; and by the appearance of those modes associated with the imide moiety, namely imide I (1786 cm^{-1}), imide II (1385 cm^{-1}) and imide III (1118 cm^{-1}). Relevant bands are indicated in *Figure 4*.

Figure 5 shows plots of the imide I mode ratioed to the 1600 cm^{-1} ring vibration for the *para*, *meta* and 50/50 mixed isomers, respectively, at 225°C as a function of time. As discussed previously, the intensity of this vibration may change slightly with conversion,[12] nevertheless, it can be used as an internal standard. It is apparent from a comparison of the *meta*, *para* and 50/50 mixed isomers at comparable times that the *para* polymer is more highly imidized than the *meta* polymer, which in turn is more highly imidized than the 50/50 mixed isomer. This was found for each temperature investigated. The shapes of the conversion curves are similar for the *meta*, *para* and 50/50 polymers: there is a fast initial imidization rate followed by a slow imidization

Table 6 Band frequencies and assignments for the *meta*, *para* and 50/50 mixed isomers of the ethyl ester of oxydianiline/pyromelletic dianhydride polyamic acid

PAAES			Imide		
Frequency (cm^{-1})	Intensity	Assignment	Frequency (cm^{-1})	Intensity	Assignment
750	m	—			
1106	w	—			
			1118	m	imide III
1138	w				
1161	m	ring hydrogen	1164	w	ring hydrogen
1250	m	amide III			
(1275)	sh	CH_3			
			1319	w	—
1327	s	C–O			
(1300)	sh	CH_2			
			1384	s	imide II
1408	w	aromatic CH bend			
1450	w	CH			
1512	w	aromatic ring	1512	w	aromatic ring
1558	m	aromatic ring			
1605	s	ring vibration of ester	1608	s	aromatic ring
1655	m	amide I			
1724	m	ester C=O			
(1670)					
			1786	s	imide I
2932	w	CH_2 stretch			
2982	w	CH_3 stretch			
3067	m	aromatic CH stretch	3075	m	aromatic CH stretch

s = Strong; m = medium; w = weak; sh = shoulder.

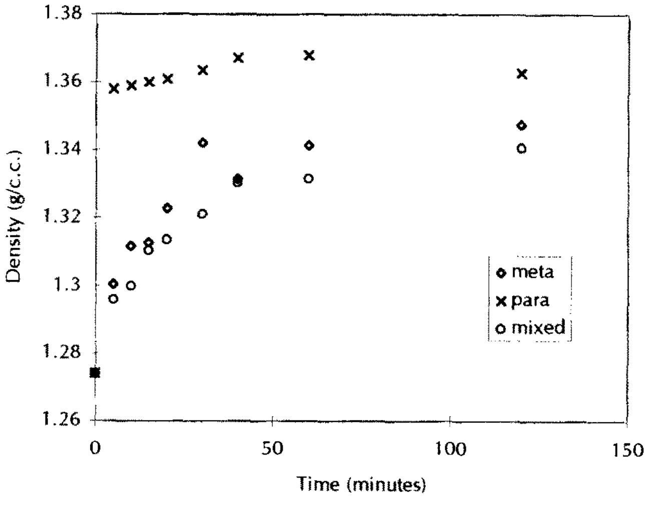

Figure 6 Densities of spun samples of *meta*, *para* and 50/50 mixed isomers cured at 215°C for times up to 1 h

to the final conversion. For the temperatures investigated the imidization rate occurred in the order: *para* > *meta* > 50/50 isomer. Similarly, at final conversion, the per cent imidization occurred in the order: *para* > *meta* > 50/50 isomer.

The highest temperature investigated was 350°C. Even at this temperature, the ester peaks still appeared in the *FT*-Raman spectra of the *meta*, *para* and 50/50 mixed isomers, indicating that full conversion to the polyimide had not been achieved for any of these polymers.

Density gradient column analysis

The densities of spun samples of *meta*, *para* and 50/50 mixed isomers cured at 215°C for times up to 1 h are plotted in *Figure 6*. Mass spectroscopic analysis confirmed that the films did not contain NMP. The cure profile of the films were similar to those obtained from the *FT*-Raman data. The *para* isomer cured the fastest, with the *meta* and 50/50 mixed isomers curing significantly more slowly. The densities of the uncured poly(amic acid ester) films for each isomer were identical, and were thus assumed to be fully amorphous. The densities of the cured films at 215°C (1.368 $g\,cc^{-1}$ *para*, 1.341 $g\,cc^{-1}$ 50/50 and 1.33 $g\,cc^{-1}$ *meta*) were all below the density of an amorphous polyimide film, reported as 1.38 $g\,cc^{-1}$ [29]. The imidization reaction was thus occurring from an amorphous polyamic acid ester to an amorphous imide structure for all of the isomers. It was not possible to determine the densities of the solid samples because the powder particles were too small. Densities of highly crystalline PMDA/ODA polyimides, made using high pressure techniques, have been reported at 1.46 ± 0.01 $g\,cm^{-3}$ [30].

DISCUSSION

We have investigated the effects of isomer composition, solvent retention and annealing on the cyclization kinetics of the polyamic acid ester to polyimide conversion. Three independent methods, namely isothermal and dynamic mass spectroscopy, density gradient analysis and *FT*-Raman spectroscopy have shown that at temperatures below 275°C the *para* isomer cured faster and to a higher degree of conversion than the *meta* isomer at a particular temperature. Under these same conditions, the 50/50 mixed isomer cured at the slowest rate and to a lower degree of conversion than either the *meta* or *para* isomers. The results were obtained from both solid samples precipitated from aqueous solution and dried, as well as from samples cast or spun from NMP solution. The mass spectroscopy data monitored the byproducts of the imidization reaction under reduced pressure, while the *FT*-Raman spectroscopy provided complimentary information on their state of cure under ambient conditions. In the case of the solid samples, not only was $T_{\max}$ $(para) < T_{\max}(meta)$ by 10°C, but $\Delta T_{1/2}(para) > \Delta T_{1/2}(meta)$, indicating that imidization began even sooner for some of the *para* ester groups. In the case of the solid 50/50 mixed isomer, $T_{\max}$ was higher than either the *meta* or *para* isomers, but $\Delta T_{1/2}$ was broad.

These results are in agreement with previous investigations in which the *para* isomer of the PMDA/ODA based poly(amic ethyl ester) was reported to have exhibited the onset of imidization *ca* 10–20°C lower than the corresponding meta isomer, using thermogravimetric analysis (t.g.a.)[3]. Forward recoil spectrometry (FRES) results for this system showed greater degrees of imidization for the *para* and 50/50 mixed isomers compared with the *meta* isomer for samples spun from NMP, but not from DMSO[31]. Increased degrees of conversion were also observed for the *para* compared to the *meta* poly(methyl esters) of PMDA/ODA using i.r. spectroscopy[32]. The results are thus in partial agreement with theoretical predictions that the *para* isomer of PMDA/ODA poly(amic acid) (and by analogy the ethyl ester derivatives) should cure to complete conversion, the *meta* isomer to 82% conversion, and a 50/50 mixed isomer to 91% conversion[17]. In this model, the polymers were assumed to be in the amorphous state above the glass transition temperature, where differences in ultimate conversion depended on whether local or long range motions were necessary to bring the COOH and amide units into close proximity to form the polyimide. For the *para* polymer, it was suggested that only short range conformational changes were required to bring about complete imidization, whereas for the *meta* isomer, there was a certain fraction of 'hard cases', where long portions of the chain had to sweep out a large volume in order to achieve the necessary arrangement for reaction.

This model did not explicitly discuss the rate dependence of the imidization. However, 'easy' cases, where only local rearrangements of COOH and amide units of the molecule were necessary for imidization were considered similar for both the *meta* and *para* configurations. Thus, if it is assumed that the conformations which can easily rearrange to imidize do so first, the rates might be expected to be similar initially for the *meta*, *para* and 50/50 isomers. One measure of the initial rate can be obtained from the isothermal mass spectrometry data, from the delay between the time at which a given preset isothermal temperature, t_{iso}, is reached and the time at which the maximum in the isothermal ion chromatogram, $t_{\max}$ of ethanol occurred. At the lowest temperature investigated, 225, $(t_{\max} - t_{\text{iso}})$ values were quite close for the *meta* and *para* isomers, but between 235 and 275°C, the *meta* isomer reached $t_{\max}$ approximately twice as slowly as the *para* isomer. At the highest temperatures, the values for all the isomers converged. These results indicate that even in the early stages of the imidization, the *para* isomer was most easily imidized. The *FT*-Raman data for these samples were not obtained at sufficient time resolution to compare rates at the early stage of the imidization. However, the density data show a large initial increase for the *para* isomer compared with either the *meta* or 50/50 mixed isomers.

If it is assumed that the 'easy' rearrangements occurred first for all the isomers, then in the later stages of the imidization, rates of imidization of the *meta* isomer might be expected to be slow with respect to those of the *para* isomer in this model. The results of the current investigation indicate that this was the case, at least at temperatures below *ca* 275°C, from data obtained using *FT*-Raman spectroscopy, density gradient analysis and mass spectroscopy.

For both the solid and spun samples, $T_{\max}$ decreased with decreasing heating rate, but $\Delta T_{1/2}$ was not significantly affected. The samples heated at slower heating rates were kept at each temperature for longer times so that a greater fraction of the ester groups imidized at a given temperature, decreasing $T_{\max}$. Conversely, at the faster heating rate, the samples were brought to a particular temperature more quickly, and all three isomers approached the same $T_{\max}$. Similarly, at high temperatures (>300°C), the isothermal ion chromatograms indicated that the rates of imidization converged for all three isomers. Although quantitative data at 100% conversions was not obtained, the degrees of conversion from the *FT*-Raman results also converged with increasing temperature.

Solvent had a dramatic effect on both $T_{\max}$ and $\Delta T_{1/2}$. A comparison of the ethanol ion chromatograms of the cast films with those of the solid samples indicated that the chromatograms of the cast films were considerably narrower and peaked at lower temperatures. The narrowing occurred in several circumstances: when excess solvent was present throughout the whole chromatogram, when only a small amount remained at the imidization temperature, and even when no NMP was observed at the imidization temperature, if the samples had been previously annealed in NMP. In the first two cases there was an asymmetry on the low temperature side of the ion chromatograms, which was not observed for the solid samples. This asymmetry was directly correlated with the presence of NMP still in the samples, as indicated by a comparison of the ethanol and NMP ion chromatograms. Imidization, as evidenced by the evolution of ethanol, started sooner when NMP was present.

The lowest values of $T_{\max}$ and $\Delta T_{1/2}$ for each isomer were obtained (under the same heating rate conditions) for the samples which contained the most solvent, i.e. those cast from NMP solution. In particular, $\Delta T_{1/2}$ narrowed by a factor of 2 to 3 for the cast samples compared with the solid samples, decreasing from 65 to 20°C for the *para* isomer and from 30 to 12°C for the *meta* isomer. The values of $T_{\max}$ for the cast samples decreased by 35°C for the *meta* isomer and by 50°C for the *para* isomer compared with the solid samples.

The amount of NMP retained in the spun films depended on the spinning speed. At lower spin speeds more of the NMP was retained by the films and at higher spin speeds less NMP was retained. With decreasing spin speed, the film thickness also increased. The spun samples represented an intermediate case between the solid and cast samples. At low spin speeds, i.e. 1000 rpm, the films were thick and retained solvent, and it took longer for the solvent to diffuse out. Annealing the samples spun at the lower speeds resulted in low values for $\Delta T_{1/2}$, comparable to those observed for the *meta* and *para* cast samples. With increasing spin speed, there were decreasing amounts of NMP in the films, and both $\Delta T_{1/2}$ and $T_{\max}$ increased. In the case of the *para* isomer, where NMP was retained the longest, $T_{\max}$ reached the same value as observed in the solid samples, but $\Delta T_{1/2}$ remained low (25°C for the sample spun at 6000 rpm vs 65°C for the solid sample). In the case of the *meta* isomer, both $\delta T_{1/2}$ and $T_{\max}$ increased at the highest spin speeds compared to the solid samples. In the case of the 50/50 mixed isomer, $\Delta T_{1/2}$ and $T_{\max}$ reached values which were essentially the same as for the solid samples.

These results are consistent with a mechanism of plasticization of the films by NMP, as has been observed for the poly(amic acids) and their ester derivatives[30]. In the dilute solution limit[33], the imidization rate peaks at about 170°C for the *meta* and *para* ester model compounds. Solvent has been shown to play an important role in the curing rates of PMDA/ODA poly(amic acids), both by direct chemical interaction with the poly(amic acid) and as a plasticizer[12,13]. In PMDA/ODA polymers and their model compounds, stable 2:1 hydrogen bonded complexes with solvent molecules were formed[34,35], so that complete removal of NMP occurred only upon imidization. In contrast, the ethyl ester derivatives do not form stoichiometric complexes with NMP, and there is no evidence of specific NMP binding. However, increased solvent retention has been reported for the *para* isomer compared with the *meta* isomer[30] and our results have shown that it was possible to remove all of the NMP from the *meta* and 50/50 mixed isomer samples before imidization began. The *para* isomer retained the NMP to higher temperatures than the *meta* isomer, and complete removal was not possible until temperatures (*ca* 120°C) at which some imidization had occurred.

The fact that the narrowing of $\Delta T_{1/2}$ remained although NMP had been removed prior to the onset of imidization indicates that annealing the films in the presence of NMP at temperatures below *ca* 120°C changes the distribution of conformational states to one more favourable for imidization. This could occur because the solvent enabled the chains to untangle and align to a more ordered, possibly mesophase state, thereby decreasing the constraints for imidization. We have no direct evidence for mesophase formation. However, narrowing of $\Delta T_{1/2}$ from mass spectroscopy data in poly(amic acids) has previously been associated with cooperative cyclodehydration reactions[36,37] and mesophase (or quasicrystalline) structures[35]. Decreased values of $\Delta T_{1/2}$ for both water or ethanol and solvent have been observed for the model compounds compared with the polymers[32,38,39], when 100% *para* films were compared with the 50/50 mixed isomer films[38], and for oriented fibres compared with films.

Mesophase formation in the case of the poly(amic ethyl esters) might be expected based on configurational statistics from dilute solution light scattering studies, which showed that the degree of stiffness, as measured by the persistence length (q) of the chains, was sufficient to support an ordered state[6,40]. Although we did not observe mesophase formation directly, as NMP was removed from the samples, the transition from viscous solution to the amorphous glassy polymer did not result in precipitation of the polymers and was better characterized as a clear gel. The density data we obtained indicated that the films were amorphous. In the case of PMDA/ODA poly(amic acids), although X-ray data indicated highly parallel alignment and nearly fully extended local chain conformations in films containing 30 wt% solids in NMP[41], there was no indication of periodicity perpendicular to the chain axis. The lack of liquid crystallinity was attributed to lack of isomeric purity.

Other poly(amic acid) films which were amorphous via X-ray diffraction, have been observed to exhibit self-ordering of the chains in the plane of the film as evidenced by conoscopic microscopy[42]. When investigated in more detail using X-ray scattering, nematic mesomorphic states at concentrations of *ca* 40–50% were observed, and improvements in the mesophase order occurred when the films were heated in the temperature range 120–135°C, prior to the onset of thermal imidization. The polyimide precursor, poly(4,4'-methylenediphenylene pyromellitamic acid) formed a liquid crystalline mesophase at 14–20 wt% solids in NMP, at which concentrations the material formed a gel upon standing. It is thus possible that mesophase formation is responsible for the narrowed distribution of imidization temperatures in the PMDA/ODA PAAES films annealed in NMP.

That the 50/50 mixed isomer had the highest $T_{\max}$ may result from differences in solid state morphology. For example, it may have more difficulty forming a mesophase. Intermolecular interactions such as crystallinity and hydrogen bonding have been observed to retard the imidization reaction in PMDA/ODA systems[13,43]. In other investigations[30] the 50/50 mixed isomer had curing characteristics more similar to the *para* isomer when spun from NMP solution. It is clear from the present investigation that $T_{\max}$ and $\Delta T_{1/2}$ can change independently depending on thermal treatment and can be affected by the presence of solvent, so it is not surprising that conflicting results have been observed.

CONCLUSIONS

The rate of cure of the *para* ethyl ester of PMDA/ODA poly(amic acid) was found to be greater than that of the *meta* isomer at temperatures below 275°C, but converged for all the isomers at higher temperatures. The per cent conversions after 1 h were also greater for the *para* isomer compared with the *meta* isomer at the temperatures investigated. The 50/50 mixed isomer cured at the slowest rate and to the lowest degree of conversion compared with either the *meta* or *para* isomers.

Although conformational characteristics of the chain were an important consideration for determining the rates and per cent conversions of polyamic esters to polyimides, solvent effects played a large role in determining the peak temperature of imidization as well as the breadth of the temperature range over which imidization occurred. Solvent affected the imidization kinetics not only through plasticization, but also through the development of orientational alignment at temperatures below the onset of the imidization reaction, so that T_{max} decreased and $\Delta T_{1/2}$ narrowed by a factor of 2–3.

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