Solvent and isomer effects on the imidization of pyromellitic dianhydride–oxydianiline-based poly(amic ethyl ester)s*

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The imidization behaviour of the isomeric poly(amic ethyl ester) (PAE) precursor molecules of the polyimide pyromellitic dianhydride–oxydianiline was followed using forward recoil spectrometry. The degree of imidization after 1 h at various temperatures was found to depend strongly on the spin-casting solvent. Films cast from dimethyl sulfoxide (DMSO) showed an imide fraction, f, which was independent of depth and of isomeric precursor (i.e. whether the precursor was *para*-PAE, *meta*-PAE or a random mixture of *meta* and *para* (mixed-PAE).) In films spun cast from *N*-methylpyrrolidone (NMP), however, fs for the *para*- and mixed-PAE were larger than that for the *meta*-PAE. In addition the fs for the *para*-PAE and mixed-PAE were found to be greater for films cast from NMP than from DMSO for any given thermal treatment. For the *meta*-PAE, f was independent of the casting solvent. Over an imidization temperature range of 180–280°C f was found to vary with depth, being lower than the bulk value over the first 3000 Å from the film surface. These observations appear to be related to a retention of the NMP with f being larger where NMP is retained.

(Keywords: polyimide; imidization; poly(amic ethyl ester))

INTRODUCTION

For electronic packaging, aromatic polyimides are attractive polymers, having good high temperature stability, a relatively low dielectric constant and useful mechanical properties. Polyimides are generally synthesized in a two-step process by the condensation reaction of a diamine and a dianhydride to form a soluble poly(amic acid) (PAA). These precursor polymers are then solvent cast to the desired form, and thermally treated to cycloimidize the polymer, liberating water and forming the final polyimide. Understanding the details of the imidization reaction is important to ensure optimal final properties, and critical in the design of a system which involves the deposition of consecutive layers.

The cycloimidization reaction is not limited, however, to the acid precursor. An ester of the PAA, for example the ethyl ester, can be cycloimidized producing ethanol rather than water. Such poly(amic alkyl ester) precursors have been developed recently[1,2]. Relative to the PAA precursors these have improved solution properties, better resistance to hydrolytic degradation, an apparent lack of exchange reactions in solutions containing different precursor polyimides, and a higher, broader imidization temperature regime which offers a wider processing window for good adhesion[1]. While a substantial amount of work has gone into understanding the imidization reaction of the PAA of pyromellitic dianhydride–oxydianiline (PMDA–ODA)[3–9], much less is known about imidization of the esters. Our study examines the thermal imidization behaviour of the poly(amic ethyl ester) (PAE) precursor of PMDA–ODA.

In the synthesis of the precursor polymer, the nucleophilic substitution reaction on the dianhydride carbonyl may result in the addition of the diamine in the *meta* or *para* position. Generally the resulting poly(amic ester) is a statistical copolymer containing 50% *meta* and 50% *para* linkages. A synthetic method has been developed which can create poly(amic alkyl ester)s with all *para* or all *meta* connections along the chain[2]. The *meta*-poly(amic alkyl ester)s have the advantage of having lower viscosities in concentrated solution, and higher imidization temperatures (T_is) than the randomized chain[2]. This paper investigates the imidization behaviour of these isomeric PAEs and, in particular, the effects that differences in polymer chain architecture and different casting solvents have on the ring-closing reaction.

Forward recoil spectrometry (FRES) has been utilized to follow the course of the imidization reaction of the PAE precursors of PMDA–ODA. The ethyl ester precursors were ideal for this study, since the leaving

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group could be labelled with deuterium. Determination of the amount and distribution of deuterium after various treatments yielded the extent of imidization as a function of depth from the surface of the polymer film after any thermal treatment. This method, described in detail elsewhere[10], has several advantages over other methods used to study imidization including d.s.c., Fourier transform infra-red (*FT*i.r.) spectroscopy and gravimetric methods. In particular, the information obtained from FRES is a direct measure of unreacted ester groups, independent of chain orientation, and provides information on the depth dependence of the imidization.

EXPERIMENTAL

Synthesis of PAEs of PMDA–ODA

Starting materials. PMDA and ODA were purchased from Aldrich Chemical and purified by sublimation. The sublimation was conducted in two stages, the first stage involving vacuum sublimation of the material through about a 12 mm thick layer of 12–32 mesh, activated alumina at temperatures in excess of 200°C (vacuum of ~33 Pa) to remove non-volatile impurities, and the second stage consisting of a straight sublimation to insure complete dryness and conversion to the anhydride. The activated alumina was obtained from EM Science. *N*-methylpyrrolidone (NMP) was distilled under vacuum from P_2O_5 and tetrahydrofuran was distilled under argon from Na. Pyridine (Aldrich) was sealed under nitrogen and used as received.

Diethyl dihydrogen pyromellitate (I). Freshly sublimed PMDA (49.5 g, 0.227 mol) was suspended in dichloromethane (~200 ml) containing ethanol (30 g, 0.577 mol). The mixture was cooled externally with ice and then dry triethylamine (46.55 g, 0.460 mol) was added dropwise under constant stirring. After the amine addition was complete, the reaction mixture was stirred for an additional 16 h under nitrogen, yielding a homogeneous solution. The dichloromethane was then evaporated under vacuum and the amorphous residue taken up in distilled water (250 ml). The aqueous solution was then cooled internally with ice and acidified with dilute, aqueous HCl. The resulting precipitate was filtered and the aqueous filtrate extracted with ethyl acetate. Evaporation of the ethyl acetate yielded, in combination with the precipitated fraction, 70.8 g (97.5%) of the desired diester after vacuum drying at 50°C for 24 h. In this experiment, additional polymers were prepared with a perdeuterated ester group using ethanol-d_6.

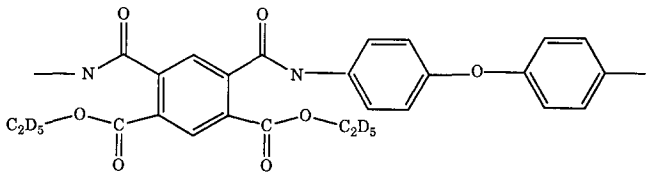
Isomer separation. The pyromellitate diester diacid I (120 g) was suspended in ethyl acetate (500 ml) and stirred for 24 h. The resulting suspension was filtered and the filtrate evaporated under vacuum. This procedure yielded 53.6 g (44.7%) of ethyl acetate soluble material corresponding mainly to the *meta*-isomer and 65.6 g (54.7%) of ethyl acetate insoluble material corresponding mainly to the *para*-isomer. The isomeric purity was ~85%. Recrystallization of the *meta*-rich isomer from butyl acetate (200 ml) yielded 36.6 g of *meta*-diethyl dihydrogen pyromellitate with an isomeric purity of >99%. Recrystallization of the *para*-rich material from butyl acetate (2 l) yielded 50.8 g of *para*-diethyl dihydrogen pyromellitate with an isomeric purity of >99%.

Diethyl pyromellitate diacyl chloride (meta- *or* para-*isomer*) (*IIa and IIb*). Diester diacid Ia or Ib (93.0 g, 0.3 mol) was suspended in ethyl acetate (~250 ml) in a 1 l three-necked flask equipped with magnetic strirrer, reflux condenser and nitrogen bubbler connected to a scrubber containing NaOH. Next, oxaloyl chloride (100 g, 0.79 mol) was added in four to five portions over a period of 8 h. Each addition of oxaloyl chloride was followed by the addition of two drops of dimethylformamide to catalyse the room temperature chlorination. Prior to addition of the last portion of oxaloyl chloride, the temperature of the reaction mixture was raised to 50°C for 3–4 h yielding a homogeneous solution and no further gas evolution. Next, the ethyl acetate was evaporated under vacuum and the crystalline residue dried under vacuum at ambient temperature. The material was then redissolved in 500 ml of boiling hexane in the case of the *meta*-isomer and cyclohexane in the case of the *para*-isomer, which had been spiked with several millilitres of oxaloyl chloride. These solutions yielded well-defined, crystalline materials upon cooling, which were filtered under nitrogen and vacuum dried at ambient temperature for 24 h.

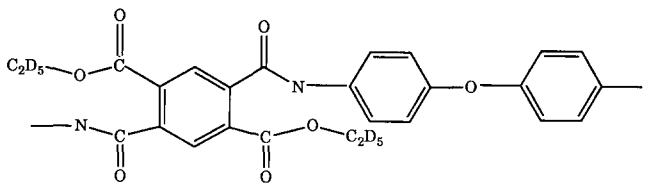
Preparation of poly(meta- *or* para-*diethyl* p,p-*oxydiphenylene pyromellitamide*) (*III*). A three-necked flask equipped with a mechanical stirrer, liquid addition funnel and nitrogen bubbler was charged with freshly sublimed ODA (2.076 g, 10.37 mmol) dry NMP (40 ml) and dry pyridine (1.62 g, 20.45 mmol). The mixture was stirred at room temperature until all the diamine had dissolved and was then cooled externally with ice until the internal temperature had dropped to 0–5°C. At this point diacyl chloride (3.546 g, 10.22 mmol) dissolved in tetrahydrofuran (~10 ml) was added gradually so as to maintain the internal temperature at 5–10°C. Once the acyl chloride addition was complete, the already viscous polymerization mixture was allowed to gradually return to ambient temperature. Stirring was continued for an additional 3 h and then the polymerization mixture was precipitated into distilled water utilizing a Waring blender. The precipitate was filtered and thoroughly washed with distilled water, followed by ethanol and finally ethyl acetate to promote drying. After vacuum drying at 50°C for 24 h, 4.83 g (99%) of the desired polymer was obtained. In this way, the pure *meta*- and *para*-isomers were prepared having deuterium substitution on the ethyl ester moiety, and are referred to as m-PAdE and p-PAdE. The chemical structures of p-PAdE and m-PAdE are shown in *Figure 1*. A polymer with random *para* and *meta* linkages along the chain was also prepared by using the unseparated diethyl dihydrogen pyromellitate monomer. This is referred to as the mixed isomer.

Sample preparation and analysis

Solutions of 8–10 wt% of each of these precursor polymers, were prepared in both NMP and dimethyl sulfoxide (DMSO). The solutions were spun cast at 600 rev min^{-1} for 60 s onto 7.6 cm diameter chromium-coated silicon wafers to form films (~2 μm thick). These were then dried at 80°C for 1 h under vacuum, and subsequently diced into pieces (~15 mm × 15 mm). The



Meta PAdE



Para PAdE

Figure 1 Repeat units for *para*-PAdE and *meta*-PAdE. The mixed isomer is a random mixture of the *para* and *meta* connections along the main chain. The deuterated ethanol will leave as a result of the cycloimidization reaction, and hence the amount of deuterium is a direct measure of the fraction of groups which have imidized

samples were grouped so that each thermal treatment contained a sample of m-PAdE, p-PAdE and mixed-PAdE spun from both NMP and DMSO. Heat treatments below 280°C were performed for 1 h in a preheated vacuum oven, while heat treatments above 280°C were done in a quartz tube furnace under flowing argon. This required a 15°C min^{-1} ramp to the desired temperature, where it was held for 1 h, and then cooled down at 5°C min^{-1}.

The imide fraction, *f*, of the sample was determined using FRES. Doubly charged helium ions were accelerated to an energy of ~2.7 MeV which impacted the sample at a glancing angle. Hydrogen and deuterium nuclei were scattered in the forward direction, passed through a mylar film, and were detected with an energy-sensitive detector. Due to conservation of energy and momentum in the elastic scattering process, deuterium nuclei have a higher energy than the hydrogen if both particles recoil from the surface of the film. Inelastic scattering events cause a reduction in the energy of particles that originate below the surface of the film and provide information on the depth distribution of the particles. Greater detail about the technique and interpretation of the FRES spectra may be found in other references[11,12].

The unreacted PAE precursor has an atomic ratio of 10 deuterium to 12 hydrogen, while the fully imidized polyimide contains no deuterium. The FRES data are utilized to determine the ratio of deuterium to hydrogen in the sample after thermal treatment. Hence, evaluating this ratio as a function of depth yields the variation in *f* in the specimen.

The residual solvent content of the solid films was determined by preparing solutions using deuterium-labelled NMP and DMSO as solvents for unlabelled (non-deuterated) PAE. Depth profiles of the solvent concentration were determined by measurement of the deuterium profiles by FRES in a manner identical to that described above.

RESULTS

A striking difference between the films cast from NMP and DMSO was the variation in *f* as a function of depth or distance from the surface. *Figure 2* shows the *f* values of p-PAdE imidized at 250°C as a function of depth for films prepared from DMSO and NMP. As can be seen from these data, for the films prepared from DMSO, *f* is independent of depth and has a value of 0.74. However, for the film prepared from NMP, at the air surface $f = 0.65$ and, with increasing distance from the surface, *f* increases gradually reaching a maximum value at $f = 0.82$ at a distance of $\sim 3 \times 10^3$ Å. With increasing distance *f* remains constant at this value which is referred to as the 'deep' imide fraction indicating the fraction of the PAdE imidized well within the sample.

Not only was the depth dependence of imidization found to depend upon the solvent for a given isomer but, as shown in *Figure 3*, for films cast from NMP imidized to 250°C, *f* depended upon the isomer of the PAdE. As indicated before, *f* increases from 0.65 at the air surface to 0.85 deep within the sample for p-PAdE. The m-PAdE, however, shows no dependence on depth and remains constant at 0.65. The mixed isomer, again shows a depth

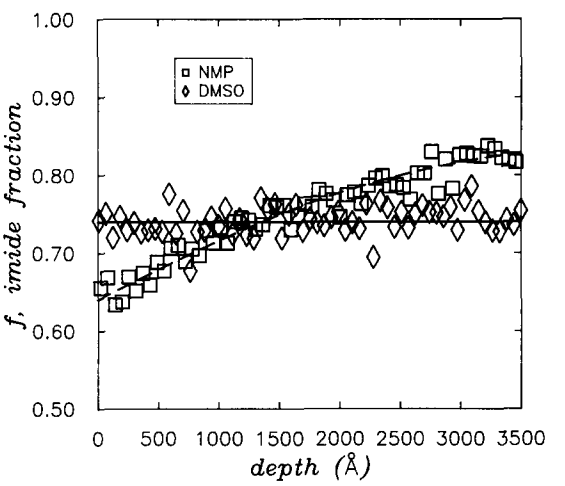


Figure 2 Depth dependence of the imidization reaction for the *para*-PAdE isomer for samples spun out of NMP and out of DMSO, after a 1 h heat treatment in a vacuum oven preheated to 250°C

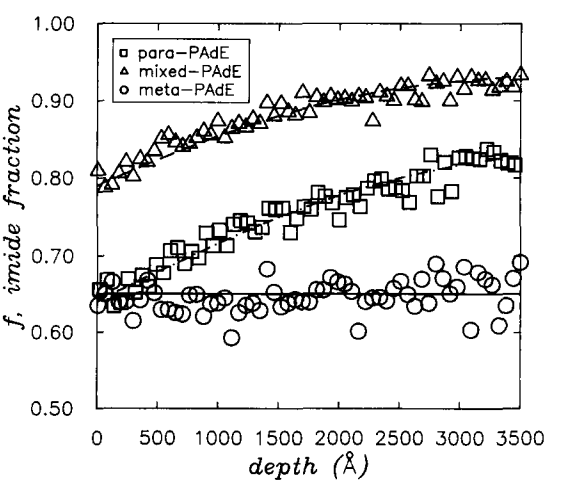


Figure 3 Depth dependence of the imidization reaction for *meta*-, *para*- and mixed-PAdE isomers spun out of NMP, after a 1 h heat treatment in a vacuum oven preheated to 250°C

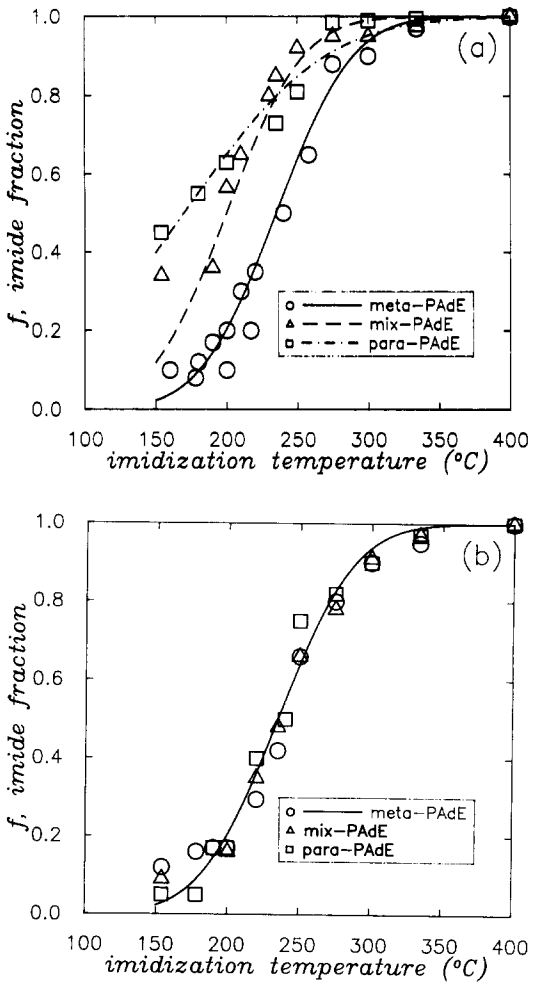


Figure 4 Imide fraction plotted *versus* imidization temperature for *meta*-, *para*- and mixed-PAdE isomers prepared from NMP (a) and DMSO (b)

dependence of f but f is uniformly greater than that seen for p-PAdE. For the mixed isomer f increases from 0.79 at the air surface, and reaches a value of 0.93 at $\sim 3 \times 10^3$ Å from the air surface and remains constant at the 'deep' imide fraction.

This 'deep' imide fraction after annealing for 1 h, was found to be very dependent on the T_i, increasing with increasing T_i. It should be noted that the temperature at which $f=0.5$ occurred at a substantially higher temperature than that of the corresponding PAA precursors, and is consistent with data reported previously[2,8,10,13]. However, for any given T_i, f depended markedly on the isomer and on the casting solvent. The deep imide fraction is plotted as a function of temperature for the *meta*-, *para*- and mixed isomers in *Figures 4a* and *b* for films cast from NMP and DMSO, respectively. In *Figure 4a*, where NMP was used as the casting solvent, the behaviour of the isomers differs. The p-PAdE precursor sample shows a higher degree of conversion to polyimide than does the m-PAdE for all T_i. The mixed-PAdE displays behaviour close to that of the p-PAdE. In contrast, *Figure 4b* shows that when DMSO is used as the casting solvent, the different isomers behave almost identically, though the *para*-isomer still displays a slightly greater tendency to imidize at a given temperature. The difference in behaviour as a result of the casting solvent is underlined in *Figures 5a*, *b* and *c* where f is plotted as a function of temperature for p-PAdE, m-PAdE and mixed-PAdE, respectively, using both solvents. It can be seen that all the precursor isomers cast from DMSO fall approximately on the same curve as the m-PAdE isomers cast from NMP. However, for the p-PAdE and mixed-PAdE, f is always greater for the films prepared from NMP. Volksen *et al.*[1] also indicate that *para*-isomers exhibit an earlier onset of imidization than *meta*-isomers and suggest it may be due to a more favourable conformation of the reactive groups of the *para*-isomer.

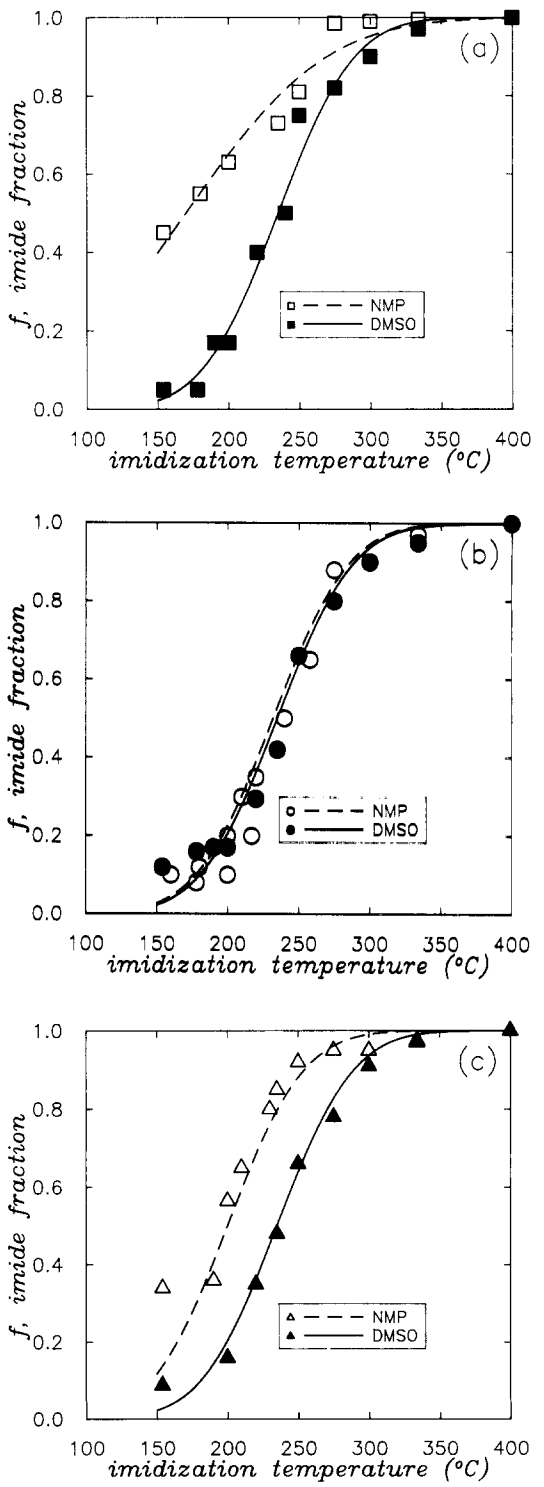


Figure 5 Imide fraction plotted *versus* imidization temperature for each of the spin-casting solvents for the *para*-PAdE isomer (a), the *meta*-PAdE isomer (b) and the mixed-PAdE isomer (c)

The dependence of f on casting solvent and depth may be better understood by determining the depth profile of the residual solvent left in the film. Using *d*-NMP and *d*-DMSO and unlabelled PAE isomers the FRES experiments can be used to determine the variation in solvent as a function of depth and the concentration of residual solvent well within the film. The concentration profile of residual NMP in p-PAE as a function of depth is shown in *Figure 6a* after drying for

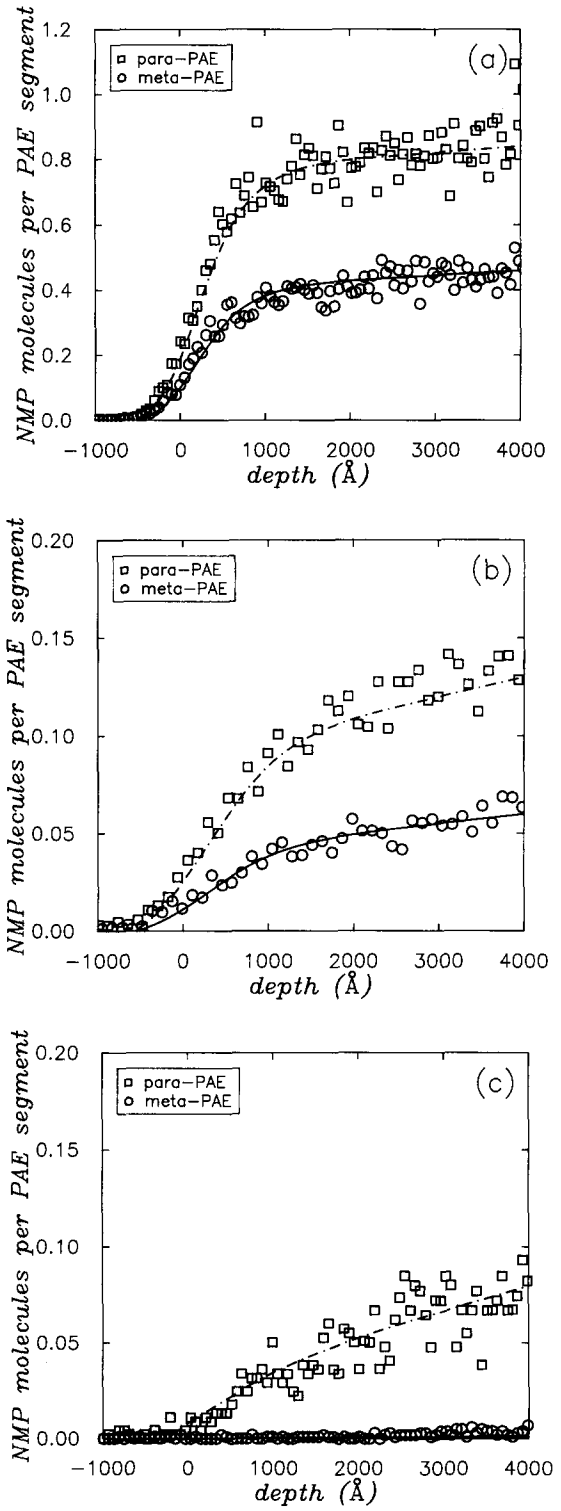


Figure 6 Solvent profiles from samples made with unlabelled polymer and *d*-NMP, were measured by FRES after drying for 1 h in a vacuum oven at 80°C (a), and then after an additional 1 h of heat treatment at 160°C (b) or 200°C (c)

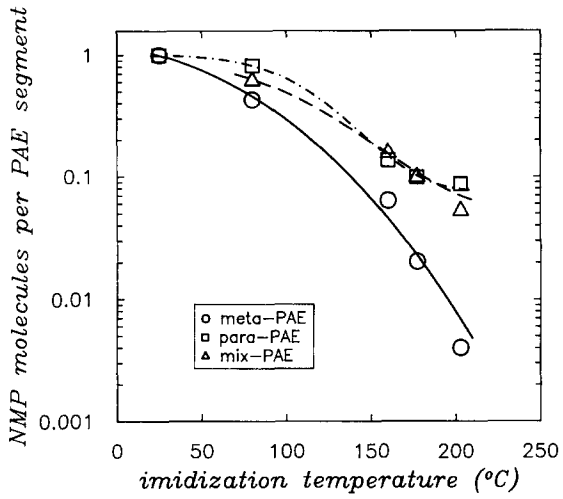


Figure 7 *d*-NMP solvent concentration 3000 Å below the air surface plotted for the *meta*-, *para*- and mixed-PAE isomers after undergoing a 1 h heat treatment in a preheated vacuum oven

1 h at room temperature and in *Figures 6b* and *c* after subsequent 1 h treatments at 160 and 200°C, respectively. As can be seen, there is a surface region of $\sim 3 \times 10^3$ Å, where the residual *d*-NMP is depleted due to a diffusion of the NMP out of the sample during heating. In addition, the amount of residual solvent in the m-PAE case is much less than that for the p-PAE. This depletion region extends over the same depth where f of p-PAdE and m-PAdE decreases below its 'deep' or bulk value. Thus it appears that the residual NMP increases the imidization kinetics of the PAEs. This behaviour is consistent with previous experiments[14,20] on PAA precursors of PMDA–ODA, which showed that the imidization of films cast from NMP depended strongly on film thickness. This dependence was attributed to the greater retention of NMP in the thicker films, which would increase the mobility of the reacting groups involved in the cycloimidization due to an enhanced mobility of the polymer chain.

DMSO, which does not produce differences in f between isomers or any depth dependence of f, is more volatile than NMP. It also is likely that DMSO is not as strongly bound as NMP to the p-PAdE and mixed-PAdE precursors. In any case, the residual levels of DMSO would be very low and do not markedly affect the imidization reaction in the way proposed for NMP.

Plotting the solvent content $\sim 3.5 \times 10^3$ Å below the surface for the *meta*, *para*- and mixed isomers demonstrates the relation between solvent retention and f. The residual solvent deep within the sample is shown in *Figure 7* as a function of T_i for each of the isomers. The solvent retention for the p-PAE and mixed-PAE are similar but greater than that for m-PAE at all temperatures where imidization occurs. After an 80°C drying step, the p-PAE contains about twice as much retained solvent than the m-PAE. With increasing T_i the difference becomes greater. *Figure 8* shows that the DMSO retention for all isomers is approximately the same and corresponds to the NMP retention seen for m-PAE. Again, the f values of all the isomers cast from DMSO are roughly the same as that for m-PAdE prepared from NMP. Further evidence that the solvent plays a crucial role in determining f was obtained by baking the mixed-PAdE prepared from both NMP and

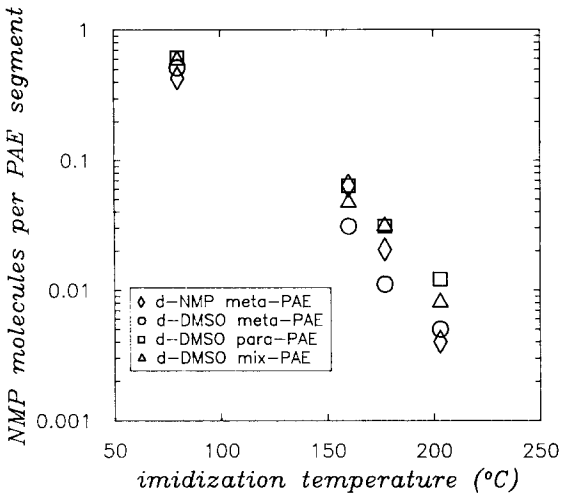


Figure 8 Retention of *d*-NMP for the *meta*-PAE isomer compared to the retention of *d*-DMSO by the *meta*-, *para*- and mixed-PAE isomers after thermal treatments

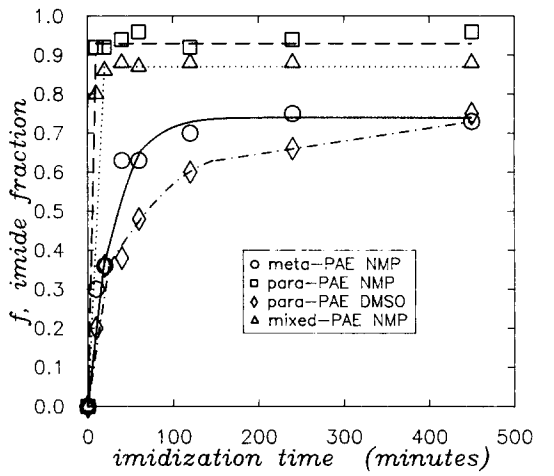


Figure 9 Imide fraction plotted as a function of time the sample was in a vacuum oven at 218°C. Samples in this imidization–time study included *meta*-, *para*- and mixed-PAdE samples prepared from NMP and *para*-PAdE samples prepared from DMSO

DMSO in an oven saturated with NMP at 185°C. It was found that f was the same for both specimens, independent of depth with $f=0.85$. This was much larger than that of the corresponding samples annealed in vacuum.

The mechanism of imidization was further explored by placing samples in an isothermal vacuum oven for varying times. *Figure 9* contains resulting f values for m-, p- and mixed-PAdE samples prepared from NMP and for p-PAdE prepared from DMSO. Consistent with our other results, for samples prepared from NMP, $f_{para} > f_{mixed} > f_{meta}$ for all time periods. The *para* and mixed samples attained a high degree of conversion after 10 min, and then did not change appreciably. In contrast, for the m-PAdE samples prepared from NMP, and the p-PAdE sample prepared from DMSO, f continued to increase with time. Many researchers have observed similar kinetics for the isothermal imidization reaction of PAA[5,14,15]. One explanation is that as the cyclization reaction proceeds the polymer chain stiffens, reducing the mobility of the reacting groups and hence slowing the reaction[15]. For both m-PAE and p-PAE, the residual *d*-NMP content of analogous m-PAE and p-PAE samples does not appear to be a function of treatment time, suggesting that the thermally released *d*-NMP left the sample within the first 10 min of heat treatment. After drying, the *d*-NMP content of the p-PAE sample was 0.82 NMP molecules per PAE segment, and after 10 min at 218°C, it fell to a value of 0.006 and remained constant. Similarly, the m-PAE sample had an initial *d*-NMP concentration of 0.43 NMP molecules per PAE segment, and after 10 min at 218°C, the *d*-NMP concentration was reduced to 0.004 NMP molecules per PAE segment and then stayed constant. About twice as much solvent leaves the *para* sample as leaves the *meta* sample (due to differing solvent contents after drying).

DISCUSSION

The presence of solvent after the initial drying step is consistent with the results reported by other authors[3,4,9] for the PAA where a NMP–PAA complex is formed. However, the depth dependence of the imidization reaction has not been reported previously. It is felt that these two observations are closely related.

For the PAA, the mechanism of the solvent catalysis has been explained by suggesting that the liberated NMP plasticizes the polymer and that the decomplexed PAA becomes more mobile, making reacting groups more available to each other, so that the reaction proceeds to a greater extent[4,9]. However, solvent content is not the only factor that determines the kinetics and extent of imidization. As the reaction proceeds, a leaving group, (water for the PAA, ethanol for the PAE), will be released. Presumably, these by-products will act as plasticizers, increasing the ease of intramolecular movements. At the same time, increasing the number of imide rings along the main chain stiffens the backbone and has the effect of slowing the reaction by reducing the availability of suitable conformations for imidization[15].

Brekner and Feger[4] have done an extensive study of the imidization reaction of PAA and its complexation with NMP. They observed an initial ratio of NMP to polymeric repeat unit of 4:1 after drying at room temperature at ~67 Pa. This ratio decreased to 2:1 after further drying at 86°C. It was postulated that the retention of solvent was due to a hydrogen bonding complexation which involved initially, at room temperature, the tertiary amine of the NMP solvent, with the hydrogen of the amide and carboxylic acid groups of the PAA. The interaction between the carboxylic acid group and the tertiary amine nitrogen of NMP is the stronger interaction, and is responsible for the stable NMP–PAA complex formed after drying at 80°C.

In the study presented here, for p-PAE an initial ratio of 1:1 was found after drying under vacuum at room temperature. This ratio is reduced to 0.82:1 after an 80°C bake, and is further decreased to 0.14:1 and 0.08:1 after 160 and 200°C heat treatments, respectively. In this case, where ethyl esters are used, there is no carboxylic acid group to donate a hydrogen, and the amount of retained solvent is considerably lower than the values reported by Brekner and Feger[4]. Nonetheless, the NMP has a profound effect on the temperature-dependent reaction behaviour.

The increase of f at any T_i for p-PAE and mixed-PAE prepared from NMP relative to those prepared from DMSO (*Figures 5a* and *c*), suggests that a solvent–PAE complexation occurs and enhances the cycloimidization

reaction. The insensitivity of the m-PAE to casting solvent correlates with a reduced solvent retention in comparison to p-PAE as shown in *Figure 2*. In fact, the *meta*-isomer appears to retain NMP and DMSO equivalently when measured on the basis of the number of solvent molecules retained per repeat unit of polymer (*Figure 8*). The fact that there was no appreciable difference in the imidization profiles for the mixed-PAdE samples prepared from NMP and DMSO, which were annealed in an NMP saturated atmosphere, supports the idea of solvent plasticization.

However, differences between the isomers still remain suggesting some fundamental role of the backbone structure. First, the m-PAE has a more kinked main chain structure than does the p-PAE, consisting of rigid units of length 9 and 18 Å, respectively[16]. The p-PAE is considerably more extended in solution than the m-PAE[17], and it would be expected that the spun-cast film of p-PAE would have a more ordered structure than that of m-PAE. These differences could cause m-PAE to have greater difficulty in attaining suitable conformations for cycloimidization. In addition the enhanced ordering of the p-PAE suggests that intermolecular associations may be more important. Sazanov *et al.*[18] have shown that PAA in amide solvents tends to form ordered structures in non-oriented films and argue that the ordering affects the cyclodehydration reaction. They postulate that amorphous regions release solvent much more readily than do the ordered regions. Using mass spectrometric thermal analysis, they show that an all *para* chain of the PAA of PMDA–ODA releases solvent in a narrow high temperature band, while the mixed-PAA releases solvent both in a broad low temperature band and a narrower high temperature band. They argue that this behaviour can be attributed to solvent removal from less and more ordered regions of the polymer film, respectively. Similar arguments would hold here where the more ordered p-PAE and mixed-PAE could retain solvent more effectively than the kinked chain *meta* structures[19]. Since free rather than complexed solvent plasticizes the film, the breakup of this ordered solvent–polymer complex should have the effect of releasing plasticizer within the temperature regime where imidization can occur easily in the presence of plasticizing solvent.

CONCLUSIONS

The imidization behaviour of isomeric PAEs of PMDA–ODA under isothermal temperature treatments was measured using FRES. Substantial differences were seen in imidization behaviour as a function of isomer, when NMP was the spin-casting solvent. In contrast, films spun out of DMSO displayed approximately the same temperature behaviour, independent of the isomeric make-up of the sample. Additionally, NMP cast films showed a smaller f in the region within 2000 Å of the surface than in the bulk, while DMSO cast films displayed a constant f throughout. Retention of solvent was seen to correlate with these observations, with more solvent remaining in areas of greater f, or samples of higher f, for equivalent thermal treatments.

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REFERENCES

1 Volksen, W., Yoon, D. Y., Hedrick, J. L. and Hofer, D. 'Materials Science of High Temperature Polymers for Microelectronics', MRS Symposia Proceedings, Anaheim, Vol. 227, p. 23
2 Volksen, W. 'Recent Advances in Polyimide and Other High Performance Polymers', Interdisciplinary Symposium, Division of Polymer Chemistry, American Chemical Society, San Diego, 1990, p. C-1
3 Brekner, M.-J. and Feger, C. *J. Polym. Sci., Polym. Chem. Edn* 1987, **25**, 2005
4 Brekner, M.-J. and Feger, C. *J. Polym. Sci., Polym. Chem. Edn* 1987, **25**, 2479
5 Kreuz, J. A., Endrey, A. L., Cay, F. P. and Sroog, C. E. *J. Polym. Sci. A1* 1966, **4**, 2607
6 Snyder, R. W. *Macromolecules* 1989, **22**, 4166
7 Numata, S., Fujisaki, K. and Kinjo, N. 'Polyimides' (Ed. K. L. Mittal), Plenum Press, New York, 1984, p. 259
8 Buchwalder, L. P. *J. Vac. Sci. Technol. A* 1989, **7** (3), 1772
9 Johnson, C. and Wunder, S. 'Proceedings/Abstracts of Third International Conference on Polyimides', 2–4 November 1988, Ellenville, Elsevier, New York, 1988, p. 70
10 Tead, S. F., Kramer, E. J., Russell, T. P. and Volksen, W. *Polymer* 1990, **31**, 520
11 Shull, K. 'Physics of Polymer Surfaces and Interfaces' (Ed. I. Sanchez), Butterworth, Boston, 1992, Ch. 9
12 Mills, P. J., Green, P. F., Palmstrom, C. J., Mayer, J. W. and Kramer, E. J. *Appl. Phys. Lett.* 1984, **45**, 957
13 Houlihan, F. 'Proceedings of American Chemical Society Division of Polymeric Materials Science and Engineering', 1988, Vol. 59, p. 225
14 Ginsburg, R. and Susko, J. R. 'Polyimides' (Ed. K. L. Mitta), Vol. 1, Plenum Press, New York, 1984, p. 237
15 Laius, L. A. and Tsapovetsky, M. I. 'Polyimides' (Ed. K. L. Mittal), Vol. 1, Plenum Press, New York, 1984, p. 295
16 Takahashi, N., Yoon, D. Y. and Parrish, W. *Macromolecules* 1984, **17**, 2583
17 Cotts, P. M. *J. Appl. Polym. Sci. Appl. Polym. Symp.* 1992, **51**, 101
18 Sazanov, Y. N., Shibayev, L. A., Dauengauer, S. A., Stepanov, N. G., Bukina, M. K., Denisov, V. M., Antonov, N. G. and Kol'tsov, A. I. *Polym. Sci. USSR* 1985, **27**, 2699
19 Huang, J.-W. and Chu, N.-J. *J. Chin. Inst. Chem. Eng.* 1991, **22**, 45
20 Diener, C. E. and Susko, J. R. 'Polyimides' (Ed. K. L. Mittal), Vol. 1, Plenum Press, New York, 1984, p. 353