Ion beam analysis of the imidization kinetics of polyamic ethyl ester

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(Received 18 April 1989; revised 7 August 1989; accepted 7 August 1989)

The extent of imidization was determined as a function of depth in films of the deuterated version of a model polyimide precursor, polyamic ethyl ester (*d*-PAE), using a novel ion beam analysis technique. Monitoring the loss of the deuterated ethyl moiety provided a precise means of evaluating the extent of imidization f as a function of the temperature of imidization and time at the imidization temperature. The imidization reaction was found to proceed uniformly as a function of depth down to 700 nm below the surface. The imidization kinetics followed a two-stage sequence in which the initial rate of imidization was rapid, up to f values of *ca.* 0.6, whereupon the reaction rate diminished sharply.

(Keywords: polyimide; imidization; ion beam analysis)

INTRODUCTION

Polyimides are a class of polymers enjoying increasing industrial applications, especially as dielectrics for electronic packaging. The importance of polyimides stems, to a large degree, from their solvent resistance and stability at temperatures above 400°C. The feature responsible for these attributes is the presence of stable aromatic rings on the polymer backbone, as opposed to the weaker aliphatic bonds found in most polymers. However, the aromaticity in the imide polymer backbone, in the absence of flexible linkages, gives rise to intermolecular associations making the polymer difficult to process in the imide form. For this reason the polymer is generally processed in its precursor form (i.e. as the polyamic acid), which is soluble in solvents such as dimethyl formamide, *N*-methyl pyrrolidone, and dimethyl sulphoxide. The polymer is subsequently cured, with the amide and acid groups of the polyamic acid combining in a cycloimidization reaction to form the imide.

Since the optimum properties of a polyimide film depend critically on the degree of imidization, it is desirable to evaluate the extent of the cycloimidization reaction in a particular sample. Conventional methods for determining the extent of cure have included differential scanning calorimetry (d.s.c.)[1,2], and infra-red spectroscopy (*F*Ti.r.)[3–7]. Disadvantages of the d.s.c. technique include ambiguities arising from other endothermic processes occurring simultaneously with the cyclization reaction, such as solvent evaporation, solvent–polymer interactions[2,8,9], and anhydride formation[8,9]. Dichroism arising from partial orientation[10,11], or segmental ordering[12–15] can affect *F*Ti.r. data, also introducing uncertainties into such studies.

In this paper we present a new approach for studying the degree of imidization in a polyimide film. The technique involves a direct measurement of the concentration of unreacted (non-imidized) groups in the polymer sample, with fewer ambiguities than those affecting d.s.c and *F*Ti.r. as mentioned above. Furthermore, the technique is unique in that the degree of cure can be measured as a function of depth in a film sample. We use a model polyimide precursor synthesized with deuterium substituted (deuterated) ester groups. The deuterium atoms are removed from the specimen in the form of deuterated ethanol (*d*-ethanol), as produced in the imidization reaction. The concentration of deuterated ester groups is determined as a function of depth by forward recoil spectrometry[16] and, therefore, gives a direct measure of the extent of imidization *versus* depth in the sample.

EXPERIMENTAL

Samples of the ethyl ester of PMDA-ODA (PAE), were synthesized in a *N*-methyl pyrrolidone solution. The ester was formed by low temperature, solution polymerization of *p,p*′-oxydianiline (ODA) with perdeuterated diethyl pyromellitate diacyl chloride (derived by the reaction of perdeutero ethanol with pyromellitic dianhydride). This polymer is referred to as *d*-PAE. The imidization reaction converting *d*-PAE to the polyimide is shown in *Figure 1*. Deuterium is lost from the polymer as the *d*-ethanol by-product generated during the cycloimidization.

Forward recoil spectrometry was used to monitor the deuterium concentration and thus the degree of imidization in a film of *d*-PAE as follows: a solution of the polymer in dimethyl sulphoxide was spun onto a 3 in silicon wafer, creating a film of approximately 10 μm thickness. The film was partially dried at 80°C, and individual samples of the *d*-PAE on silicon were cut. The films were annealed to cycloimidize the *d*-PAE, in vacuum or in an argon atmosphere, for a time t at imidization temperatures T_i of 150, 200, 250, 300, 350, and 400°C. (Some samples were also held at room temperature with no heating, and are referred to as

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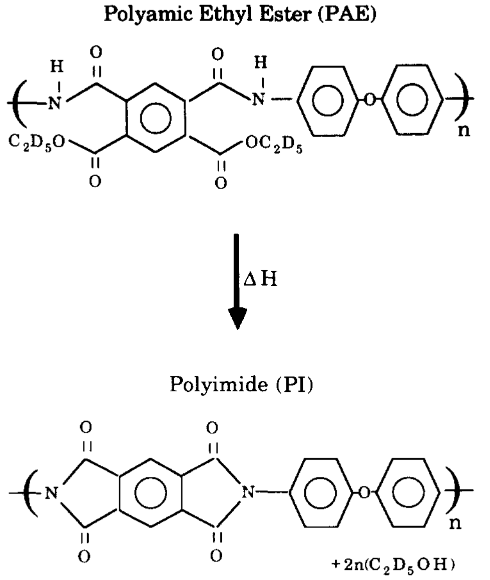

Figure 1 Imidization of deuterated polyamic ethyl ester (*d*-PAE) to PMDA-ODA polyimide, with the evolution of *d*-ethyl alcohol as the reaction product

having a T_i of 80°C.) Following the anneal, the films were cooled rapidly to room temperature and then analysed by forward recoil spectrometry to obtain the deuterium concentration as a function of depth. From the forward recoil spectrometry data the degree of cure could be determined as a function of depth in a given film sample.

RESULTS AND DISCUSSION

Figure 2 shows the forward recoil spectra for two *d*-PAE samples with T_i values of 80°C (upper points) and 250°C (lower points). The forward recoil spectra result from the accumulation of hydrogen and deuterium ions recoiling from the *d*-PAE film, under the impact of a 3 MeV $^4He^{2+}$ ion beam. The highest energy ions, which form the 'edge' near channel 300, correspond to deuterium ions recoiling from the surface of the film. The edge near channel 200 marks the point where surface hydrogen ions (which have 0.5 the mass of deuterium ions, and therefore recoil with only about 0.7 the energy) enter the spectrum.

Depth information is present in the spectra, with lower channel numbers or ion energies corresponding to ions emerging from greater depths in the film sample. This depth–energy relationship results from energy losses (due to inelastic collisions) suffered by the incident ion beam as it penetrates the film and similar losses by the recoiling hydrogen or deuterium ions as they pass through the film en route to the sample surface. The overlap of the hydrogen and the deuterium spectra begins with deuterium ions arriving from depths greater than 0.7 μm from the film surface, and therefore determines the measuring 'window' of the technique. The peak seen near channel 125 corresponds to a resonance at 2.14 MeV in the $^4He^{2+}$–deuterium scattering cross-section. The resonance energy is reached when the $^4He^{2+}$ ion beam has penetrated the sample to about 1 μm in depth.

Comparing the relative spectra from the samples treated at 80 and 250°C, one sees a decrease in the yield from the specimen heated to 250°C. This corresponds to the loss of one hydrogen from the amide group and five deuterium atoms from the *d*-ethyl group during imidization, as shown in *Figure 1*. A simulation curve (solid line in *Figure 2*) was fit to each set of data, using the known stoichiometry change upon curing and the degree of imidization *f* (the fraction of imide groups in the sample) as the only adjustable parameter.

A small deviation of the simulation from the data, in the form of an overestimation of the deuterium concentration at the sample surface, can be seen in the 80°C sample. A similar deviation was seen in other *d*-PAE samples, and was found to be an increasing function of the beam dose accumulated during measurement of the forward recoil spectra. It was surmised that the source of this phenomenon was ion beam induced dissociation of the *d*-ethyl group from the polymer, which subsequently left the sample surface into the forward recoil spectrometry chamber vacuum. Forward recoil spectrometry measurements taken at liquid nitrogen temperatures reduced this form of beam damage, through not entirely. From such

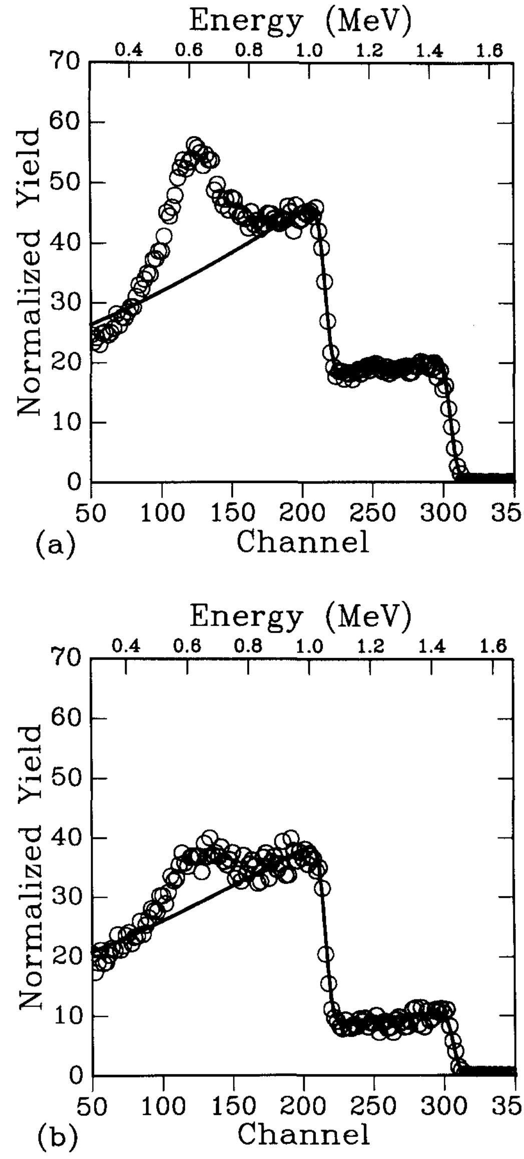

Figure 2 Forward recoil spectra of *d*-PAE films after imidization at a temperature T_i. The solid lines represent a simulation with a depth-independent degree of imidization *f* as the variable in a best fit. (a) $T_i = 80$°C (60 min anneal). No imidization; (b) $T_i = 250$°C (90 min anneal). $f = 0.6$

low temperature measurements it was found that the damage did not significantly affect the value of f determined from the fitting procedure.

One of the unique features of the forward recoil spectrometry technique is its capacity to deliver depth information regarding the degree of cure in the *d*-PAE film. The simulations shown in *Figure 2* were created assuming a constant, depth independent value of f. In general it was found (apart from the surface damage caused by the ion beam, as noted earlier) that the assumption of depth invariance for the degree of imidization yielded good agreement with the experimental data in the 0.7 μm measurement window available to the technique. This depth invariance is interesting when compared with the result noted[4,6] for the conversion of polyamic acid (PAA) to PMDA-ODA polyimide, namely that PAA cycloimidizes more rapidly when the specimen thickness is increased (due possibly to a greater retention of solvent in a thicker film). Our result indicates that either the mechanisms causing accelerated imidization of thicker samples are not operative in our 0.7 μm measurement window, or they are not of importance in the cycloimidization of the polymer *d*-PAE.

Two separate studies determined the dependence of the imide fraction f on the imidization time and temperature T_i. *Figure 3* shows the data obtained from the first study, where f was determined as a function of time, at a constant T_i of 250°C. The cycloimidization appears to have two stages. At early times the reaction takes place at a high rate, reaching an imide fraction of $f = 0.5$ in 30 min. Later, the reaction rate is dramatically reduced, leaving imide formation incomplete even after 21 h of annealing.

The solid line in *Figure 3* represents a fit of the short time data to a first-order reaction rate model, i.e.

$$\frac{dr}{dt} = -kr \tag{1}$$

where r is the concentration of amide groups left unreacted at a given time and k is the reaction rate constant. The rate constant can be determined by noting that

$$f = 1 - r \tag{2}$$

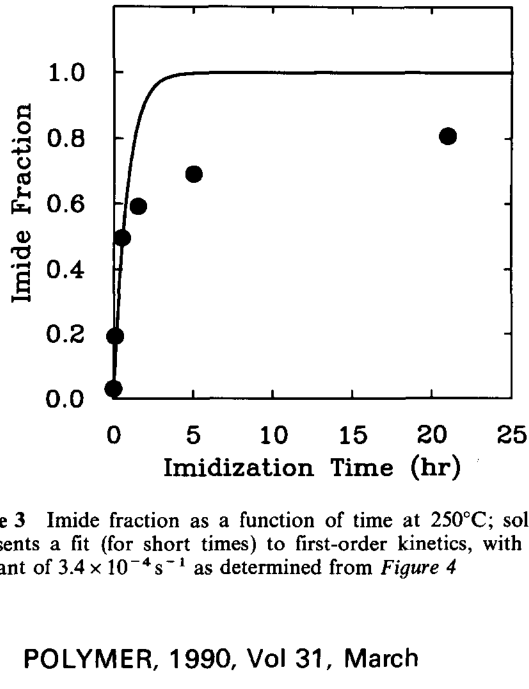

Figure 3 Imide fraction as a function of time at 250°C; solid line represents a fit (for short times) to first-order kinetics, with a rate constant of $3.4 \times 10^{-4}\,s^{-1}$ as determined from *Figure 4*

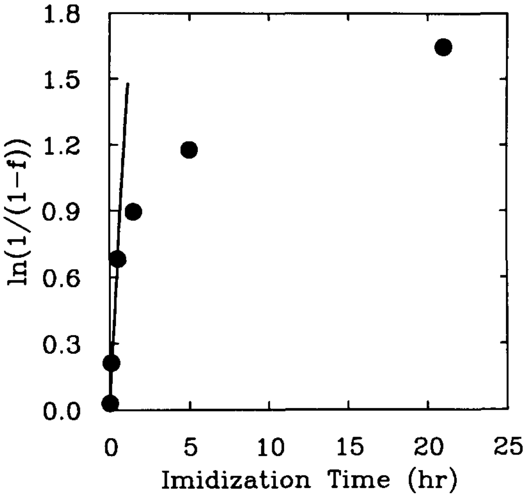

Figure 4 Data from *Figure 3*, replotted to determine the reaction constant k. Short time fit has slope $k = 3.4 \times 10^{-4}\,s^{-1}$

is the concentration of the imide groups formed, or the imide fraction, and therefore,

$$f = 1 - e^{-kt} \tag{3}$$

If equation (3) applies, then the quantity $\ln(1/1-f)$ should vary linearly with time, with slope k. As can be seen in *Figure 4*, while a first-order kinetic model may hold for short times, the reaction deviates considerably from the model thereafter. The rate constant determined from a linear regression of the data at early times is $3.4 \times 10^{-4}\,s^{-1}$. Substitution of this value in equation (3) yields the solid line in *Figure 3*.

The failure of the cycloimidization of *d*-PAE to follow a simple, first-order model for the reaction kinetics, is similar to that reported by others for the cycloimidization of PAA[1,5,7,17]. Several arguments have been made to account for the observed slowing down of the imidization reaction, including polymer–solvent interactions, competing chemical reactions, and the increased glass transition temperature (T_g) with imidization. The latter effect is important because cycloimidization, being an intramolecular reaction, requires the polymer chain to undergo conformational changes to complete the imidization. The polymer motion associated with the conformational changes is slowed by the increased T_g, inhibiting the reaction. Competing reactions such as anhydride formation and intermolecular imidization reactions[8,9] may also serve to retard the reaction kinetics. Finally, while the presence of solvent molecules would normally impart more mobility to the polymer system, enhancing the reaction rate, possible complexation between the PAE molecule and the solvent molecules, as found with PAA[8,9], may also hinder imidization.

A second study was made to determine the temperature dependence of the degree of imidization. *Figure 5* shows the imide fraction measured after 1 h of annealing, for various imidization temperatures T_i. The imidization reaction is *ca.* 50% complete after 1 h at 250°C and complete after 1 h at 350°C. The solid line represents an approximation based on equation (1) and an Arrhenius-type relationship for the reaction rate constant,

$$k = k_0 \exp\left(-\frac{\Delta H}{RT}\right) \tag{4}$$

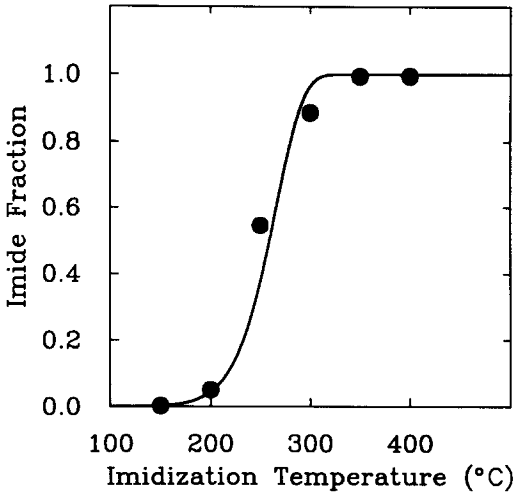

Figure 5 Imide fraction as a function of imidization temperature T_i after 1 h of annealing. Solid line represents a fit to an Arrhenius form, with excess enthalpy 97 kJ mol^{-1}

where ΔH is the excess enthalpy of imide formation, and R is the molar gas constant. The values used for the enthalpy (97 kJ mol^{-1}), and k_0 (6×10^5 s^{-1}) were empirically chosen to yield the best fit. However, these values do not necessarily represent meaningful physical quantities for this reaction, since the 1 h imidization time may put the reaction in the first(fast) stage for the lower annealing temperatures, and the second (slow) stage for the higher imidization temperatures[5].

CONCLUSIONS

We have shown that a novel ion beam analysis technique can serve to determine unambiguously the imide fraction f in films of *d*-PAE. The technique is unique in allowing the determination of the depth profile of the degree of imidization and, within the upper 0.7 μm of the film, a depth invariance of f was found.

The imide fraction was determined as a function of imidization time and temperature. Our results for the reaction kinetics support the two-stage model of polyimide cyclization. A high reaction rate, following first-order kinetics, is present at short times, followed by a second stage in which the rate constant is dramatically reduced. The temperature dependence of the reaction could be fit empirically assuming first order kinetics and an Arrhenius form for the rate constant.

ACKNOWLEDGEMENTS

We would like to acknowledge the support of this study by the Semiconductor Research Corporation, through the Electronic Packaging program. We are also grateful for the use of facilities of the Materials Science Center, Cornell University, which is funded by the DMR-MRL program of the NSF. We thank Dr Philip Miller for his contributions, and useful discussions with Dr George Schmitt are appreciated.

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