Polyimide foams derived from a high T_g polyimide with grafted poly(α-methylstyrene)

J. L. Hedrick and R. DiPietro
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, USA
and C. J. G. Plummer and J. Hilborn
Ecole Polytechnique Federale de Lausanne, 1015 Lausanne, Switzerland
and R. Jérôme
Université de Liège, Sart Tilman, Liège, Belgium

Abstract
A new route to high-T_g, thermally stable polyimide foams has been developed. Foams were prepared by casting microphase-separated graft copolymers comprising a thermally stable main chain, polyimide, and a thermally labile graft, poly(α-methylstyrene). The copolymer compositions were designed so that the thermally labile block would be the dispersed phase. This can unzip to its monomer upon heating, and the decomposition product diffuses out of the film, leaving pores embedded in a matrix of the thermally stable component. The copolymers were synthesized through either the poly(amic acid) precursor, followed by chemical cyclodehydration to the imide form, or the poly(amic alkyl ester) precursor followed by thermal imidization. The decomposition of the α-methylstyrene in the block copolymer was studied by thermogravimetric, dynamic mechanical and thermomechanical analyses. Mild decomposition conditions were required to avoid rapid depolymerization of the α-methylstyrene and excessive plasticization of the polyimide matrix. The foams showed pore sizes with diameters ranging from less than 20 nm to over 1 μm, depending upon the synthetic route employed, and the reduction in the mass density was generally consistent with the starting composition.

Keywords: polyimide foams; block copolymer; plasticization

INTRODUCTION

A key feature in the fabrication of microelectronic components and devices is the dielectric constant of the insulating materials. These materials must also withstand severe thermal, chemical and mechanical stresses associated with microelectronics fabrication, and inorganic alumina or silicon oxides have been shown to satisfy most of those criteria. Polymeric insulators, on the other hand, have several key attractive features including low dielectric constant and ease of processing. There are few polymers which satisfy the criteria for microelectronics fabrication, and polyimides have emerged as the favoured class of materials[1]. Although polyimides meet most of the requirements for microelectronic applications, it would be desirable to improve their electrical performance by further reducing the dielectric constant. A new approach has been developed to reduce the dielectric constant while maintaining the thermal and mechanical properties. This involved the generation of a foam or porous structure, in which the reduction in the dielectric constant is achieved by replacing a proportion of the polymer with air, which has a dielectric constant of 1. For thin-film microelectronic applications, the size of the pores must be much smaller than the film thickness in order to maintain the integrity of the insulating layer and the circuitry deposited on the film. We are currently able to produce high-temperature polymer foams with pore sizes in the nanometre regime, which may therefore be termed 'nanofoams'. The technique is based on micro-phase-separated block copolymers comprising a thermally labile component dispersed in a thermally stable matrix[2-5]. On heating, the thermally unstable block undergoes thermolysis, leaving pores with sizes commensurate with the initial copolymer morphology. In addition to the pore size, the pore shape is also important. It is necessary for microelectronics applications that the pore interconnectivity be minimal and that the pores be of the close-cell type, to avoid the formation of pathways for solvent penetration. The usefulness of the block copolymer approach to nanofoam formation is therefore limited owing to the formation of more interconnected (cylindrical or lamellar) structures as the volume fraction of the thermally labile component approaches 30%.

Nanofoams have been prepared using poly(propylene oxide) (PPO) or poly(methyl methacrylate) (PMMA) as the labile component in a polyimide or polyphenylquinoxaline (PPQ) matrix[2]. In PPO- and PMMA-based triblock copolymers, a 10—18% reduction in density was observed on decomposition of the labile component, and a small-angle X-ray scattering (SAXS) indicated pores sizes in the 100 Å range. Transmission electron microscopy (TEM) has confirmed the highly interconnected nature of the porous morphology obtained from triblock copolymers showed markedly different behaviour[4]. Regardless of the composition of the initial copolymer, the foams showed discrete spherical voids with minimal interconnectivity. The graft architecture thus appears to allow discrete or non-interconnected morphologies for copolymers containing relatively high proportions of the thermally labile phase.

Poly(α-methylstyrene) (PMS) has been shown to be ideally suited for use as the thermally labile coblock, since

well-defined functional oligomers can be prepared, and it depolymerizes quantitatively to the monomer, which can diffuse through the matrix[5]. This occurs at approximately 290°C, which is sufficiently high to allow conventional film processing and solvent removal, but is also well below the T_g of typical polyimides used in microelectronics fabrication. Thus, a substantial processing window is defined. Foams derived imide/α-methyl-styrene-based triblock copolymers nevertheless showed interconnected porous structures, even for low PMS contents[5]. The degradation product, α-methylstyrene, was found to plasticize the polyimide, and, on evolution from the film, acted as a 'blowing agent', increasing the pore size and interconnectivity (porosities as high as 60% could be achieved for such systems). In the light of the results for imide-PPO graft copolymers described above, it is therefore of interest to prepare imide—α-methyl-styrene graft copolymers as a means of obtaining foams with discrete pores.

Here we discuss the synthesis and foam formation for imideα-methylstyrene graft copolymers in which the imide component was derived from a pyromellitic dianhydride with 1,1 -bis(4-aminophenyl)-l -phenyl-2,2,2-trifluoroethane (3FDA—PMDA), since this was the polyimide used in the imide-α-methylstyrene triblock study, allowing direct comparisons. The 3FDA— PMDA polyimide has a T_g of 440°C and a decomposition temperature of 500°C, comfortably fulfilling the requirements of many microelectronic applications. 3FDA—PMDA polyimide is also soluble in common organic solvents, so that significant synthetic flexibility is obtainable through thermal, chemical or solution imidization. The choice of processing route has previously been shown to have major influence on the morphology of foams obtained from the imide—α-methylstyrene triblock copolymers . We therefore consider both chemically imidized graft copolymers and thermally imidized films cast from the poly(amic alkyl ester) precursor.
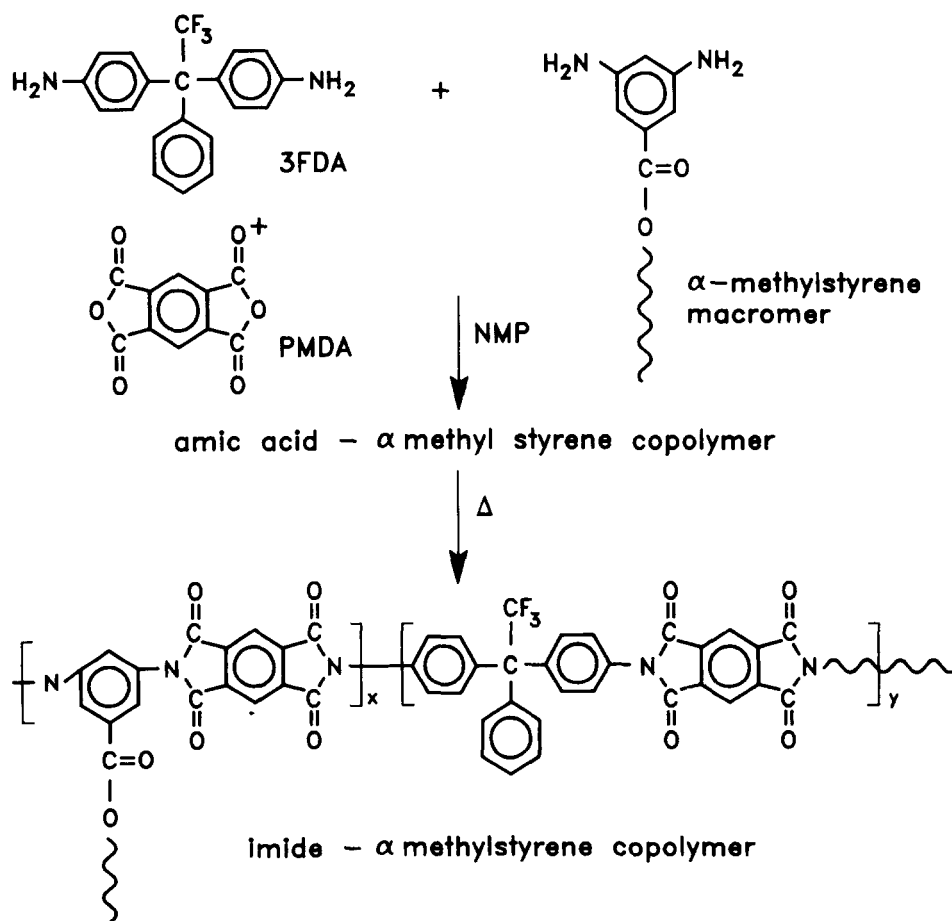
Scheme I
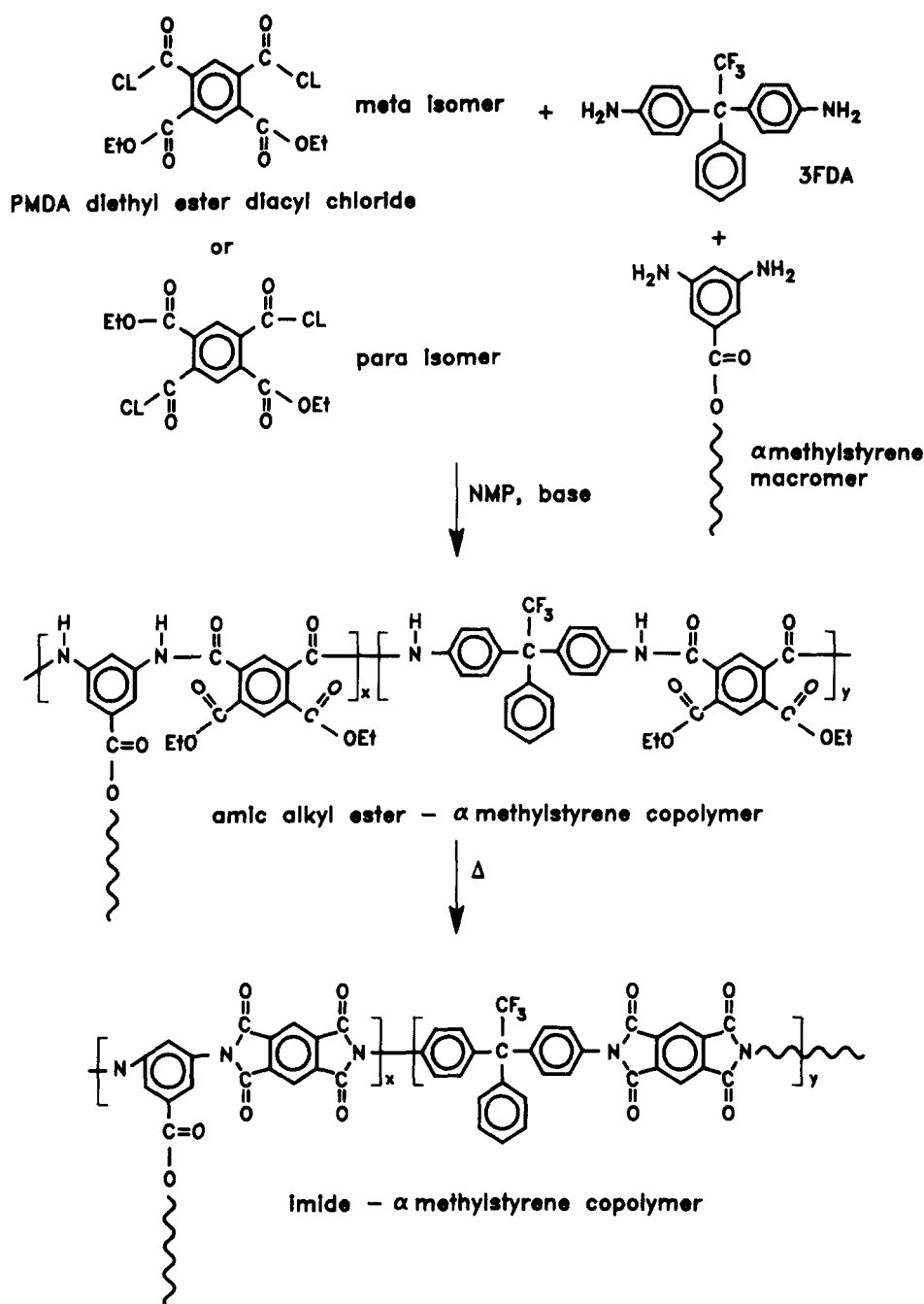
Scheme 2

EXPERIMENTAL

Materials

N-methyl-2-pyrrolidone (NMP), pyridine and acetic anhydride were purchased from Aldrich and used without further purification. The PMDA (Chriskev Co.) was sublimed three times prior to use. Diethyl pyromellitate diacyl chloride was prepared according to a procedure described by Volksen *et al.*[6] and the 3FDA was prepared following Rogers *et al.*[7].

Polymerizations

The hydroxyl functional α-methylstyrene oligomer, with a molecular weight of 18 000 gmol^{-1}, was prepared according to a literature procedure.[5] It was then reacted with 2,5-dinitrophenyl chloroformate, and hydrogenation over Pearlman's catalyst provided the aromatic diamino end-group necessary for the graft copolymerization[5]. In the first synthesis route considered, 3FDA-PMDA imide-α-methylstyrene copolymers were prepared via the poly(amic acid) precursor route followed by imidization *(Scheme 1)*. Solid PMDA (1.2000g, 0.0055 mol) was added to a solution of the α-methylstyrene oligomer (1.0000 g, 0.000055 mol) and 3FDA (1.8644 g, 0.0054

mol), to yield the target poly(amic acid) solution. The polymerizations were performed in an NMP-tetrahydrofuran (THF) (75/25) solvent mixture with a solids content of approximately 10wt%. Although both the 3FDA-PMDA poly(amic acid) and PMS are individually soluble in NMP, mixtures of the homo-polymers with the molecular weights under consideration here formed cloudy solutions. Addition of 25% THF, on the other hand, gave clear solutions and minimized homopolymer contamination after copolym-erization. Imidization of the poly(amic acid) solution was accomplished chemically with excess acetic anhydride and pyridine (6—8 h at 65°C).

Table 1   Characteristics of 3FDAPMDA imide-α-methylstyrene graft copolymers

| Sample | Imide form | α-Methylstyrene composition (wt%) | | Volume fraction of α-methylstyrene (%) |
		Charge	Incorporated	
1	Imide	15	15	17.5
2	Imide	25	25	29.0
3	*Meta*	10	10	12.0
4	*Meta*	15	14	17.0
5	*Meta*	25	23	26.7
6	*Para*	25	27	31.5

The second synthetic route to the imide-α-methyl-styrene graft copolymers was the poly(amic alkyl ester) route *(Scheme 2)*. This precursor may be isolated, characterized and given selective solvent rinses to remove possible homopolymer contamination prior to imidization. Furthermore, it is important to note that there are two isomeric forms of PMDS which can be separated and isolated at the monomer stage and subsequently polymerized. In our experiments, both the *meta* and *para* isomers of PMDA diethyl ester diacyl chloride were used, to study their effects on the subsequent foam. The synthesis involved the incremental addition of PMDA diethyl ester diacyl chloride (1.5600g, 0.00449 mol) dissolved in methylene chloride to a solution of the α-methylstyrene oligomer (1.0000 g, 0.00005mol) and 3FDA (1.519g, 0.04438mol) and NMP containing pyridine (0.7100g, 0.00897 mol) as the acid acceptor. The solids content was maintained between 12 and 15% in each case. The polymerizations were allowed to proceed overnight, and the products isolated in a water—methanol mixture, rinsed with methanol and dried in a vacuum oven.

Several different 3FDA—PMDA imide-α-methyl-styrene copolymers were prepared in the fully imidized form (copolymers 1 and 2, *Table 1)* and from the poly(amic alkyl ester) precursor (copolymers 3-6, *Table I)*. Copolymers 3-5 were prepared from the *meta* isomer of PMDA diethyl ester diacyl chloride, whereas copolymer 6 was prepared from the *para* isomer. For this study, only one PMS block length was investigated (18 000 g mol^{-1}). The α-methylstyrene contents of 15 and 25wt% were intentionally maintained low in order to produce discrete phases of α-methylstyrene embedded in the polyimide matrix. The α-methylstyrene contents was assessed gravimetrically from the weight retention after decomposition of the thermally labile block. For almost every copolymer synthesized, the final α-methylstyrene content agreed closely with that charged. The use of the α-methylstyrene oligomer which is difunctional at one chain end with the polyimide monomers produces a graft architecture where the α-methylstyrene component comprises the graft or pendant blocks. The average molecular weight of the α-methylstyrene graft is identical to that of the preformed oligomer. Furthermore, for such an architecture where the labile block is pendent to the matrix chain axis, decomposition of the labile coblock does not result in molecular weight degradation of the polyimide matrix.

Foam formation
The successful generation of a nanofoam requires the ability to process the block copolymer by conventional methods. The PMS decomposition temperature is sufficiently high to allow removal of common solvents prior to void formation, and after solvent removal the labile block can be decomposed by a subsequent thermal treatment. The copolymers were dissolved in NMP at a concentration of 9-15% solids. Transparent coatings 1025 μm thickness were obtained by spin coating at 2000 rpm on 2.54 cm diameter silicon wafers or by doctor blading. Thermal imidization was accomplished by heating the polymer films to 265° C at 5°Cmin^{-1} and maintaining them at 265°C for 1.5h in a nitrogen atmosphere. Previous studies have shown that this is near the temperature and time limit for quantitative α-methylstyrene retention[5]. Approximately 95% of the poly(amic alkyl ester) was converted to the imide by this treatment. However, it should be pointed out that the block copolymers were extremely brittle, and freestanding films were difficult to obtain. The films were then heated over a 4 h period to 325°C and held at this temperature for 2 h to effect the decomposition of the α-methylstyrene coblock.

Characterization
Glass transition temperatures, taken as the midpoint of the change in the slope of the heat flow rate, were measures with a DuPont 2090 differential scanning calorimeter at a heating rate of 10°C min^{-1}. A Polymer

Laboratories' Dynamic Mechanical Thermal Analyzer (DMTA) operating in tension at 10 Hz with a heating rate of 10°C min^{-1} was used to assess the dynamic mechanical properties. Isothermal and variable-temperature thermogravimetric analysis (t.g.a.) measurements were performed on a Perkin-Elmer mode TGA-7 in a nitrogen atmosphere (10°Cmin^{-1}). Density measurements were obtained with a density gradient column containing water and calcium nitrate. The column was calibrated against a set of beads of known densities at 25°C. At least two specimens were used for each density measurement. *FTi.r,* measurements were made on an IBM Instruments IR44 with an MCT detector[8].

Selected samples were prepared for transmission electron microscopy (TEM) using the Reichert-Jung Ultracut E ultramicrotome. Film samples were mounted in epoxy resin, and thin sections were taken parallel and perpendicular to the plane of the films at room temperature. These sections were then observed using the Phillips 300 TEM at an accelerating voltage of 100 kV. Image analysis software for the TEM images was written using the National Instruments Labview 81 programming language, incorporating Graftek Image Concept V.i = 81 image-handling subroutines.

RESULTS

Dynamic mechanical and dynamic thermal analysis

The dynamic mechanical results for selected copolymers are shown in *Figure I.* Two glass transitions were observed in each case, indicative of microphase-separated morphologies. The transition observed near 60°C is similar to that seen for the α-methylstyrene oligomer. Furthermore, the damping peaks associated with the α-methylstyrene transitions were sharp, particularly that of copolymer 6, derived from the *para* isomer, indicating that the phases were pure with sharp boundaries. The imide transitions tended to be comparable to that of the parent polyimide (~450°C). In addition, a modulus drop in the proximity of 320°C could be observed. Interestingly, this temperature is consistent with the decomposition temperature of the α-methylstyrene coblock, as shown by the variable-temperature thermogram *(Figure 2).* These data strongly suggest that the α-methylstyrene monomer generated as the degradation product strongly interacts with the 3 FDA-PMDA polyimide, which results in plasticization of the matrix.

Thermal mechanical analysis was also used to study the structure and stability of the copolymer as a function of temperature. For these experiments, a small tensile deformation was applied during heating, and the deformation as a function of temperature for copolymer 1 is shown in *Figure 3*. As expected, up to approximately 160°C the standard thermal expansion is observed. However, near the T_g of the α-methylstyrene a contraction due to a relaxation of the thermal stresses is observed.

Subsequent thermal expansion of the film is observed up to approximately 300°C, where a contraction in the sample was observed. This is consistent with the formation and simultaneous collapse, or at least partial collapse, of the foam structure, and further illustrates the significance of plasticization. Finally, the polyimide T_g can be observed at about 440°C, consistent with the dynamic mechanical spectra.
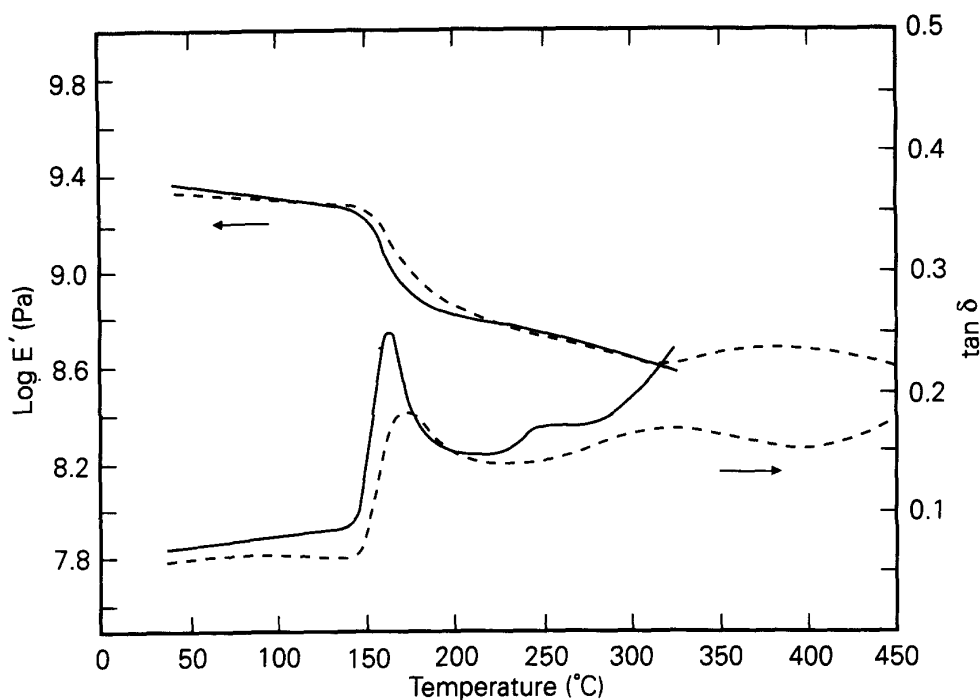

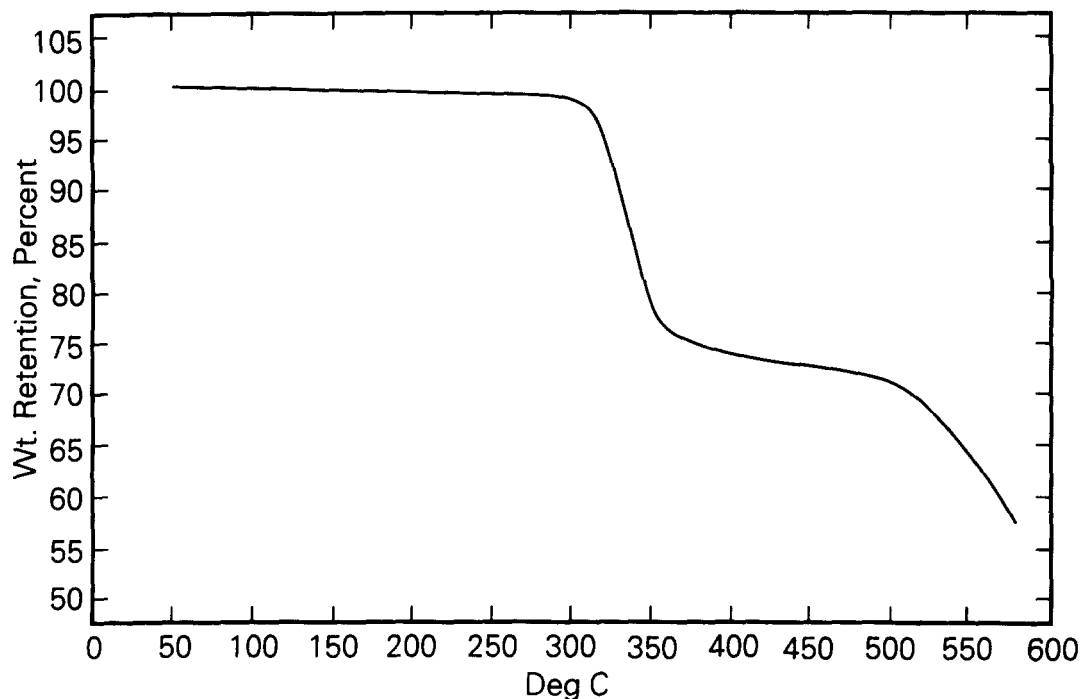*Figure 1   Dynamic mechanical analysis for copolymers 2 (—) and 6 (-----)*
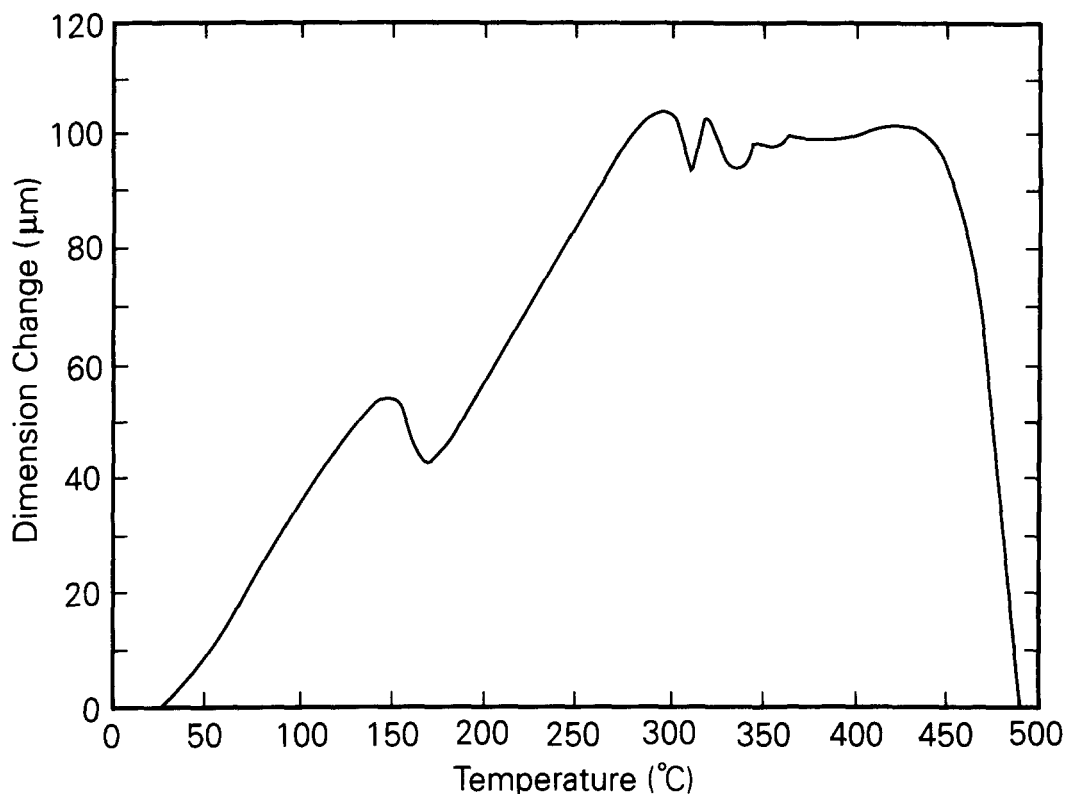
Figure 2   T.g.a. of copolymer 2

Figure 3   Thermomechanical analysis of copolymer 1

Morphology

Interpretation of the porosity values measured by flotation in the density gradient column for the foamed polymers was difficult. In most cases this method yielded values substantially lower than expected. During the course of the measurement the film would initially settle at a specific height in the column, but with time the sample would slowly move towards higher densities. In previous studies this was shown to result from fluid

penetrating the pores, giving a density similar to the homopolymer[5]. To avoid these problems, infrared spectroscopy was used to determine the void content in the foamed copolymers[8]. By independently measuring the film thickness, the absorbance (calibrated from measurements on unfoamed imide films) and the refractive index determined from the interference fringes, we were able to obtain results in quantitative agreement with the density column method. The porosities of the foamed copolymers are shown in *Table 2*. In most cases, the foams showed porosities consistent with the volume fraction of the α-methylstyrene in the copolymer.

Table 2   Characteristics of 3FDA-PMDA imide foams

Sample	Total volume fraction of α-methylstyrene	Porosity (%)
1	17.5	8
2	29.0	29
3	12.0	8
4	17.0	22
5	26.7	24
6	31.5	28

Figure 4 shows selected transmission electron micrographs for different copolymers. These reflect not only the variations in porosity, but also a remarkable variation in structure according to the synthetic route employed. Microtomed slices of the foams obtained by the ester route copolymers (4 and 6) contained very coarse voids, with rough surfaces and diameters of up to 1 μm or more, as shown in *Figure 4a*. These images must nevertheless be treated with caution since, in some cases, the voids appeared to contain some internal structure, which was probably severely damaged by the microtom-ing, as shown in *Figure 4b*-—note also the presence of smaller voids with diameters of approximately 50 nm in this section. The films obtained from copolymer 5, on the other hand, had a very different internal structure; here the voided regions of the films were highly interconnected and adopted a coarse ribbon-like morphology with a very high void content (there was also some degree of organization of the void ribbons in sections taken in the plane of the films, as shown in *Figure 4e)*. The chemically imidized foams had much finer structures *(Figure 4d)*. For essentially unconnected voids with apparently spherical or ovoid morphologies were observed (although a variety of other structures was present, which may have been contributed to by damage during preparation). For copolymer 2, the void density was apparently higher with a somewhat high degree of interconnectivity locally, although the mean void size appeared lower (see *Table 2)*. The structures observed in the slices did not vary greatly with the direction of the cut, but it must be remembered that these are essentially two-dimensional sections though a three-dimensional sample, so that the degree of interconnectivity may be higher than suggested by microtoming. For example, small circular holes may represent sections through higher aspect ratio structures extending out of the plane of the slices.

A more thorough analysis of these structures to obtain void size distributions and volume fractions was difficult, not only because of the variable geometry of the voids, but also owing to the finite thicknesses of the slices. Where spherical or nearly spherical voids could be assumed, one can estimate the various moments of the distribution of R, the radius of the assumed spherical voids, and the void volume fraction, φ, from images of films of different thicknesses using[9]

$$\langle r \rangle = \frac{\pi \langle R^2 \rangle + 2t \langle R \rangle}{4 \langle R \rangle + 2t}$$

$$\langle r^2 \rangle = \frac{4 \langle R^3 \rangle + 3t \langle R^2 \rangle}{6 \langle R \rangle + 3t} \tag{1}$$

$$\phi_a = \frac{4 \langle R^3 \rangle + 3t \langle R^2 \rangle}{4 \langle R^3 \rangle}$$

where t is the film thickness and r is the equivalent disc radius calculated for each hole in a given image from $2/\pi a^{1/2}$, where a is the hole area. The total area fraction of holes, φ_a, were obtained by converting TEM images into binary form using a suitable threshold and then using the standard image analysis routines referred to in the Experimental section. The assumption of spherical voiding is clearly questionable. However, the estimates from direct observations of void volume fractions for copolymers 1, 4 and 6, where this assumption seemed most justified, were in reasonable agreement with values obtained from the absorbance measurements as shown in *Table 2,* which suggests that even if the voids do contain internal structure, this represents a very small proportion of the total volume.

In the remaining films, estimates of the void volume fractions were obtained by optical densitometry of the TEM

plates using the method employed by Kramer[10] to determine volume fractions in crazes. This is complicated by assumptions relating to the uniformity of the film thickness and the linearity of the sensitivity of the TEM plates. It does not allow any estimation of void dimensions: those given for copolymers 2 and 5 in *Table 2* were simply obtained by inspection of the TEM plates.
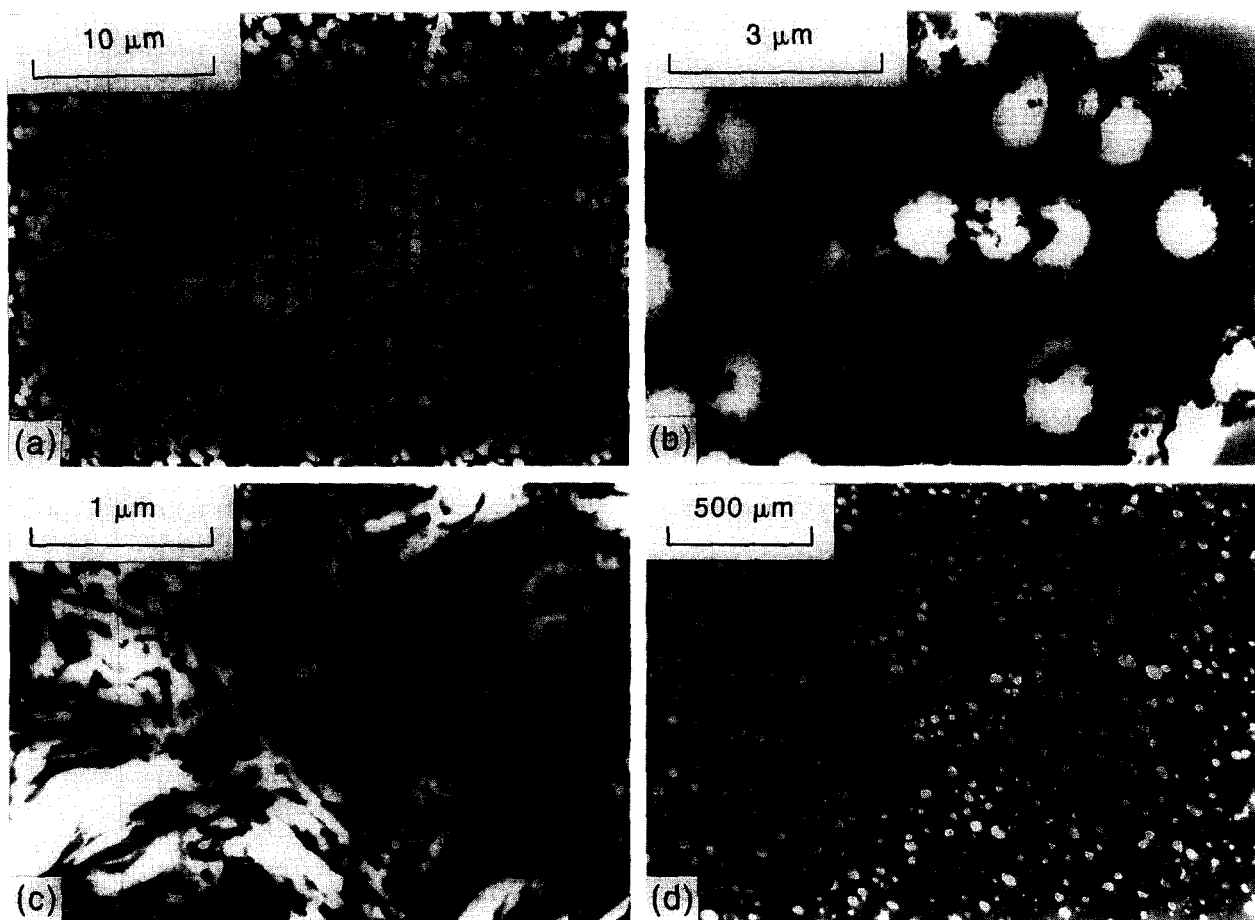

Figure 4 Microtomed sections of foams from various copolymers (the compositions given are those prior to foaming): (a) transverse section of para 3FDA-PMDA-25 wt% PMS; (b) detail of (a) showing smaller voids and internal structure in the large voids; (c) longitudinal section of meta 3FDA-PMDA-25wt% PMS; (d) transverse section of imide-15 wt% PMS

DISCUSSION

Glassy polymers are well known to foam by blowing of supersaturated gas, for example CO_2 introduced at high pressure. If the gas acts as a plasticizing agent, on release of the pressure at a sufficiently high temperature T where $T < T_g$ of the plasticized polymer, bubbles will nucleate, possibly at sites of high free volume (physical ageing has been demonstrated to lower the bubble nucleation density in certain systems). Such situations may lead to bimodal distributions of pores, since those which nucleate first are able to grow rapidly, the high solute concentration driving void growth and plasticizing the matrix. Later-forming voids may either be unstable owing to Ostwald ripening mechanisms or else undergo only limited growth owing to the diminished solute content at relatively long times. Such foams are typically characterized by micrometre sized circular voids, and often a skin layer containing little cores voiding, presumably since the solute concentration is always low close to the sample surface.

Here the situation is different in that blowing is not needed to obtain porosity. Decomposition of the PMS-rich phase regions can, in principle, simply leave behind holes whose morphology reflects the initial morphology (given a sufficiently stable matrix). However, as we have seen, the matrix is plasticized by the PMS monomer. Thus, for the poly(amic alkyl ester)-based copolymers 3-6, where imidization does not go to completion prior to PMS decomposition and the T_g, the matrix is sufficiently plasticized for blowing to occur. That is, T is at some point less than the sample temperature. Ind~eed, for the thermally imidized foams obtained via the ester route we see coarse voiding, and, similarly, foams from the triblock polymer by this route high void contents. As stated in

the introduction, these latter also showed highly interconnected structures, similar to those obtained here for copolymer 5, and are consistent with those for the triblock polymers.

However, non-interconnected spherical highly voided regions in copolymers 4 and 6 were not seen in the triblock copolymers. This would appear not to be related to the initial microstructures since the polymer architecture should ensure that phase separation is limited to much shorter spatial ranges in all cases. These structures might be taken to imply a competitive growth mechanism; large voids grow with solute diffusing from the rest of the sample as in the pressure-induced foams described at the beginning of this section. However, there is no apparent surface depletion of voids, and the highly porous spherical regions apparently contain internal structure. Furthermore, we have seen similar structures in essentially two-dimensional films (that is, with a film thickness very much less than the diameter of the highly voided regions), and preliminary *in situ* TEM observations of films suggest that the highly voided patches appear first as regions of increased mass density which subsequently undergo massive nucleation. Clearly, in a highly plasticized matrix, Ostwald ripening processes will be highly unfavourable to subsequent void stability in the surrounding material.

In the chemically imidized foams (copolymers 1 and 2), the imide T_g at the decomposition temperature is higher than that of the thermally imidized films, and, as a result, we do not see this coarse distribution of voids. This is consistent with the previous study of the imide α-methylstyrene triblock copolymers, although here the structures are less connected.

SUMMARY

A new means of preparing polyimide foams with pore sizes in the nanometre to micrometre regime has been demonstrated. Microphase-separated block copolymers comprised of a polyimide as the matrix or dominant phase with a thermally unstable material, PMS, have been prepared. The copolymers were designed in such a way as to allow conventional solvent processing (spin coating and doctor blading, for example), and, upon a subsequent thermal treatment, the thermally unstable block undergoes thermolysis, leaving pores with a size and shape dictated, in principle, by the initial block copolymer morphology. The copolymers were prepared through either the poly(amic acid) precursor or the poly(amic alkyl ester) route (using both the *meta* and *para* isomers). The α-methylstyrene compositions in the copolymer were deliberately maintained low so as to produce discrete domains of the thermally labile component in a high-temperature polymer matrix. Microphase-separated morphologies were observed in all cases. TEM and infrared measurements were used to assess the porosity. The results show that the foam structure depended strongly on the degree of plasticiza-tion of the polyimide matrix by the α-methylstyrene monomer. TEM measurements showed that the sizes of the pores generated, ranging from 40 nm to over 1 *μm,* were larger than the initial copolymer morphologies. This discrepancy in the pore size was attributed to a plasticization of the polyimide matrix coupled with rapid volatilization of the PMS, which served as a blowing agent.

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