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Polyimide foams prepared from homopolymer/copolymer mixtures

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A new route has been developed for the synthesis of thermally stable polymer foams with high glass transition temperatures. Compositionally asymmetric microphase-separated block copolymers were prepared where the minor component, poly(α-methylstyrene), is thermally labile and the major component, polyimide, is thermally stable. The minor component can unzip, to its monomer upon heating, and the decomposition products diffuse out of the film leaving behind pores embedded in a matrix of the thermally stable component. The addition of homopolymer of the thermally labile component to the block copolymer offered one means to increase the volume fraction of voids while maintaining a discrete cell structure. Mild decomposition conditions were required to avoid rapid depolymerization of the α-methylstyrene and subsequent plasticization of the polyimide matrix. The foams showed pore sizes with diameters ranging from 40 nm to just over 1 μm, depending on the copolymer used in the mixture, along with the expected increase in porosity.

(Keywords: polyimide; foams; synthesis)

Introduction

An alternative methodology to low dielectric constant, high temperature polymers has been developed. The reduction in the dielectric constant is achieved by generating a foam, replacing some of the polymer with air which has a dielectric constant of 1. Foams have been prepared from microphase-separated block copolymers composed of a thermally stable and a thermally labile block where the latter is the dispersed phase[1–4]. Upon heating, the thermally unstable block undergoes thermolysis leaving pores whose size and shape are dictated by the initial copolymer morphology. High temperature foams have been successfully prepared by this route with pore sizes less than 10 nm; this is crucial for microelectronic applications where the pore size must be much smaller than the film thickness and the underlying microelectronic features. It is also mandatory that the pores be of the closed cell type, since interconnectivity will lead to shorts and solvent entrapment in the fabrication of a microelectronic device. Consequently, the block copolymer approach is limited to volume fractions of the thermally labile coblock of <30%, since above these compositions more interconnected morphologies are found. Previous investigations have shown, however, that the volume fraction of voids generated in the foam was significantly less than the initial volume fraction of the thermally labile material in the copolymer[1–4]. This results from a collapse of smaller pores due to the surface tension of the pores and the plasticization of the matrix by the decomposition products of the thermally labile block. These results suggest a limiting void size and volume fraction achievable by this approach. Adding homopolymer of the labile component to the block copolymers offers one possible means by which the volume fractions of voids can be increased while maintaining a discrete closed cell structure. Mixtures of the imide α-methylstyrene (αMS) block copolymers with poly(α-methylstyrene) (PαMS) homopolymer are described in this article.

Experimental

N-Methyl-2-pyrrolidone (NMP), pyridine and acetic anhydride were purchased from Aldrich and used without further purification. Pyromellitic dianhydride (PMDA) (Chriskev Co.) and 4,4′-oxydianiline (ODA) were sublimed three times prior to use. Diethyl pyromellitate diacyl chloride was prepared according to a procedure described by Volksen *et al.*[5]. The 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA) was prepared according to literature procedures[6]. Preparation of the PαMS and the imide–αMS copolymers has been described previously[4].

The copolymers and block copolymer/homopolymer mixtures were dissolved in NMP and spin-coated or doctor-bladed onto Si wafers to produce films 10–25 μm thick. Samples were heated under nitrogen at 5°C min^{-1} to remove the solvent, and were held at 265°C to imidize the polymer. Foams were generated by heating the imidized films to 325°C over a 4 h period and holding at that temperature for 2 h to decompose the αMS block.

Thermal analyses were obtained with a DuPont 2090 instrument at a heating rate of 10°C min^{-1}. A DuPont Dynamic Mechanical Analyzer with a heating rate of 10°C min^{-1} in the tension mode was used to measure the dynamic mechanical properties. Thermal gravimetric analysis (t.g.a.) measurements were performed on a Perkin–Elmer model TGA-7 under a nitrogen atmosphere. Porosity was determined by i.r. spectroscopy

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*To whom correspondence should be addressed using a Fourier transformed infra-red spectrometer (IBM Instruments IR44), with MCT detector[7]. Transmission electron microscopy (TEM) was performed on a Phillips 12 520 Instrument at 100 kV. Copolymer films were cast from a dilute solution in NMP onto a glass plate; they were imidized and foamed then removed from the glass plate and ultramicrotomed at room temperature.

Results and discussion

The polyimide matrix derived from 3FDA/PMDA is soluble in solvents like NMP, has a glass transition temperature, T_g, of 440°C, and a polymer decomposition temperature in excess of 500°C (ref. 6). The block copolymers and homopolymer used in the mixtures were prepared either by the chemical imidization of the poly(amic acid), **1**, or by thermal imidization of the poly(amic alkyl ester) precursor, **2**, PαMS was used as the thermally labile component since it depolymerizes at ~ 290°C, which is significantly lower than the T_g of the polyimide[8]. To produce an initial copolymer morphology with discrete PαMS microdomains, copolymers with αMS compositions ranging from 10 to 30% were prepared. While this should be suitable for the generation of a foam, the degradation product of PαMS plasticizes the 3FDA/PMDA polyimide and the depolymerization is so rapid that it acts as a 'blowing agent', producing pore sizes larger than that expected from the initial copolymer morphology. TEM measurements showed that the pore sizes ranged from 15 to 1800 nm. These effects were more pronounced with the copolymers derived from the poly(amic alkyl ester) precursor, since, at the cure temperatures, the full T_g of the polyimide was not realized.

Mixtures of the PαMS homopolymer (M_w = 9600 g mole^{-1}) with the 3FDA/PMDA amic ester α-methylstyrene copolymers were dissolved in NMP, cast and cured at 265°C for 1.5 h to remove the solvent and effect imidization. The low molecular weight of the PαMS was chosen to ensure that the homopolymer dissolved in the PαMS microdomain of the copolymer, which had a molecular weight of 18 000. Volksen *et al.*[5] found that the imidization of the poly(amic ethyl ester) derived from PMDA/ODA occurred from 240 to 355°C, with a maximum rate at 255°C. However, the decomposition of the αMS restricted the imidization conditions to 1.5 h annealing at 265°C, which is near the limit of quantitative αMS retention. Two series of mixtures were studied, where the volume fraction of the PαMS homopolymer was varied using copolymers **3** and **4** in which the fraction of PαMS in the copolymer was 18% and 30%, respectively (*Table 1*). All the mixtures were transparent, indicating that the PαMS homopolymer mixed with the PαMS block of the copolymer. Two additional sets of blends were prepared from imide–αMS triblock copolymers, where the molecular weight of the PαMS block was 12 000 g mol^{-1} and the fraction of PαMS in the copolymer was 10 or 25 wt%, denoted as copolymers **5** and **6**, respectively. Mixtures were prepared by the addition of αMS homopolymer with molecular weights of 9600 or 1000 g mol^{-1} to each of the copolymers. A summary of the mixtures studied is shown in *Table 2*. All the mixtures were transparent, showing no evidence of a macroscopic phase separation.

Table 1 Copolymer/homoplymer blends[a]

Copolymer or blend	Total volume fraction of αMS[b]	Porosity (%)
3	18	15
3a	23	20
3b	29	44
3c	36	47
3d	39	40
3e	44	42
4	30	35
4a	34	28
4b	39	24
4c	44	–

[a] PαMS molecular weight was 9600 g mol^{-1}

[b] Includes the αMS in the homopolymer and the copolymer

Table 2 Copolymer/homopolymer blends

Copolymer or blend	Total volume fraction of αMS	Porosity (%)	Molecular weight of PαMS homopolymer (g mol^{-1})
5	12		–
5a	14	>50	9600
5b	54	38	9600
5c	55	–	1000
6	29		–
6a	36	>50	9600
6b	54	30	9600
6c	37	42	1000

The dynamic mechanical analyses for selected mixtures are shown in *Figures 1* and *2*. In the copolymers, two transitions were observed in each case, indicative of microphase separation[4]. Similar modulus temperature profiles are also seen for the block copolymer/homopolymer blends. The transition occurring near 160°C, similar to that seen for the αMS oligomer used in the synthesis, is sharp, suggesting that the phases are pure with sharp boundaries. The higher temperature transition can be attributed to the T_g of the imide matrix. A modulus drop near 320°C is also observed, which can arise from the plasticization of the polyimide matrix by the αMS monomer generated in the depolymerization of PαMS. The high diffusivity of the monomer, however, ensures that the plasticization of the polyimide matrix is short-lived, as evidenced by the modulus increase above 320°C.

The thermogram of copolymer **6** and blends **6a** and **6c**

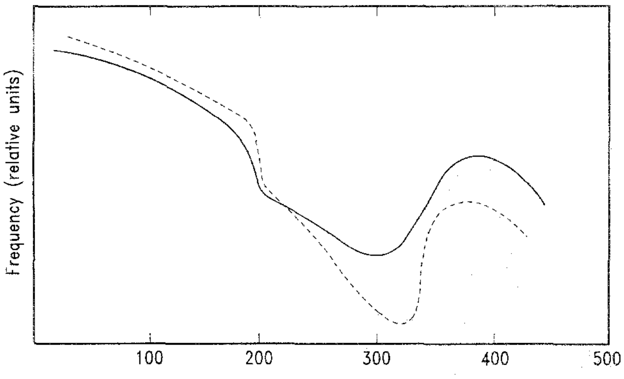

Figure 1 Dynamic mechanical analysis of blend **3d** (——) and **4b** (-----)

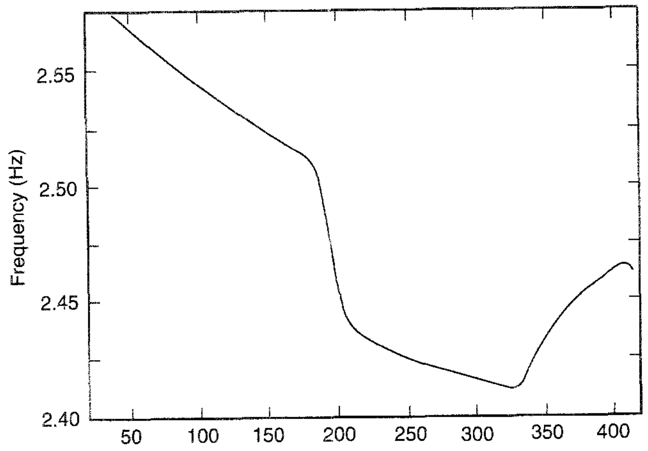

Figure 2 Dynamic mechanical analysis of blend **5a**

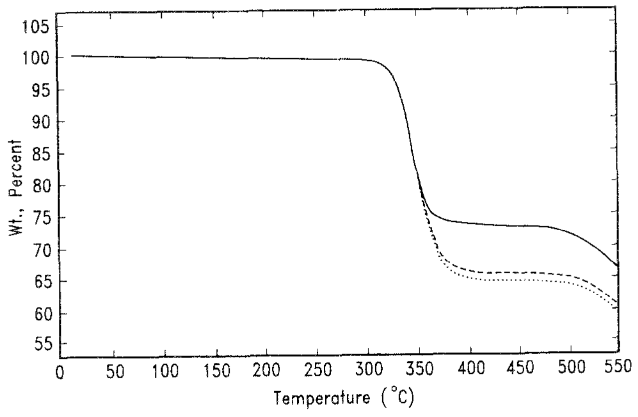

Figure 3 Thermogravimetric analysis of copolymer **6** (——) and blends **6a** (-----) and **6c** (········)

in *Figure 3* shows that the PαMS in the copolymer and homopolymer degrades at ~ 320°C. The sharpness of the weight loss profile clearly demonstrates that the degradation product, αMS, is readily evolved from the sample. However, the retention of the foam structure depends on a balance between the decomposition rate and the permittivity of the αMS in the imide matrix. Since the αMS is soluble in the imide matrix, then the diffusion of αMS in the imide matrix dictates the length of time that the matrix is plasticized by the αMS, i.e. the residence time of the αMS in the matrix. Consequently, the heating rate of the experiment is critical. The optimum thermal treatment was found to be 265°C for 1.5 h followed by a slow heating to 325°C over a 4 h period and holding at temperature (325°C) for 2 h (ref. 4).

The porosity values, as measured by i.r. spectroscopy[7], for the copolymers and copolymer/homopolymer mixtures are shown in *Tables 1* and *2*. For mixtures using copolymer **3**, an expected increase in porosity with the addition of PαMS homopolymer is seen, with values as high as 47%. Furthermore, the porosity, to within the experimental errors of the i.r. technique, agrees well with the total PαMS volume fraction in the mixture[7]. Mixtures of copolymer **4** with PαMS homopolymer show markedly different behaviour. It appears that the addition of PαMS homopolymer to the copolymer adversely affected the final porosity. From *Table 1* it is seen that the porosity decreased in all cases. The mixtures prepared from the fully imidized copolymers (copolymers **5** and **6**) shown in *Table 2* showed similar porosities to those prepared from copolymers **3** and **4**.

While the i.r. measurements indicate that foams were successfully generated, no information on the pore size was obtained. The opacity of the films suggests a pore size much larger than the initial block copolymer morphology. The transition electron micrographs of a typical microtomed section of a copolymer **3** and several blends **3c** and 3e, prepared via the poly(amic alkyl ester) route, after the decomposition of the αMS phase are

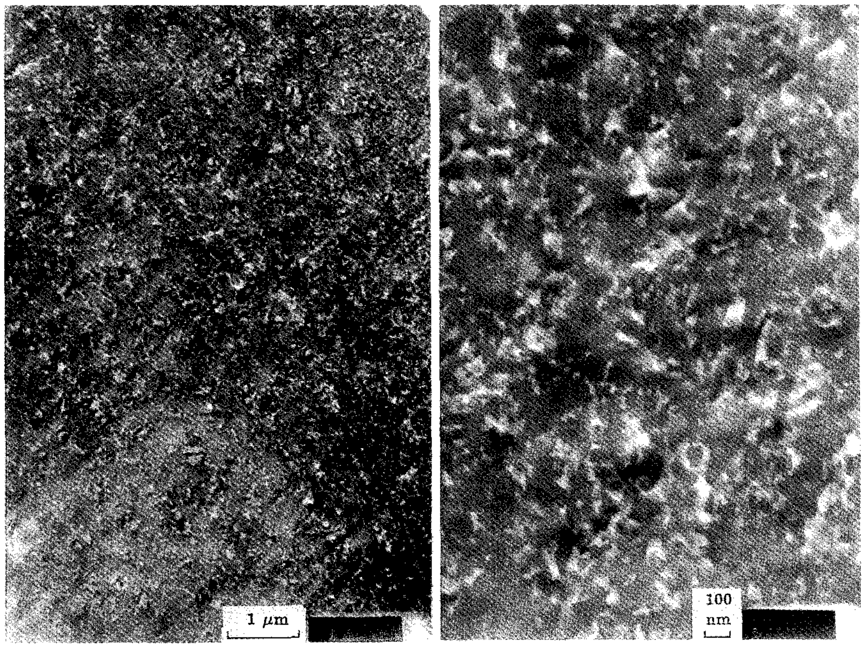

Figure 4 TEM micrograph of copolymer **3** (left 18 750×, right 67 000×)

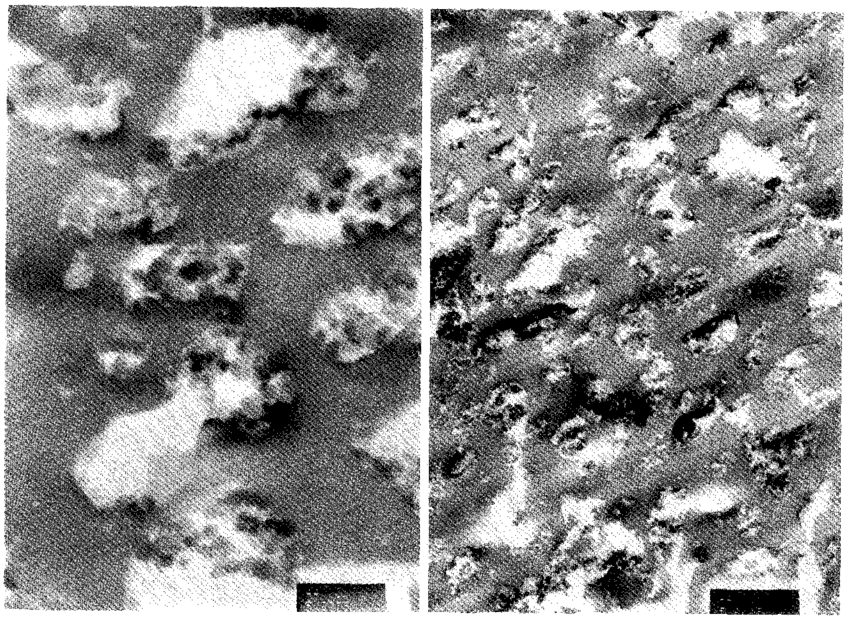

Figure 5 TEM micrograph of blend **3c** (right 18 750×, left 67 000×)

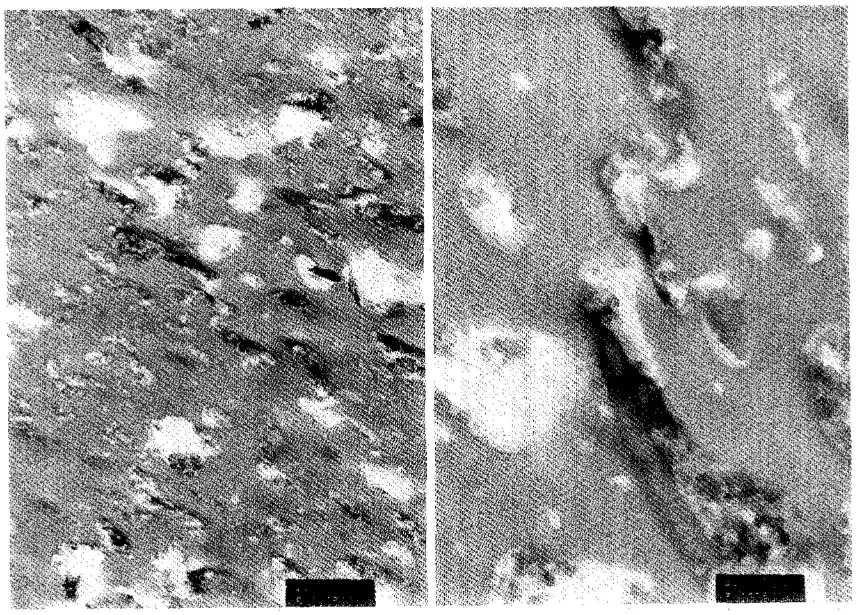

Figure 6 TEM micrograph of blend **3e** (left 18 750×, right 67 000×)

shown in *Figures 4–6*. The dark regions of the micrographs correspond to the polyimide phase. For the copolymer, it is evident that a porous structure is obtained from the micrograph, with pores having cross-sections ranging from 20 to 200 nm. The opacity arising from the foam is believed to result from plasticization of the matrix from the αMS formed together with a partial blowing and/or coalescence of these pores. Markedly different behaviour was found for the block copolymer/homopolymer mixtures derived from the poly(amic alkyl ester) precursor. The micrographs clearly show the formation of a cellular structure with pores nearly 1 μm in size, irrespective of the copolymer used or the blend composition. These pores are unlike those described above for the copolymer and, once again, they are considerably larger than the initial block copolymer morphology. However, unlike the block copolymer foams described above, this cellular structure is composed of discrete spherical pores.

The comparison of the foams produced from these copolymer mixtures provides some insight into the control of the pore size. The major difference in the mixtures prepared from copolymers **3** and **4** is the fraction of PαMS in the copolymer. In the first case only 18% of the copolymer is of PαMS, whereas, in the latter, 30% of the copolymer is PαMS. In terms of the morphology, the former case will generate microphases of the PαMS that are well dispersed in the polyimide matrix. Increasing the PαMS content by the addition of the homopolymer will tend to increase the size of the PαMS microdomains and decrease the separation distance. Copolymers with the higher PαMS content will have a tendency to produce more interconnected structures, or, if the microdomains are well dispersed, the separation distance between the microdomains will be small. Addition of the PαMS homopolymer will simply increase the size of the microdomains and promote interconnectivity. Consider now the concentration of the αMS monomer in the imide matrix during the decomposition of the PαMS block and homopolymer. The smaller the separation distance between the microdomains, the greater will be the concentration of the αMS monomer which, in turn, leads to a greater plasticization of the matrix and, consequently, a lower matrix T_g. This will promote a coalescence of the pores and facilitate the blowing process. Both will lead to pores with sizes larger than expected, which is observed.

Foams prepared from copolymer/homopolymer mixtures, where the fully imidized form of the copolymer was used, were translucent or opaque. As in the other mixtures, this shows that the pore sizes are comparable to the wavelength of light and are much larger than the microdomains of the initial copolymer. Shown in *Figures 7* and *8* are electron micrographs of copolymer **6** and its mixture **6c**. As before, the dark regions of the micrographs correspond to the polyimide phase. Clearly, a porous structure was obtained, with pores having cross-sections ranging from 10–180 nm. Although the pores are larger than the microdomains of the initial block copolymer, they are significantly smaller than those found in the poly(amic alkyl ester) analogues. This suggests that the polyimide matrix is plasticized by the αMS and that the αMS acts as a blowing agent. It is

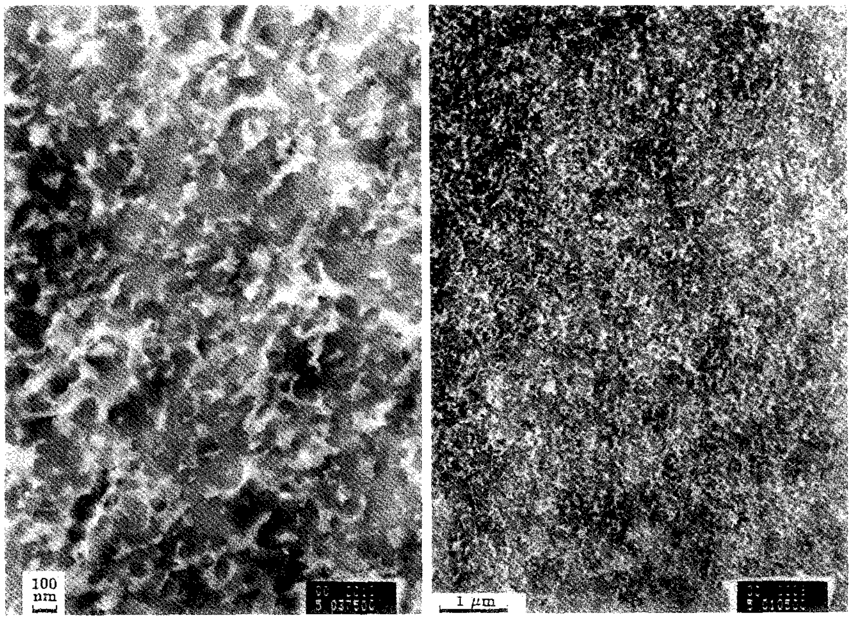

Figure 7 TEM micrograph of copolymer **6** (right 18 750×, left 67 000×)

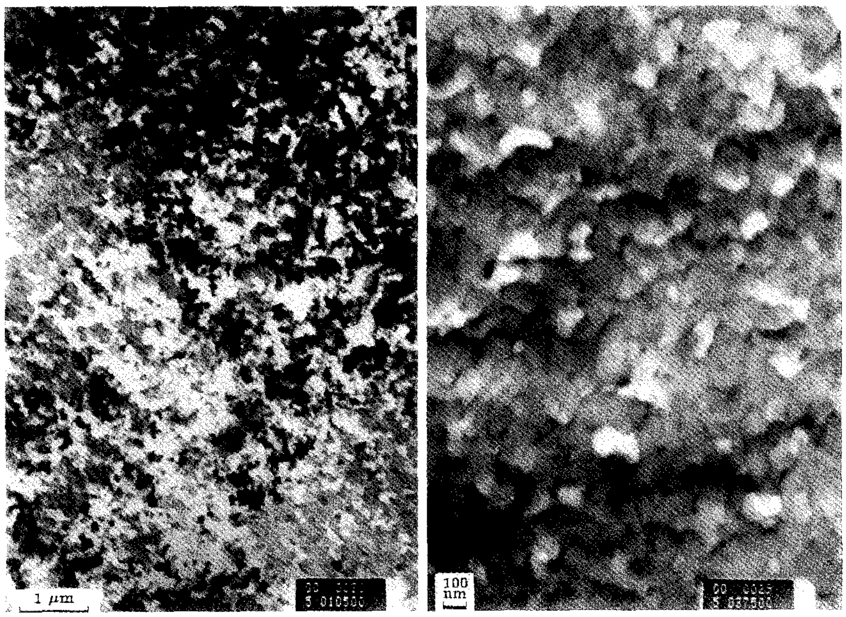

Figure 8 TEM micrograph of blend **6c** (left 18 750×, right 67 000×)

apparent that the diffusion of the αMS in the polyimide matrix is greater for these materials than for the copolymers prepared via the poly(amic alkyl ester) route. This can be attributed to a lower T_g of the matrix due to an incomplete imidization of the poly(amic alkyl ester).

Summary

A new means of preparing polyimide nanofoams has been demonstrated. Microphase-separated block copolymers have been prepared, composed of a thermally stable polyimide as the matrix or dominant phase with a thermally unstable material. Homopolymer of the labile component was added to the block copolymer so as to increase the volume fraction of voids while maintaining the discrete spherical structure. The αMS compositions in the copolymer were maintained low so as to promote the formation of discrete domains of the thermally labile component in the high temperature polymer matrix. The molecular weight of the PαMS homopolymer was kept low to ensure that the homopolymer dissolved in the αMS domains of the copolymer. Microphase-separated morphologies were observed in all cases. TEM and i.r. measurements demonstrated that a porous film could be generated by the decomposition of the αMS block. However, the size of the pores in the resultant foam was much larger than the size of the αMS microdomains in the initial mixture. This discrepancy in the pore size can be attributed to a plasticization of the polyimide matrix coupled with rapid volatilization of the PαMS, which served effectively as a blowing agent.

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