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The use of styrenic copolymers to generate polyimide nanofoams

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New routes for the synthesis of high T_g thermally stable polymer foams with pore sizes in the nanometre regime have been developed. Foams were prepared by casting well-defined microphase-separated block copolymers comprising a thermally stable block and a thermally labile material. At properly designed volume fractions, the morphology provides a matrix of the thermally stable material with the thermally labile material as the dispersed phase. Upon thermal treatment, the thermally unstable block undergoes thermolysis generating pores, the size and shape of which are dictated by the initial copolymer morphology. Several labile blocks were surveyed including polystyrene, poly(α-methylstyrene) and several α-methylstyrene/styrene copolymers. Each of these polymers can unzip to its monomer upon heating; however, the rate is substantially slower for polystyrene. The copolymers were synthesized through either the poly(amic acid) precursor, followed by chemical imidization to the polyimide form, or the poly(amic alkyl ester) precursor followed by thermal imidization. The decomposition of the labile coblock was studied by thermogravimetric and dynamic mechanical analysis. Upon decomposition, the foams showed pore sizes in the nanometre regime along with the expected reduction in mass density.

(Keywords: polyimide foams; block copolymers; synthesis route)

INTRODUCTION

For microelectronic fabrication, polymeric insulators have several attractive advantages over inorganic materials such as alumina and silicon oxides. These include lower dielectric constants and ease of processing[1], with polyimides emerging as prime candidates for polymeric insulators. To further reduce the dielectric properties of polyimides, perfluoroalkyl groups have been incorporated and, while this approach produces films with dielectric constants below 3.0, it is often at the expense of both solvent resistance and mechanical properties. In an effort to circumvent these problems, a new approach has been developed to reduce the dielectric constant while maintaining the thermal and mechanical properties. The reduction in the dielectric constant is achieved by replacing a proportion of the polymer with air (dielectric constant of 1), which leads to a foam or porous structure. 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 have demonstrated a procedure for the production of high temperature polymer foams with pore sizes in the nanometre regime, which we have termed 'nanofoams'. This technique is based on microphase-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.

Nanofoams have been prepared using poly(propylene oxide) (PPO) or poly(methyl methacrylate) (PMMA) as the labile component in a polyimide or poly(phenylquinoxaline) (PPQ) matrix[2]. In PPO- and PMMA-based triblock copolymers, a 10–18% reduction in density is observed on decomposition of the labile component, and small-angle X-ray scattering (SAXS) shows pores sizes in the region of 10nm. Poly(α-methylstyrene) also appeared to be ideally suited for use as the thermally labile coblock, since well-defined functional oligomers can be prepared, and, unlike PPO, it depolymerizes quantitatively by unzipping to the monomer (zip length of $\sim$ 1200)[5]. The decomposition temperature of $\sim$ 290°C is also well below the glass transition temperature (T_g) of typical polyimides, and significantly lower than the decomposition temperature of PMMA prepared by group transfer methods. However, foams derived from imide/α-methylstyrene-based triblock copolymers have interconnected microporous structures and not the

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expected nanopores, even for low α-methylstyrene contents[5]. A plausible explanation for this is that the decomposition rate of the poly(α-methylstyrene) block was considerably faster than the diffusion rate through the polyimides surveyed, and the degradation product, α-methylstyrene, plasticized the polyimide matrix and acted as a 'blowing agent', increasing the pore size and interconnectivity. In fact, porosities as high as 60% with pore sizes in the 200 nm range have been observed for some systems.

To overcome this pore expansion and coarsening, some or all of the α-methylstyrene units can be replaced with styrene. By comparison, polystyrene has a zip length of only 60 which slows the rate of decomposition[6,7]. Also for anionically prepared polystyrene the decomposition temperature is $\sim 340°C$ which is sufficiently high to allow imidization, if required, and solvent loss, but is sufficiently below the T_gs of the selected polyimides investigated to afford an ample processing window. In this study, we wish to report the use of polystyrene and styrene/α-methylstyrene copolymers as labile blocks to generate polyimide nanofoams for microelectronic applications.

EXPERIMENTAL

Materials

N-methyl-2-pyrrolidone (NMP), pyridine and acetic anhydride were purchased from Aldrich and used without further purification. The 9,9'-bis(4-aminophenyl) fluorene (FDA) and pyromellitic dianhydride (PMDA) (Chriskev Co.) were sublimed three times prior to use. The α -methylstyrene and styrene were dried over CaH_2 at 25°C, and distilled over fluorenlithium before polymerization. Ethylene oxide was also dried over CaH_2 and distilled over n-BuLi before use. The 1,1-bis-(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA) was prepared according to a literature procedure[8]. The diethyl pyromellitate diacyl chloride was prepared according to a literature procedure[9].

Synthesis of hydroxyl-terminated polystyrene oligomers. Styrene was polymerized in tetrahydrofuran (THF) at −78°C, using sec-BuLi as an initiator. Polymerization was carried out under dry nitrogen, in a previously flamed-treated glass reactor equipped with rubber septums. Dry THF was added via a stainless steel capillary, followed by 1 ml of α-methylstyrene. The initiator was added dropwise to the previously cooled (−78°C) THF until a red colour persisted, followed by the requisite amount of sec-BuLi. The necessary amount of monomer was added ([St] = 1 M) and polymerized for 3 h at −78°C. Finally, a five fold molar excess of ethylene oxide was added. The reactor temperature was allowed to increase slowly from −78 to 25°C. After 3 h at 25%, acidic methanol was added to the polymerization medium. Then the unreacted ethylene oxide and part of THF were distilled off, and the polymer was finally precipitated into methanol, filtered and dried under vacuum at 60°C.

Aminophenyl carbonate-terminated polystyrene. To a 250 ml round-bottomed flask equipped with a stir bar and Ar inlet were added 15.0 g (0.00125 mol) of 14 K polystyrene (hydroxy-terminated), 100 ml of dry THF, 0.38 g (0.001875 mol) of *p*-nitrophenylchloroformate and 0.15 g (0.001875 mol) of pyridine, and the mixture stirred at ambient temperature overnight. The resulting suspension was filtered on a medium fit, evaporated on a rotary evaporator and taken up in ether (some THF may be necessary for complete dissolution). The solution was allowed to stand for 1 h, filtered and evaporated to a clear semi-solid. This material was then taken up in 150 ml of dry THF and hydrogenated for 48 h over 500 mg of Pearlman's catalyst [$Pd(OH)_2$] at ambient temperature and 276 kPa (40 psi) of hydrogen. The suspension was filtered on Celite, concentrated and redissolved in 500 ml of Ch_2Cl_2. The resulting solution was washed with 3 × 250 ml of $NaHCO_3$, 3 × 250 ml of water, concentrated and redissolved in 100 ml of THF. The product was isolated by slow addition of this solution to 800 ml of well-stirred methanol, filtration and drying at 50°C and 27 Pa (0.2 mm Hg) overnight to yield 13.9 g of the target compound as a white powder.

Amino-terminated polystyrene by TEMPO route

A solution of t-BOC protected derivative of 4,4'-azobis(4-cyanovaleric acid) (1.00 g, 151 mmol) and 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (486 mg, 3.0 mmol) in styrene (47.1 g, 453 mmol, 300 equiv.) was heated with stirring at 130°C under argon for 72 h. During this time the reaction mixture increased in viscosity and eventually solidified. The reaction mixture was then dissolved in tetrahydrofuran (50 ml) and precipitated into methanol (2 l) and the white precipitate collected by vacuum filtration to give the mono t-BOC protected polystyrene as a white solid (43.1 g, 89.0%; $M_{n(gpc)} = 13\,500$).

The mono t-BOC protected polystyrene (5.00 g, 0.357 mmol equiv.) was dissolved in dichloromethane (25 ml), trifluoroacetic acid (2.5 ml) was added dropwise and stirring continued under argon for 16 h. The reaction mixture was then evaporated to dryness, redissolved in dichloromethane (100 ml), washed with saturated aqueous sodium carbonate (3 × 100 ml), dried and evaporated to dryness. The crude product was then purified by precipitation into methanol (500 ml) from dichloromethane (10 ml). The desired monoamino-terminated polystyrene, **1d**, was obtained as a white solid (4.72 g, 94.4%; $M_{n(tit.)} = 13\,000$; $M_{n(gpc)} = 13\,500$).

Block copolymer formation

(A) Amic acid route. First, the amino-functional styrene oligomer (1.000 g, 0.0000384 mol) and 3FDA (3.1260 g, 0.00913 mol) were charged into a flask together with 25 ml of NMP/THF (3/1) solvent mixture. The PMDA (2.0000 g, 0.00916 mol) was later added to the solution at 5°C, yielding the target poly(amic acid) in 24 h. Imidization of the poly(amic acid) was accomplished chemically with an acetic anhydride/pyridine mixture. In the case of chemical imidization, a threefold excess of acetic anhydride and pyridine was added and slowly heated to 60°C and for 10–12 h. The resulting polymers were precipitated in methanol and heated (80°C) in a vacuum oven for 24 h. The resulting polymer was isolated from a water/methanol mixture, rinsed with isopropyl alcohol and dried in a vacuum oven (50°C).

(B) Amic ester route. The amic ester/styrene triblock copolymers were prepared by the co-reaction of the amino-terminated styrene oligomers with 3FDA and PMDA; diethyl ester diacyl chloride in NMP in the presence of *N*-methylmorpholine[2-5]. A detailed procedure designed to prepare an amic ester–α-methylstyrene copolymer with a styrene composition of $\sim$ 15% is now provided.

A three-necked flask equipped with an overhead stirrer and addition funnel was charged with the styrene oligomer (1.0000 g, 0.000038 mol) and 3FDA (1.9591 g, 0.00572 mol), carefully rinsed in with 20 ml of NMP. Throughout the polymerization N_2 was passed through the system. The solution was then cooled to −5°C, and pyridine (0.9017 g, 0.0114 mol) was added to the solution. The PMDA diethyl ester diacyl chloride (2.1000 g, 0.00576 mol) was dissolved in $\sim$ 75 ml of methylene chloride, and added in increments over a 2 h period so as to approach the stoichiometric end point slowly. The polymerization was allowed to proceed overnight and the polymer was isolated by precipitation in methanol/water mixture. The precipitate was rinsed with water to remove excess salts and then cyclohexane to remove possible homopolymer contamination, and dried in a vacuum oven.

Foam formation

The copolymers were dissolved in NMP at a concentration of 9–15% solids. Coatings 10–25 μm in thickness were obtained by doctor blading. The removal of the solvent and imidization, if required, were accomplished by heating the polymer films to 300°C at 5°C min^{-1} and maintaining them at 300°C for 2 h in a nitrogen atmosphere. The films were then heated over a 4 h period to 340°C and held at this temperature for 4.5 h to effect the decomposition of the styrenic coblock.

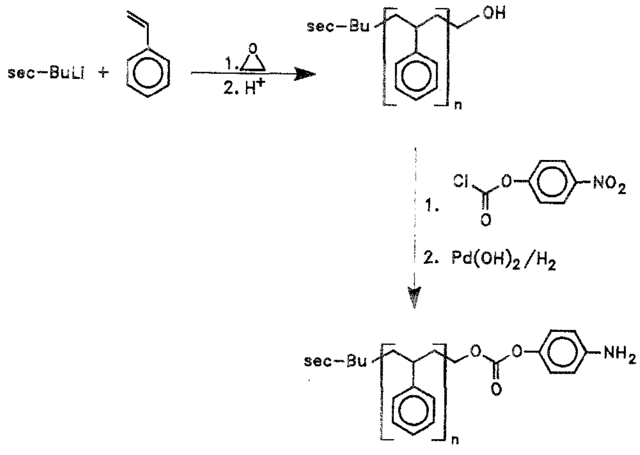
Characterization

Glass transition temperatures, taken as the midpoint of the change in the slope of the baseline, were measured on a Du Pont 1090 instrument at a heating rate of 10°C min^{-1}. A polymer Laboratories' Dynamic Mechanical Thermal Analyzer operating at 10 Hz with a heating rate of 10°C min^{-1} in the tension mode was used to measure the dynamic mechanical properties. Isothermal and variable temperature (5°C min^{-1} heating rate) thermal gravimetric analysis (T.G.A.) measurements were performed on a Perkin–Elmer model TGA-7 in a nitrogen atmosphere. Density measurements were obtained with a density gradient column composed of 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.

Fourier transform infra-red, (*FT*I.R.) measurements were made on an IBM Instruments IR44 with an MCT detector. Transmission electron microscopy (TEM) was performed on a Phillips I2 520 Instrument operating at 100 kV. The samples for TEM were prepared by ultramicrotoming the films at room temperature.

RESULTS AND DISCUSSION

Two polyimides were examined as the thermally stable block. The first polyimide, derived from pyromellitic dianhydride and 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA/PMDA), was used since this was the polyimide used in the previous study with poly(α-methylstyrene) as the labile coblock, thus allowing direct comparisons[5]. 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[8]. 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 a major influence on the morphology of foams obtained from 3FDA/PMDA imide α-methylstyrene triblock copolymers[5]. We therefore consider both chemically imidized copolymers and thermally imidized films cast from the poly(amic alkyl ester) precursor. The second polyimide surveyed was derived from pyromellitic dianhydride and 9,9'-bis(4-aminophenyl) fluorene (PMDA/FDA). This polyimide is not soluble in the fully imidized form and has a T_g in excess of 500°C, thus minimizing the possibility of plasticization by the degradation products upon thermolysis of the labile coblock. Since the PMDA/FDA polyimide is not soluble, the copolymers were prepared through the soluble/processable poly(amic alkyl ester) route.



Scheme 1

Two synthetic routes were surveyed as a means to amino-terminates styrene oligomers: an anionic and a free radical approach. In the first case, a hydroxyl-terminated polystyrene oligomer was prepared by the living anionic polymerization of styrene in THF, at −78°C (*Scheme 1*). The polymerization was initiated with sec-BuLi and end-capped with ethylene oxide. The monofunctional hydroxy-terminated styrene oligomer was converted into the monoamino derivative using the aminophenyl carbonate route in a manner similar to that previously reported for the derivatization of α-methylstyrene oligomers. The hydroxyl-terminates tyrene oligomer was reacted with 4-nitrophenylchloroformate to form a nitrophenyl carbonate end group, and hydrogenation over Pearlman's catalyst gave the corresponding amine. For all experiments, a monohydroxyl styrene oligomer with a nominal molecular weight of 14 000 g mol^{-1} was employed, **1a**. Comparison of molecular weights, determined by gel permeation chromatography (g.p.c.) and titration, confirmed

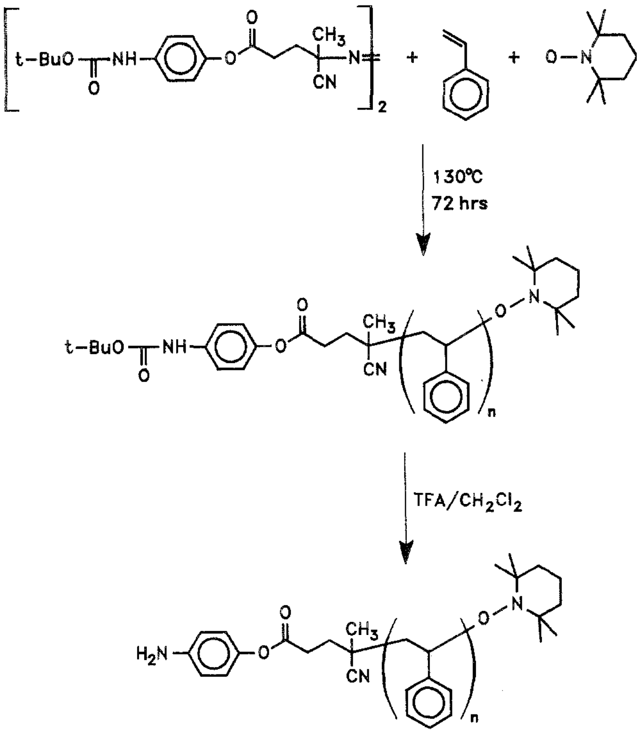
Table 1 Characteristics of aromatic amine-functional thermally labile oligomers

Sample entry	Thermally labile block type	Polymerization method	Molecular weight (g mol^{-1})	T_g (°C)
1a	Poly(α-methylstyrene)	Anionic	12 000	155
1b	Polystyrene	Anionic	14 000	100
1c	Styrene/α-methylstyrene copolymer	4/1	14 000	100
1d	Polystyrene	Free radical	13 000	100

the introduction of a single amine end group. In a similar fashion, an α-methylstyrene oligomer (**1a**) and three styrene/α-methylstyrene oligomers were prepared with styrene to α-methylstyrene compositions of 4 : 1, 1 : 1 and 1 : 4. The characteristics of the samples are also shown in *Table 1*.

An amino-functionalized polystyrene **1d** could also be prepared by a novel 'living' free-radical polymerization procedure using the appropriately functionalized AIBN initiator and 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as the 'counter' radical[10] (*Scheme 2*). For example, we have recently demonstrated[11] that polymerization of styrene with a t-BOC protected AIBN derivative, in the presence of TEMPO, leads to polystyrenes which have low polydispersity (1.20), controlled molecular weights, and a single functional chain end. Monoamino-terminated polystyrene derivatives can, therefore, be prepared which have a polydispersity and functionality similar to that prepared by anionic methods (see *Table 1*).

Polystyrene should be ideally suited for use as the thermally labile block, since well-defined functional oligomers can be prepared and the polymer depolymerizes to monomer at a rate substantially slower than that of poly(α-methylstyrene)[12]. T.g.a. of the polystyrene oligomers prepared by both the anionic and free radical approach, shown in *Figure 1*, clearly shows a rapid and quantitative degradation for each oligomer. The polystyrene prepared via anionic polymerization degrades at a temperature substantially higher than the free radically polymerized analogue. This is not surprising since it has been demonstrated that the TEMPO chain end present in the free radically prepared polystyrene is thermally unstable and on thermolysis yields a free radical end group. This free radical could then lead to unzipping of the polymer chain at a lower temperature than for other end groups, such as the sec-Bu group present in anionically prepared polystyrene. T.g.a. results of the three styrene/α-methylstyrene copolymers are shown in *Figure 2*, and analysis clearly demonstrates that the incorporation of α-methylstyrene lowers the



Scheme 2

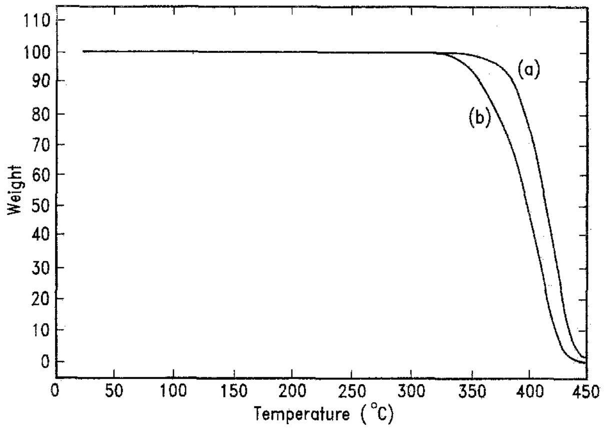


Figure 1 Thermogravimetric analysis of polystyrene prepared by (a) anionic and (b) free radical methods

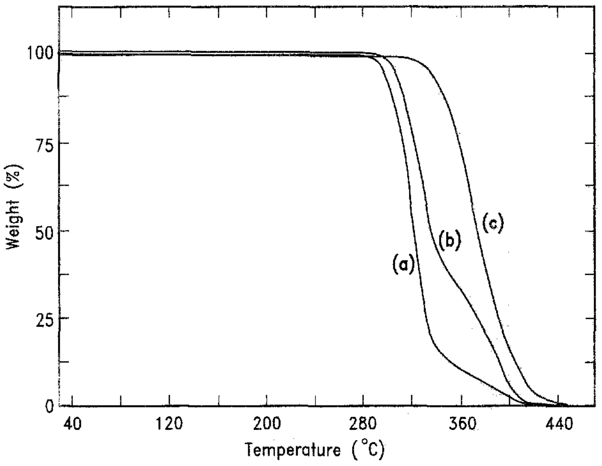
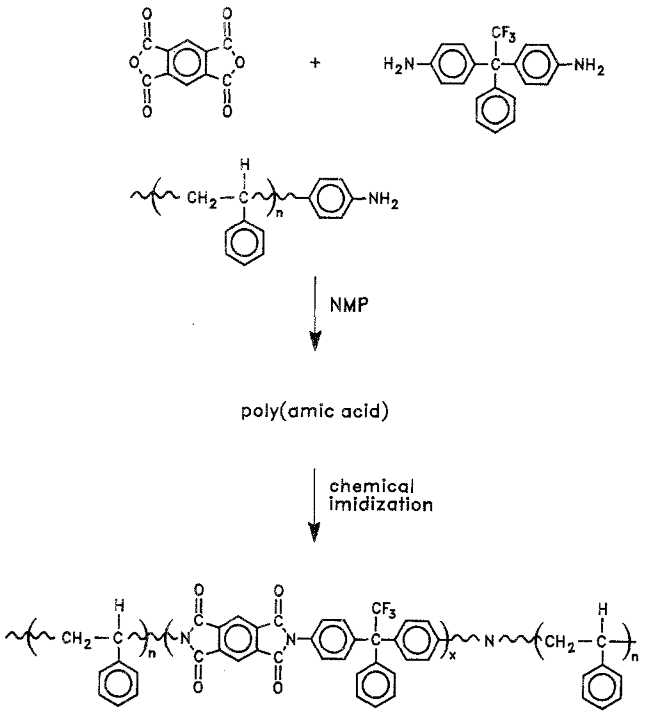


Figure 2 Thermogravimetric analysis of styrene/α-methylstyrene copolymers having styrene to α-methylstyrene ratios of (a) 1 : 4, (b) 1 : 1 and (c) 4 : 1



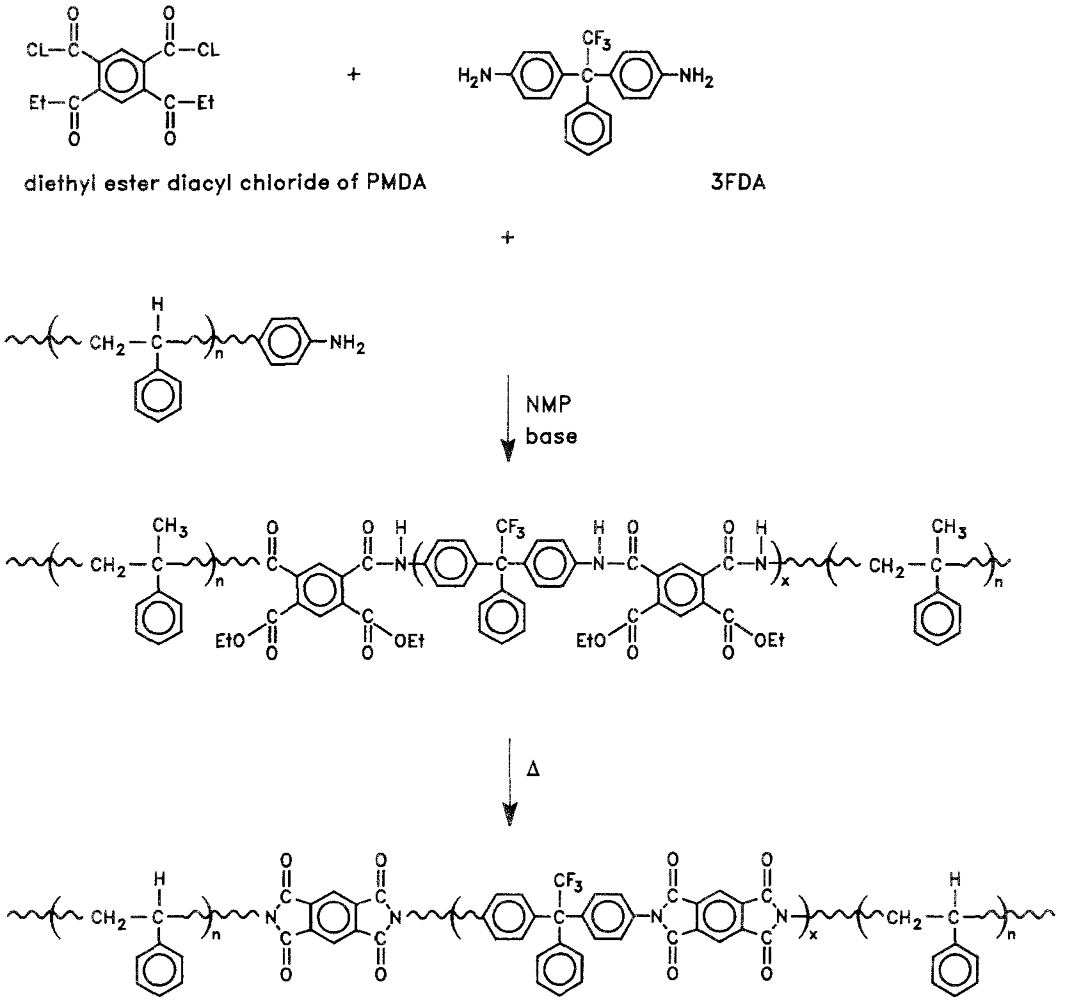
Scheme 3

Table 2 Swelling of 3FDA/PMDA and FDA/PMDA polyimides and calculated solubility parameters

Polyimide	Styrene uptake (wt%)	α-methylstyrene uptake (wt%)	Calculated solubility parameter
3FDA/PMDA	28	120	18.33
FDA/PMDA	–	98	19.28

decomposition temperature. For our experiments, we focused on the styrene/α-methylstyrene copolymer with a monomer ratio of 4 : 1 (styrene to α-methylstyrene) (**1c**), since the α-methylstyrene units should serve to initiate the degradation of the copolymer at temperatures lower than that of polystyrene, but at a slower rate than poly(α-methylstyrene). In addition, the primary degradation product of the polystyrene, styrene, shows considerably less solubility in the polyimide matrices than α-methylstyrene (*Table 2*). These combined observations suggest that plasticization followed by blowing and coarsening processes should be minimized by the use of polystyrene as the labile phase.

The 3FDA/PMDA-based copolymers were prepared via the poly(amic acid) precursor route followed by chemical imidization or via the poly(amic alkyl ester) route followed by thermal imidization (*Schemes 3* and *4*, respectively). The synthesis of the poly(amic acid)



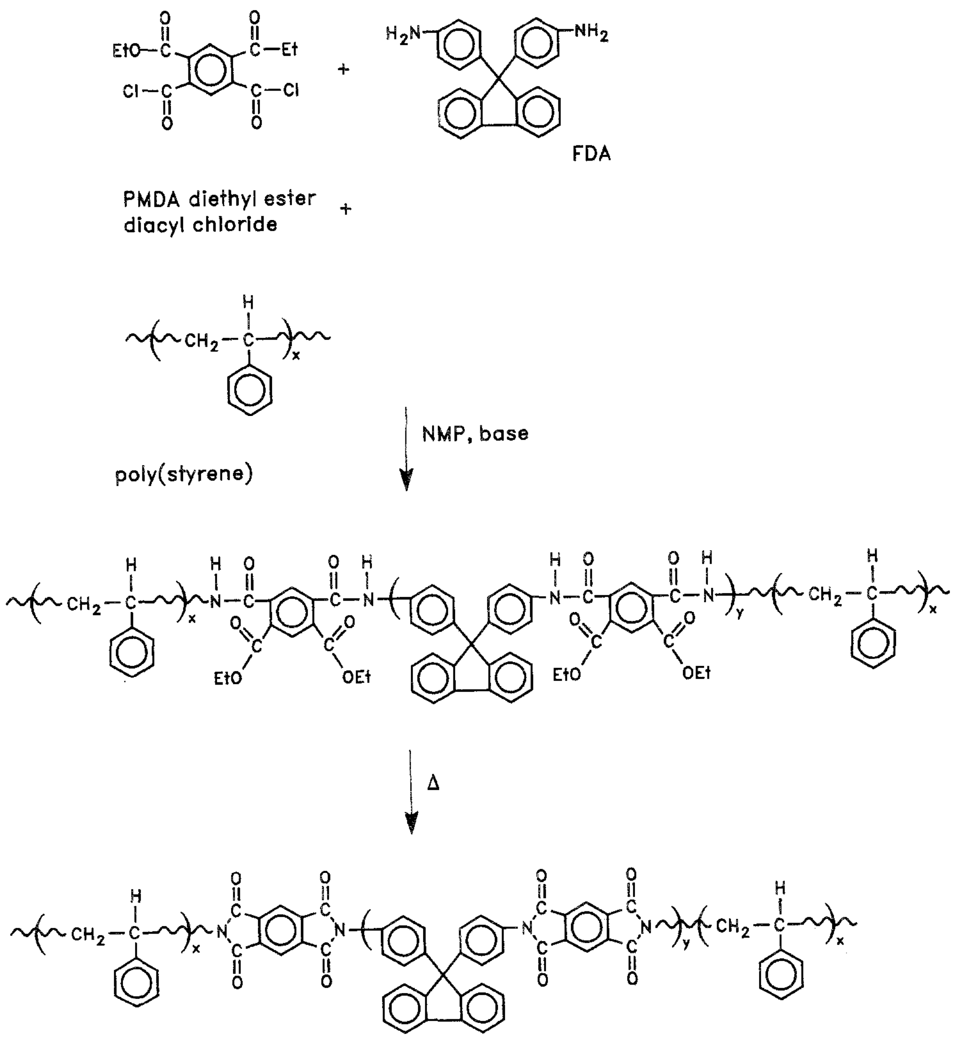
Scheme 4

involved the addition of solid PMDA to a solution of the styrene oligomer and 3FDA to yield the corresponding poly(amic acid)s. The polymerizations were performed in NMP at room temperature for 24 h with a solids content of ~ 10% (w/v). Chemical imidization of the poly(amic acid) solutions was carried out *in situ* by reaction with excess acetic anhydride and pyridine for 6–8 h at 100°C. The copolymers were subjected to repeated toluene rinses in order to remove any unreacted styrene homopolymer.

The insolubility of the PMDA/FDA polyimide required the use of an alternative synthetic route to well-defined imide block copolymers (i.e. poly(amic alkyl ester) precursor) (*Scheme 5*). Since this precursor is soluble in a variety of solvents, the synthesis is flexible allowing for a greater structural variety in the polyimide backbone as well as in the coblock type, length and composition[9]. The hydrolytically stable poly(amic alkyl ester) precursors can be isolated, characterized, and washed to remove possible homopolymer contamination prior to imidization. The synthesis involved the incremental addition of PMDA diethyl ester chloride in methylene chloride to a solution of the oligomer and FDA in NMP containing pyridine as the acid acceptor (*Scheme 3*). In our experiment, the *meta* isomer of PMDA diethyl ester diacyl chloride was used primarily due to its enhanced solubility, and to facilitate comparison with previous studies. The solids composition was maintained at ~ 15% for each of the polymerizations. The copolymers were isolated in a methanol/water mixture, rinsed with water to remove remaining salts, rinsed with methanol and toluene followed by drying at 50°C (24 h) under vacuum. To facilitate comparison between the imide and alkyl ester precursor, the 3FDA/PMDA-based block copolymer was also prepared via the poly(amic alkyl ester) route as shown in *Scheme 2*.

The use of monofunctional oligomers in the polyimide syntheses described above affords an ABA triblock copolymer architecture, where the thermally labile component comprises the terminal A blocks and the stable polyimide is the B block. Therefore, the average molecule weight of the A blocks is identical to that of the preformed oligomers, while the molecular weight of the central B block is controlled by the stoichiometric imbalance between the dianhydride and diamine. It should be noted that upon thermal decomposition of the labile coblock, the molecular weight of the polyimide block should remain the same. This is important for mechanical and physical property considerations.

The 3FDA/PMDA imide-based copolymers prepared



Scheme 5

Table 3 Characteristics of 3FDA/PMDA polyimide-based block copolymers

Sample entry	Polyimide form	Thermally labile block type (synthetic method)	Thermally labile block composition (wt%) Charge	Incorporated ^{1}H n.m.r.	Incorporated T.g.a.	Volume fraction of labile block (%)
2	Chemically imidized	Styrene (anionic)	15	–	15	18
3	Chemically imidized	Styrene/α-methylstyrene (anionic)	15	–	14	18
4	Poly(amic alkyl ester)	Styrene (anionic)	20	18	19	22
5	Poly(amic alkyl ester)	Styrene/α-methylstyrene (anionic)	20	15	14	18
6	Chemically imidized	Styrene (free radical)	15	–	9	11
7	Poly(amic alkyl ester)	Styrene (free radical)	20	19	15	18

are shown in *Table 3*. Owing to the solubility of the 3FDA/PMDA polyimide, copolymers were prepared in both the full imidized form (copolymers **2** and **3**) and in the poly(amic alkyl ester) precursor to the polyimide (copolymers **4**–**7**). The labile coblocks examined include polystyrene, prepared by both anionic (oligomer **1b**) and free radical (oligomer **1d**) methods, and a (4 : 1) styrene/α-methylstyrene copolymer (oligomer **1c**). In contrast, the FDA/PMDA imide/α-methylstyrene, FDA/PMDA imide/styrene, FDA/PMDA imide/α-methylstyrene/styrene copolymers (copolymers **8**–**11**) were only prepared via the poly(amic alkyl ester) precursor route and the characteristics of these copolymers are shown in *Table 4*. The weight percentage, or loading, of the labile blocks in the copolymers was intentionally maintained low ($\sim$ 20 wt%) in order to produce discrete spherical domains of the block embedded in the polyimide matrix. At higher loadings, phase separation of the block could, in principle, produce cylindrical or more interconnected structures which are undesirable. The loading of the labile block in the copolymer was assessed by T.G.A. and by ^{1}H nuclear magnetic resonance spectroscopy (n.m.r.). For essentially all cases, the loading of the labile block agreed closely with that theoretically expected from the feed ratios (*Tables 3* and *4*).

The initial step in the generation of polyimide foams requires the preparation of thin films followed by curing to remove solvent and, if required, effect imidization. It is important to effect this curing without degrading the thermally labile coblock or leaving residual solvent in the copolymer since this results in plasticization and a diminished processing window (i.e. temperature difference between the decomposition temperature of the labile block and the T_g of the polyimide matrix). In previous studies with the imide/α-methylstyrene copolymers, the cure temperature was limited by the decomposition temperature of the α-methylstyrene coblock to 265°C. While this treatment was sufficient to remove the solvent, the degree of imidization was restricted to $\sim$ 94%, thus lowering the T_g of the polyimide and again decreasing the process window. The polystyrene and styrene/α-methylstyrene copolymers, on the other hand, show decomposition temperatures significantly higher than that of poly(α-methylstyrene) which permits higher cure temperatures and allows the 'ultimate' T_g of the polyimide to be obtained. The processing conditions used for these copolymers include casting films from NMP followed by a slow temperature ramp at 4°C min^{-1} to 300°C, where the films are held for 2h. ^{1}H n.m.r. studies show no residual casting solvent, quantitative imidization and retention of the labile block. Furthermore, the cured films of each copolymer were transparent with no evidence of large-scale phase separation, which is characteristic of homopolymer contamination.

Dynamic mechanical analysis was used to assess the morphology of the copolymers. It is essential that separation occurs with high phase purity in order to obtain a nanofoam while minimizing collapse. The results of dynamic mechanical analysis for the FDA/PMDA/α-methylstyrene copolymers are shown in *Figure 3*. Two transitions are observed in each case, indicative of microphase-separated morphologies. The transition occurring near 160°C is similar to that seen for the α-methylstyrene oligomer used in the synthesis and the damping peaks associated with the α-methylstyrene transition are sharp, indicating that the phases are not only pure but have discrete boundaries. The transition of the imide block shows a strong dependence on the

Table 4 Characteristics of FDA/PMDA poly(amic alkyl ester)-based block copolymers

Sample entry	Thermally labile coblock type	Thermally labile block composition (wt%) Charge	Incorporated ^{1}H n.m.r.	Incorporated T.g.a.	Volume fraction of labile block (%)
8	α-Methylstyrene (**1a**)	15	15	14	16
9	α-Methylstyrene (**1a**)	25	21	24	28
10	Styrene (**1b**)	15	16	15	17
11	α-Methylstyrene/styrene (1/4) copolymer (**1c**)	15	16	–	17

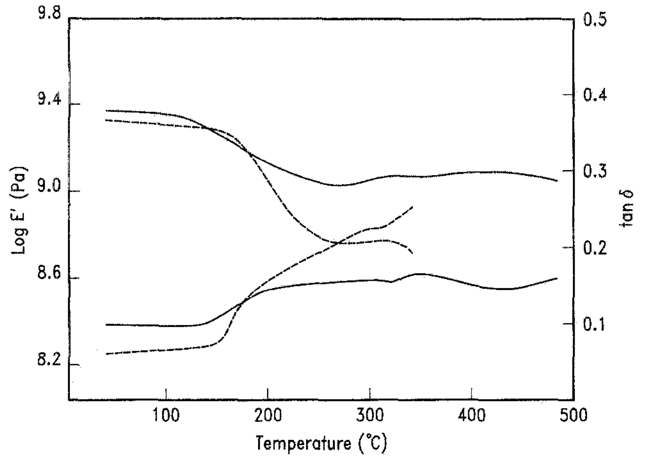


Figure 3 Dynamic mechanical analysis of copolymers **8** (—) and **9** (- - -)

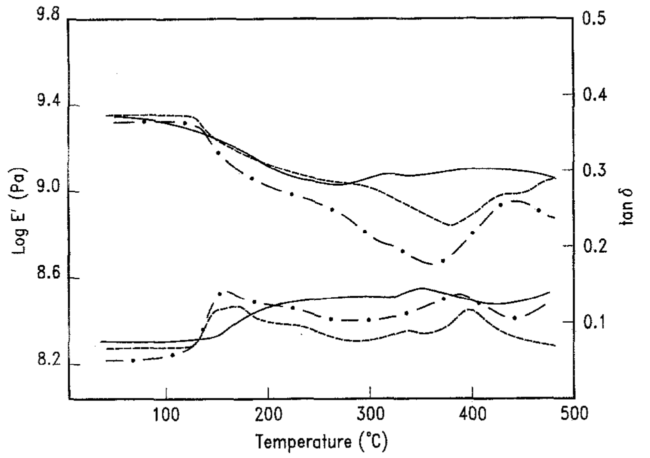


Figure 4 Dynamic mechanical analysis of copolymers **8** (—), **10** (–•–) and **11** (- - -)

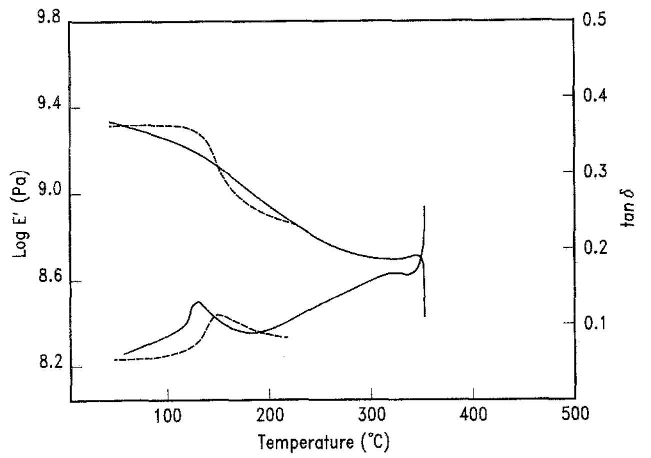


Figure 5 Dynamic mechanical analysis of copolymers **4** (—) and **5** (- - -)

fraction of the α-methylstyrene in the copolymer, as previously reported for the 3FDA/PMDA/α-methylstyrene copolymers[5]. The copolymer containing ~ 15 wt% α-methylstyrene composition (copolymer **8**) shows a modulus–temperature profile which is nearly identical to that of the polyimide homopolymer. However, the copolymer containing the higher α-methylstyrene fraction (copolymer **9**) shows an imide transition which is substantially depressed. Furthermore, the transition appears at nearly the same temperature (~ 320°C) as the decomposition temperature of poly(α-methylstyrene) and is similar to those observed in the previous studies.

The dynamic mechanical spectra for the FDA/PMDA-based copolymers with polystyrene, poly(α-methylstyrene) and styrene α-methylstyrene coblocks are shown in *Figure 4*. As in the previous discussion, two transitions are observed confirming the microphase-separated morphologies. The transitions for the styrene, styrene/α-methylstyrene and α-methylstyrene can clearly be observed at ~ 100, 140 and 160°C, respectively, and the transitions are nearly identical to those observed for the oligomers used in the synthesis. The transition for the imide block is not observed since the T_g is in excess of the decomposition temperature. However, a modulus drop just above 300°C can be observed, consistent with the decomposition of the labile coblock. For the labile block compositions surveyed, plasticization of the polyimide block was minimal. An increase in modulus is then observed as the degradation products are evolved, followed by a modulus invariance up to ~ 500°C. Likewise, similar modulus–temperature profiles are also observed for the 3FDA/PMDA-based copolymers (i.e. two transitions) (*Figure 5*). The transitions for the styrene and styrene/α-methylstyrene blocks for copolymers **4** and **5**, respectively, are sharp and nearly identical to that of the oligomers. However, the imide transitions are significantly depressed and are in the proximity of the degradation temperature of the labile coblock. The plasticization of the imide block by the degradation of products is consistent with the styrene and α-methylstyrene uptake by 3FDA/PMDA polyimide (*Table 2*). Furthermore, estimates of the solubility parameters of PMDA/FDA and 2FDA/PMDA polyimides were calculated by summing the different groups in the monomer and are also shown in *Table 2*. As can be seen, the solubility parameters for the polyimides are similar, which suggests that the degradation products would tend to be soluble in the polyimides.

Previous studies have shown that the retention of the foam structure depends upon a balance between the rate of decomposition of the labile coblock, the solubility of the degradation products in the imide matrix and the rate at which these products diffuse out of the matrix. If the rate of decomposition is significantly higher than the diffusion coefficient, accumulation of the degradation products in the polyimide matrix occurs, which leads to blowing and coarsening of the voids. In the case of the imide/α-methylstyrene copolymers, the α-methylstyrene block thermally degrades by depolymerization at extremely high rates, and since the degradation products strongly interact with the polyimide matrix, plasticization and blowing occurs, leading to pores significantly larger than expected. To overcome this blowing, we have attempted to decrease the depolymerization rate and amount of swelling by examining polystyrene and styrene/α-methylstyrene copolymers as the labile blocks. Shown in *Figures 6* and *7* are the dynamic mechanical spectra of two copolymer series together with their thermal gravimetric data. The FDA/PMDA styrene and styrene/α-methylstyrene (copolymers **10** and **11**) show a modulus drop in the proximity of the decomposition

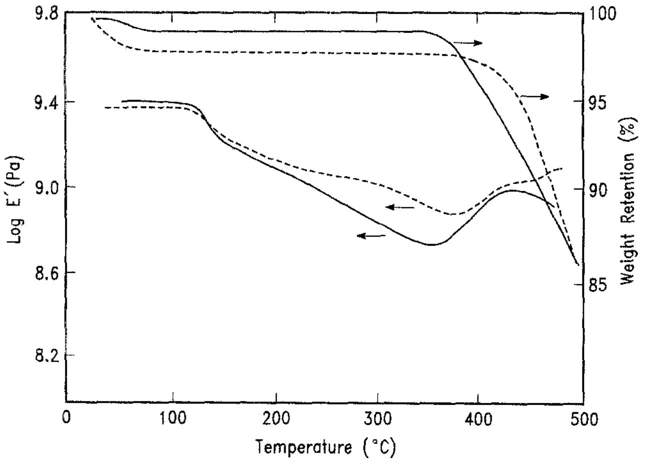


Figure 6 Dynamic mechanical analysis and thermogravimetric analysis of copolymers **11** (- - -) and **10** (—)

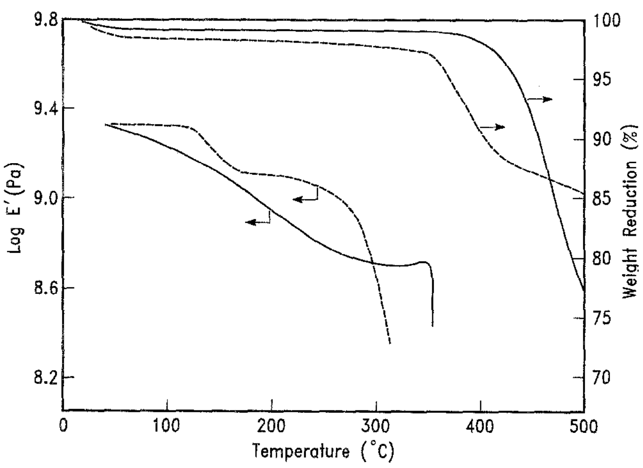


Figure 7 Dynamic mechanical analysis and thermogravimetric analysis of copolymers **4** (—) and **7** (- - -)

temperature of the labile coblock. Likewise, t.g.a. shows the onset of weight loss in the temperature regime where the respective labile blocks degrade. It is important to note that the temperature range over which degradation occurs is broad (~ 100°C) as evidenced by the weight loss and the modulus increase as the by-products are expelled. The 3FDA/PMDA imide styrene copolymers showed significantly different behaviour, and the data were further complicated by the synthetic route employed for the coblock styrene. Upon degradation of the labile block, a T_g is induced in the poly-imide block, irrespective of the polystyrene oligomer employed. The T_g of the imide block for the copolymers prepared with the free radically polymerized polystyrene block is ~ 40°C lower than that of the copolymer where the styrene block is prepared by anionic methods. In each copolymer, the evolution of by-products, as evidenced by t.g.a., is slow and over a broad range. These combined observations (i.e. plasticization, temperature range over which degradation occurs, etc.) should provide significant insight into the design of the requisite foaming conditions to generate a nanofoam.

As discussed, the successful generation of a nanofoam depends upon the extent to which the decomposition products of the thermally labile group plasticize the polyimide matrix. This depends upon the relationship between the residence time of the decomposition products in the matrix in comparison to the heating rate. The T_g of the matrix will vary with the amount of degradation products in the matrix which continually decreases, and optimally the T_g of the matrix should be greater than the sample temperature. Previous studies have shown that both the heating rate and residence time at final temperature are crucial variables in minimizing plasticization and optimizing foam content. The optimum cure schedule, as determined by density measurements of the foam generated, was found to be 300°C for 2 h to effect imidization and solvent removal, followed by a slow heating to 350°C over a 5 h period and holding at temperature for 10 h. Isothermal gravimetric analysis shows quantitative degradation of the styrenic coblock.

The formation of the foam was assessed by density measurements. The density values for the 3FDA/PMDA- and FDA/PMDA-based copolymers are shown in *Tables 5* and *6*, respectively. The density values of the polyimides 3FDA/PMDA and FDA/PMDA are 1.34 and 1.29 $\mathrm{g\,cm^{-3}}$ respectively (*Tables 5* and *6*). The densities of the foams range from 1.19 to 1.25 $\mathrm{g\,cm^{-3}}$ which is consistent with approximately 3–12% of the film being occupied by voids. These data show that the porosity obtained is considerably less than the volume fraction of labile block incorporated in the copolymer, or the foam efficiency is poor. However, the interpretation of the porosity values measured by flotation in the density gradient column for the foamed polymers was difficult. Clearly, 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 the fluid penetrating the pores, giving a density similar to that of the homopolymer[5]. To avoid these problems, infra-red 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 as determined by i.r. were inconsistent since the films were cloudy or even opaque in some cases, scattering the i.r. beam.

Transmission electron microscopy was used to assess the size of the pores. The translucency or opacity, in some cases, suggested a pore size significantly larger than the microphase-separated domains of the styrene or styrene/α-methylstyrene labile coblock. Shown in *Figures 8* and *9* are TEM micrographs of typical microtomed sections of copolymers **4** and **5**, respectively, prepared from the anionically synthesized labile coblocks via the poly(amic alkyl ester) route. The dark regions of the micrographs correspond to the polyimide phase, while the light regions correspond to the pores. Clearly, a highly porous structure is obtained with pores having cross-sections ranging from 20 to 60 nm for copolymer **5** and from 40 to 60 nm for copolymer **4**. These pores are several times larger than would be anticipated from the initial block copolymer morphology and, as expected, the films were somewhat translucent. However, it should be pointed out that these pores are

Table 5 Characteristics of 3FDA/PMDA polyimide foams

Copolymer entry	Initial labile block composition (vol%)	Density (g cm^{-3})	Volume fraction of voids (porosity) (%)
3FDA/PMDA polyimide (control)	–	1.35	–
2	18	1.24	8.2
3	18	1.26	7.0
4	22	–	–
5	18	–	–
6	11	1.22	9.0
7	18	1.23	8.2

Table 6 Characteristics of FDA/PMDA polyimide foams

Copolymer entry	Initial labile block composition (vol%)	Density (g cm^{-3})	Volume fraction of voids (porosity) (%)
FDA/PMDA polyimide (control)	–	1.29	–
8	15	1.25	3
9	25	1.2	7
10	15	1.19	8.0
11	15	1.19	8.0

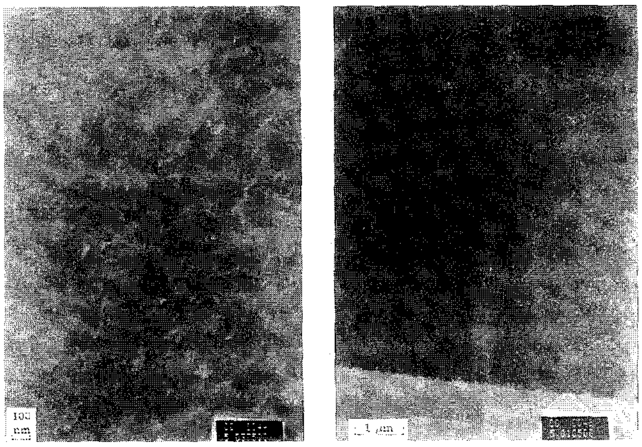


Figure 8 TEM micrographs of foam derived from copolymer 4

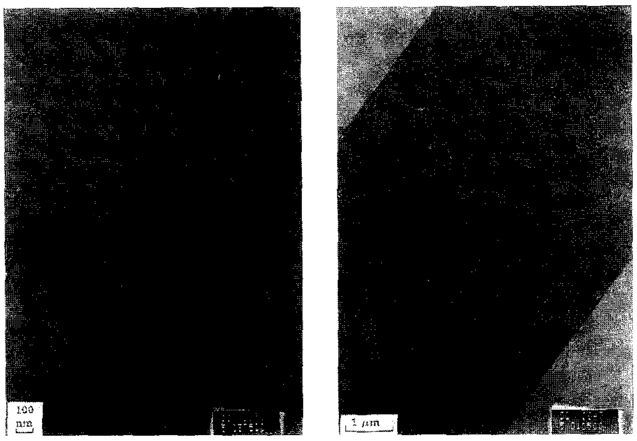


Figure 9 TEM micrographs of foam derived from copolymer 5

significantly smaller than those observed from the polyimide foams where α-methylstyrene was used as the labile coblock. The pore shapes are elongated with minimal interconnectivity between the pores. Conversely, the foams prepared from copolymer **7**, synthesized with the free radically polymerized polystyrene via the poly(amic alkyl ester) route, showed an even larger distribution in pore size (~ 20–250 nm), thus giving rise to the observed opacity in the films (*Figure 10*).

TEM micrographs of foams prepared from the FDA/PMDA polyimide are shown in *Figures 11–13*. The foam derived from copolymer **8** was clear, and, consistent with this observation, the pore size was between 10 and 20 nm. The pores were discrete with no evidence of coarsening. However, the observed porosity, by microscopy and density measurements is considerably less than that expected from the α-methylstyrene charge, clearly indicating significant collapse of the foam. It is important to note, however, that this is the first example of a nanofoam prepared from the thermolysis of poly(α-methylstyrene). Higher compositions of α-methylstyrene (copolymer **9**) lead to significantly larger pores (~ 50 – 250 nm), more interconnectivity and the films become opaque (*Figure 12*). The use of styrene and α-methylstyrene/styrene copolymers as the labile coblock with FDA/PMDA polyimide produced foams with pore sizes in the range 20–150 nm (*Figure 13*). Although the pores are discrete, the pore structure is elongated, analogous to the α-methylstyrene-based foams.

The key difference between the copolymers derived from the anionically and free radically prepared polystyrene is the distribution of pore sizes in the respective foams (copolymers **4** and **7**). In each case, the void sizes are larger than would be expected from the radius of gyration of the polystyrene. The larger pore size, in each

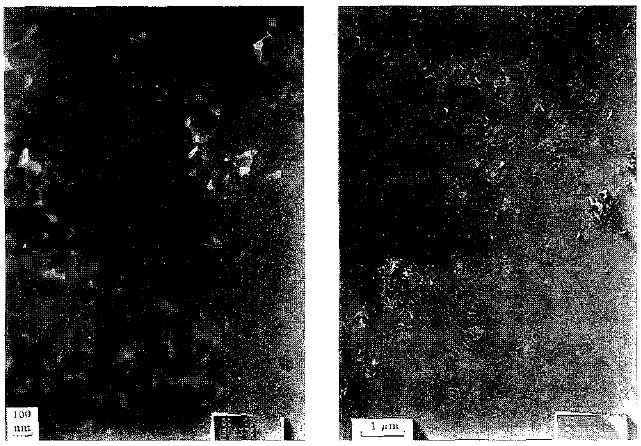


Figure 10 TEM micrographs of foam derived from copolymer **7**

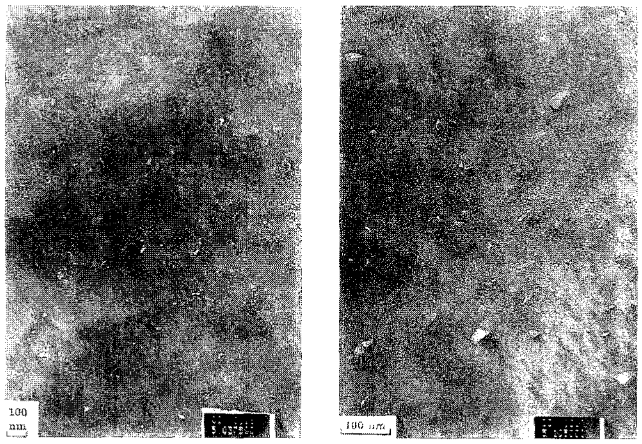


Figure 11 TEM micrographs of foam derived from copolymer **8**

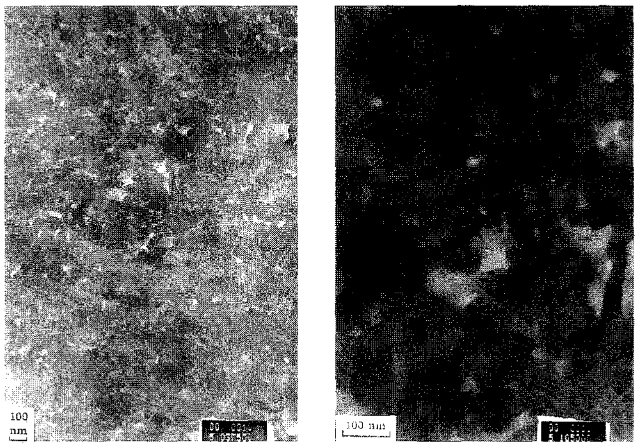


Figure 12 TEM micrographs of foam derived from copolymer **9**

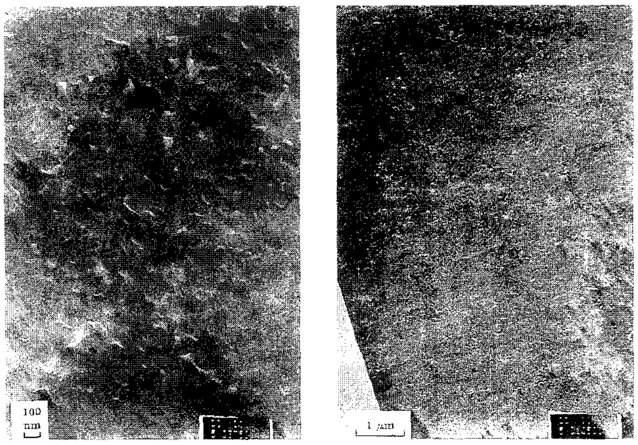


Figure 13 TEM micrographs of foam derived from copolymer **13**

case, can be explained by an effective blowing of the 3FDA/PMDA polyimide matrix or by a coalescence of pores generated during the initial stages of foaming. The larger pore size distribution associated with the foamed copolymer **7** is believed to result from the lower decomposition temperature of the free radically polymerized styrene coblock (*Figure 2*). Upon degradation of the polystyrene, plasticization of the polyimide matrix can be observed, as judged by the manifestation of the T_g (~ 300°C) (*Figure 7*). However, the degradation temperature range is broad (~ 50°C) (*Figure 2*), and, coupled with the low interaction of styrene with the polyimide (*Table 2*), the evolution of styrene from the copolymer is not observed until ~ 360°C (*Figure 7*). The long residence time of styrene in the matrix is believed to allow coarsening of the voids and give rise to the opacity in the films. The higher decomposition temperature of the anionically polymerized polystyrene effectively reduces the residence time of the degradation products, since at this temperature the volatility is much higher, thereby minimizing the void size distribution (i.e. coarsening and/or blowing). The foams derived from the chemically imidized copolymers showed nanofoam formation, irrespective of the labile coblock employed. These data are consistent with previous reports from the imide α-methylstyrene copolymers.

The foams derived from the PMDA/FDA imide-based copolymers showed pore sizes which reflect minimal blowing and/or coalescence, irrespective of the labile block type. These results are not surprising as PMDA/FDA polyimide has excellent solvent resistance and a T_g in excess of 500°C, which minimizes the possibility of plasticization. These observations, coupled with the inherently open structure of such 'cardo' polyimides (as evidence by the low density of the polyimide), should allow the balance of diffusion *versus* plasticization to favour nanofoam formation. However, for higher fractions of the α-methylstyrene block in PMDA/PDA polyimide, a saturation concentration of the α-methylstyrene in the imide matrix is reached. Although the rate at which the α-methylstyrene is removed is rapid, within the time scale defined by the plasticized imide matrix, the removal is not rapid enough and leads to an enhanced pore size.

SUMMARY

A route to high T_g thermally stable polyimide foams has been developed which uses microphase-separated ABA block copolymers comprising a thermally stable polyimide central block and a thermally labile terminal block. The copolymers were designed so that the thermally labile block would be the dispersed phase. Several labile blocks were surveyed including polystyrene, poly(α-methylstyrene) and several α-methylstyrene/styrene copolymers. Each of these blocks can unzip to

its monomer upon heating; however, the rate is substantially slower for polystyrene. In addition, two synthetic routes were employed for the styrene block, anionic and free radical, and the polymer decomposition temperatures and rates were substantially different for each. The copolymers were synthesized through either the poly(amic acid) precursor, followed by chemical imidization to the polyimide form, or the poly(amic alkyl ester) precursor followed by thermal imidization. The decomposition of the labile coblock was followed by thermogravimetric, dynamic mechanical and thermomechanical analyses. Mild decomposition conditions were employed so as to avoid rapid depolymerization and excessive plasticization of the polyimide from the degradation by-products upon thermolysis of the labile block. The foam prepared from the anionically prepared labile coblocks showed pore sizes with diameters in the 100 nm region, along with a 7–12% reduction in density. The reduced decomposition rate afforded by the polystyrene minimized the plasticization and blowing observed in previous studies. Conversely, the copolymers prepared with the free radically polymerized polystyrene blocks showed markedly different behaviour. In this case, a large distribution of pore sizes was observed, and the larger size is attributed to the lower decomposition temperature.

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