

# High temperature nanofoams derived from rigid and semi-rigid polyimides

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(Received 1 July 1993; revised 19 January 1995)

A means of generating high temperature polymer foams which leads to pore sizes in the nanometre regime has been developed. Foams were prepared by casting block copolymers comprising a thermally stable block and a thermally labile material, such that the morphology provides a matrix of the thermally stable material with the thermally labile material as the dispersed phase. Upon a thermal treatment the thermally unstable block undergoes thermolysis, leaving pores where the size and shape are dictated by the initial copolymer morphology. Multiblock and triblock copolymers, comprising rigid, semi-rigid and flexible polyimide matrices with either poly(propylene oxide) or poly(methyl methacrylate) as the thermally labile coblocks, were prepared. The copolymer synthesis was carried out through the poly(amic alkyl ester) precursor to the polyimide since this precursor is stable and allows for isolation and characterization prior to imidization. Microphase-separated morphologies were observed for all copolymers irrespective of block type or length by both dynamic mechanical and small-angle X-ray scattering techniques. Upon decomposition of the propylene oxide or methyl methacrylate coblock, reductions in the film thickness and the total integrated scattering were found for those copolymers derived from rigid and semi-rigid polyimide matrices, thus indicating a collapse of the foam as it was being formed. Conversely, copolymers based on the flexible polyimide produced stable foams upon decomposition of the labile coblocks.

(Keywords: high temperature foams; block copolymers; polyimides)

## INTRODUCTION

Polymeric materials have become increasingly important as interlayer dielectrics, passivation layers and structural resins. Polymeric insulators have several key attractive features including low dielectric constant and ease of processing<sup>1</sup>. These materials must withstand severe thermal, chemical and mechanical stresses associated with microelectronics fabrication, and polymeric materials have many shortcomings when compared with the inorganic alternatives such as alumina or silicon oxides. There are few organic polymers that satisfy the criteria for microelectronics fabrication and polyimides have emerged as the favoured class of materials. In particular, semi-rigid aromatic polyimides, e.g. poly(4,4'-oxydiphenylene-pyromellitimide) (PMDA/ODA), have proved to be the most suitable high performance polymers for this application due to their processability in the poly(amic acid) precursor form and the excellent final properties obtained after thermal cure. These properties, including low thermal expansion coefficient and high modulus, can be attributed, in part, to the liquid crystalline type ordering in the solid state<sup>2,3</sup>. Although polyimides meet most of the material requirements for microelectronics applications, it would be desirable to improve the electrical performance of these materials by reducing the dielectric constant.

One approach to reducing the dielectric constant substantially while maintaining the desired thermal and mechanical properties of the aromatic polyimide is to generate a polyimide foam. The reduction in the dielectric constant is simply achieved by replacing the polymer with air, which has a dielectric constant of 1. However, there are restraints on the materials. It is obvious that the pore size must be much smaller than the film thickness and any microelectronic features. Secondly, it is necessary that the pores be closed cell, i.e. the connectivity between pores must be minimal. Thirdly, the volume fraction of the voids must be as high as possible. Each of these can alter the mechanical properties of the film and structural stability of the foam. Failure to meet these restrictions will lead to collapse of the foam or to a foam with limited use.

Polyimide foams that have been developed primarily for the aerospace and transportation industries show high compressive strength, low dielectric constant, low density, good thermal stability and, unlike other organic foams, tend to be self-extinguishing when burned<sup>4</sup>. The routes to the preparation of polyimide foams include foaming agents<sup>5–7</sup>, partial degradation generating a foaming agent<sup>8–14</sup>, the inclusion of glass or carbon microspheres<sup>15–19</sup>, and microwave processing<sup>20</sup>. The use of foaming agents and reactive systems are the most common routes to polyimide foams and tend to give the most well-defined and controlled pore structures. It has been shown that polyimides can be swollen with volatile organic

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compounds such as chlorinated hydrocarbons<sup>6</sup>, acetone<sup>7</sup> or with higher temperature foaming agents such as 5-phenyldihydro-1,3,4-oxadiazoles to produce foamed structures upon injection moulding<sup>5</sup>. Polyimides foams have also been prepared by the reaction of dianhydrides with diisocyanates<sup>8–11</sup> or by the diester form<sup>14</sup> of dianhydrides with diamines producing either carbon dioxide or alcohol, respectively, as the condensation by-product to serve as the foaming gas. Alternatively, nadimide-functional oligomers have been shown to undergo a rearrangement upon curing to evolve volatiles in which foam structures can be prepared. Most of the high temperature polymer foams reported to date do not satisfy the requirements for applications in microelectronics and, hence, have not found any practical use for thin film applications.

An alternative means of generating a high temperature polymer foam leads to pore sizes in the nanometre regime. Foams can be prepared from block copolymers comprising thermally stable and thermally labile materials, where the latter constitutes the dispersed phase<sup>21</sup>. Upon a thermal treatment, the thermally unstable block undergoes thermolysis leaving pores, the size and shape of which are dictated by the initial copolymer morphology. Herein, triblock copolymers comprising a poly(phenylquinoxaline) (PPQ) and either poly(propylene oxide) (PO) or poly(methyl methacrylate) (PMMA), the thermally labile coblocks, are shown to produce nanofoams with a dielectric constant substantially lower than that of the pure matrix polymer. PPQ was chosen as the matrix due to its thermal stability, high glass transition temperature ( $T_g$ ) and good processability<sup>22–24</sup>. Upon decomposition of the thermally unstable blocks, a 10–15% reduction in density was observed, consistent with the initial PO or PMMA composition, and the resulting PPQ foams showed dielectric constants of  $\sim 2.4$ , substantially lower than that of PPQ (2.8). Small-angle X-ray scattering and transmission electron microscopy showed pore sizes of  $\sim 100$  Å. Although the PPQ based foams provide a useful model to demonstrate the feasibility of the copolymer approach to nanofoam formation, they are not practical materials for microelectronics applications due to the fact that these materials are soluble only in selected chlorinated solvents and *m*-cresol. Therefore, the polyimides, as a class of materials, are the most appropriate candidates and in this article the application of this foam formation methodology to imide–propylene oxide and imide–methyl methacrylate copolymers will be discussed.

## EXPERIMENTAL

### Materials

4,4'-Oxydianiline (ODA; Davos Chemical Company) and pyromellitic dianhydride (PMDA; Chriskev Company) were used without further purification. *N*-methyl-2-pyrrolidone (NMP) was vacuum distilled from  $P_2O_5$  prior to use. 1,4-Bis[6-(3-aminophenoxy)-3-phenyl-2-quinoxaliny]benzene was prepared according to a literature procedure<sup>25</sup>. Monofunctional propylene oxide oligomers (PO) with molecular weight of 5000 and  $10\,000\text{ g mol}^{-1}$  were kindly supplied by Dow Chemical and were dried *in vacuo* prior to use. The 1.9M phosgene/toluene solution was obtained from Fluka and was used as received. The difunctional propylene

oxide oligomer of molecular weight  $4200\text{ g mol}^{-1}$  was kindly supplied by Texaco. Poly(methyl methacrylate), prepared by group transfer polymerization, was kindly supplied by Du Pont.

**Diethyl pyromellitate diacyl chloride.** PMDA (50.0 g, 0.230 mol) was suspended in 250 ml of dry ethanol and refluxed for 3 h, yielding a clear solution<sup>26</sup>. Evaporation of the ethanol followed by vacuum drying at  $50^\circ\text{C}$  for 24 h gave diethyl dihydrogen pyromellitate (mixed isomers) in quantitative yield. The material was then suspended in  $\sim 200$  ml of dry ethyl acetate in a 500 ml three-necked flask equipped with magnetic stirrers, reflux condenser and  $N_2$  bubbler. Next, oxalyl chloride (75 g, 0.591 mol) was added in three portions over a period of 8–10 h, each addition being followed by one or two drops of dimethylformamide (DMF). The DMF allowed the reaction to proceed at ambient temperature, as evidenced by vigorous gas evolution. Stirring was continued overnight and the reaction mixture was then heated to  $\sim 60^\circ\text{C}$  in a water bath for an additional 6 h (total run time was  $\sim 28$  h). The ethyl acetate was then stripped and the residue dried under vacuum at room temperature overnight. The product was twice recrystallized from approximately 150 ml of hexane and vacuum dried. The yield was approximately 75% with a slight enrichment of the *para*-isomer (*meta/para* ratio of  $\sim 45/55$ ).  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.30 and 7.92 (d, 1H, *meta*-Ar-H), 8.10 (s, 1H, *para*-Ar-H), 4.50–4.38 (q, 4H, methylene), 1.39–1.36 (t, 6H, methyl).

**Preparation of BPDA diimide dimethyl ester diacid.** 3,3',4,4'-Biphenyltetracarboxylic diimide (17.65 g, 0.060 mol) was slurried in 45 ml anhydrous methanol. Triethylamine (0.6 mmol, 0.084 ml) was added as a catalyst and the mixture was refluxed for 8 h. After cooling, the excess methanol was distilled off on a rotary evaporator under reduced pressure using aliquots of ethyl acetate ( $4 \times 50$  ml). The weight of the slurry was adjusted to 60 g with ethyl acetate.

**Preparation of BPDA dimethyl ester diacyl chloride.** The slurry of the BPDA dimethyl ester diacid was cooled in an ice bath and oxalyl chloride (22.8 g, 180 mmol) was added with stirring. The bath was removed and the solution was slowly warmed to  $45^\circ\text{C}$  and held at temperature overnight. The excess oxalyl chloride was removed along with the solvent on a rotary evaporator, using aliquotic addition of solvent to ensure complete removal of the oxalyl chloride. Tetrahydrofuran (THF) was then added to prepare a 24.6% solution.

### Oligomer and polymer synthesis

**Amine end-capped propylene oxide oligomers.** The general method for functionalization of PO oligomers with an amine end group is given for the  $5000\text{ g mol}^{-1}$  hydroxyl-terminated oligomer. A 250 ml three-necked round bottomed flask fitted with a dry ice condenser and a nitrogen inlet was charged with PO (25.14 g, 5.028 mmol), followed by 70 ml of methylene chloride. Upon dissolution of the PO, 5 ml of pyridine was added. To this, a solution of 4-nitrophenyl chloroformate (1.0135 g, 5.028 mmol) dissolved in 20 ml of

methylene chloride was added dropwise (0–5°C) in a nitrogen atmosphere. The reaction was allowed to return to ambient temperature and proceed overnight. The reaction mixture was diluted with 125 ml of methylene chloride and rinsed with acid (5% HCl), water, sodium bicarbonate and water. The solution was dried (magnesium sulfate) and concentrated, yielding an oil. I.r. (neat)  $\nu$  ( $\text{cm}^{-1}$ ): 1770 (carbonate), 1520 (nitro).  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.2 (m), 3.5 (m), 7.35 (d, OPh end group), 8.3 (d,  $\text{NO}_2\text{Ph}$  end group). The end-capped PO oligomer (20.8 g) was then dissolved in 100 ml of THF with 0.875 g of catalyst (10% Pd on carbon). The reaction mixture was exposed to a hydrogen atmosphere (24 h) to effect hydrogenation of the nitro group.  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.2 (m), 3.5 (m), 6.7 (OPh end group), 7.05 (d, Ph end group).

*Chloroformate-terminated poly(propylene oxide).* The chloroformate-terminated PO oligomers were prepared by the general procedure described below for a 2300  $\text{g mol}^{-1}$  monofunctional hydroxyl-terminated PO oligomer. A 50 ml three-necked round bottomed flask was charged with the hydroxyl-terminated PO (2.85 g, 1.24 mmol), and then fitted with a dry ice condenser, nitrogen inlet and magnetic stir bar. To the PO was added 20 ml of a 20% phosgene in toluene solution (0.038 mmol), and the reaction mixture was heated to 50°C for 3 h. The excess phosgene and toluene were removed with a strong nitrogen flow through the reaction vessel to an aqueous base trap. After removal of the majority of the volatiles, the dry ice condenser was replaced with a stopper and the residual volatiles were removed *in vacuo*. The resulting oligomer was characterized by i.r., which showed the loss of the –OH stretch at 3500  $\text{cm}^{-1}$  and the appearance of a sharp band at 1780  $\text{cm}^{-1}$  characteristic of a chloroformate C=O stretch.

*Amine end-capped PMMA. Block copolymer synthesis of PMDA/ODA and PO using the oligomer–oligomer approach.* The block copolymers derived from the poly(amic ethyl ester) of PMDA–ODA and PO were prepared by the following general procedure described below. A solution of 6.00 g (0.50 mmol) of amine-terminated poly(amic alkyl ester) oligomer ( $M_n = 12\,000 \text{ g mol}^{-1}$ ) in 40 ml of NMP was charged and cooled in an ice bath. To this solution was added 2.85 g (1.24 mmol) of a chloroformate-terminated PO oligomer ( $M_n = 2300 \text{ g mol}^{-1}$ ) in 40 ml of THF. This was followed by the dropwise addition of 2 ml of pyridine. The solution was stirred at 0°C for 3 h, then warmed to room temperature overnight. The polymer was precipitated by addition of the polymerization mixture to 3:1 methanol/water solution in a blender. The polymer was washed with methanol, twice with water, four times with methanol and dried overnight to afford 6.2 g (75% yield) of the block copolymer as a white powder.

The copolymer composition was characterized by  $^1\text{H}$  n.m.r. by comparison of the integral of the resonances from the PO block to the ethyl resonances of the poly(amic alkyl ester). The resulting triblock copolymer had a PO composition of 22 wt% (theoretical = 27.4 wt%). The multiblock copolymers of PO with the poly(amic alkyl ester) of PMDA–ODA were prepared by

analogy to the triblock system. In this case, difunctional propylene oxide oligomers were used.

*Block copolymer synthesis of BPDA/PDA and PO using the monomers–oligomer approach.* The BPDA dimethyl ester diacyl chloride was placed in a 500 ml round bottomed flask equipped with an overhead stirrer and two dropping funnels. One funnel contained a solution of amine-terminated PO oligomer (2.472 mmol, 4.87 g) of molecular weight 1970  $\text{g mol}^{-1}$  in triethylamine (4.92 mmol, 0.50 g) and NMP (84.88 g). The second funnel contained a 4.81 wt% solution of PDA (57.12 mmol, 6.17 g) in NMP along with pyridine (121.17 mmol, 9.58 g). The acyl chloride solution was cooled to 5°C in an ice/acetone bath and the PO solution was added dropwise, followed by addition of the PDA solution. At the end of the PO addition, there was a slight amount of precipitate which disappeared during the addition of PDA solution. Another precipitate formed at the end of the PDA addition so the mixture appeared opalescent. Following addition of the amines, the ice/acetone bath was removed and the solution was allowed to warm to 15°C when aniline (0.81 mmol, 0.74 ml) was added to cap the polymer. The reaction was allowed to proceed overnight. The polymer was then precipitated into water, washed with methanol, and dried in the vacuum oven to yield 26.3 g of polymer.  $^1\text{H}$  n.m.r. of the polymer in dimethylsulfoxide ( $\text{DMSO}$ )- $d_6$  indicates a 9.5% PO incorporation in the polymer.

*Block copolymer synthesis of PMDA/ODA and PO or PMMA using a monomers–oligomer approach.* The amic ester–aryl ether–propylene oxide copolymers were prepared by the co-reaction of the propylene oxide oligomers with ODA and PMDA diethyl ester diacyl chloride in NMP in the presence of *N*-methylmorpholine. A detailed procedure designed to prepare an amic ester–propylene oxide copolymer with a propylene oxide oligomer of 5000  $\text{g mol}^{-1}$  molecular weight and 30 wt% propylene oxide composition is provided. A three-necked flask equipped with an overhead stirrer and addition funnel was charged with PO (1.2000 g, 0.975 mmol) and ODA (0.9005 g, 4.497 mmol), carefully rinsed in with 20 ml of NMP. Throughout the polymerization  $\text{N}_2$  was passed through the system. The solution was then cooled to –5°C, and *N*-methylmorpholine (1.1076 g, 10.94 mmol) was added to the solution. The PMDA diethyl ester diacyl chloride was dissolved in ~25 ml of methylene chloride, and added in increments of approximately half over a 2 h period so as to slowly approach the stoichiometric end point. The polymerizations were allowed to proceed overnight, and the polymer was isolated by precipitation in methanol/water, rinsed with water (to remove excess salts), subjected to a methanol rinse (to remove possible homopolymer contamination) and dried in a vacuum oven. The imide–methyl methacrylate copolymers were prepared and isolated in an analogous fashion using an amine-functional PMMA oligomer.

*Block copolymer synthesis of PMDA/PDA with PO using a monomers–oligomer approach.* The imide–propylene oxide copolymers, where the imide component was derived from PMDA and PDA, were prepared in an

analogous fashion to that described above. To a three-necked flask equipped with an overhead stirrer, nitrogen inlet and addition funnel, PDA (0.8018 g, 7.41 mmol), PO (1.500 g, 0.35 mmol) and *N*-methylmorpholine (1.5723 g) were charged and carefully washed in with NMP. The diacyl chloride of PMDA (2.6181 g, 7.72 mmol) was dissolved in methylene chloride and added dropwise over 2 h. The reaction mixture was then stirred for another hour. The resulting copolymer was precipitated in a water/methanol (40/60) mixture and dried under vacuum at 40°C for 48 h.

### Measurements

Dielectric measurements on the polymer films were carried out using a HP multifrequency analyser. Medium frequency (10 kHz to 2 MHz) capacitance and loss tangents were measured in the temperature range 25–100°C. The specimens for dielectric measurements were prepared by vacuum deposition of 3 mm diameter gold electrodes on the spin-coated polymer films with the back surface of the Si wafer serving as the other electrode. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured on a Du Pont DSC 1090 instrument with a heating rate of 10°C min<sup>-1</sup>. The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) at 10 Hz and a heating rate of 10°C min<sup>-1</sup> in the tension mode. Isothermal and variable temperature (5°C min<sup>-1</sup> 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 made from carbon tetrachloride and xylene. The column was calibrated against a set of beads of known densities at 25°C. At least three specimens were used for each density measurement. Small-angle X-ray scattering (SAXS) measurements were performed on a Kratky camera using a 60 µm entrance slit with Ni-filtered Cu irradiation from a Rigaku 18 kW rotating anode generator operated at 100 kV and 40 mA.

### Foam formation

The copolymers were dissolved in NMP at a concentration of 9–15% solids. Coatings of 10 µm thickness were obtained by spin coating at 2000 rev min<sup>-1</sup> on 2.54 cm diameter Si wafers. Removal of the solvent and imidization was accomplished by heating the polymer films to 265°C at 5°C min<sup>-1</sup> and maintaining them at 265°C for 1.5 h in a nitrogen atmosphere. The films were then cooled to room temperature, reheated to 275°C at a rate of 5°C min<sup>-1</sup> and maintained at 275°C for 9 h in air for the case of the PO based copolymers. The PMMA based copolymers were heated to 350°C (5 h) in air.

## RESULTS AND DISCUSSION

Successful implementation of the block copolymer approach to polyimide nanofoams relied, in part, on the successful synthesis of block copolymers of polyimides with the thermally decomposable block. To this end, poly(amic alkyl esters) were employed as the soluble precursor to the polyimide block, since this scheme can be applied to rigid, high *T<sub>g</sub>* polyimides and allows for isolation, purification and characterization of a

processable form of the copolymer. Two types of thermally decomposable block were studied, poly(propylene oxide) (PO) and poly(methyl methacrylate) (PMMA). Both of these polymer systems are known to decompose in the range 250–300°C, significantly below the *T<sub>g</sub>*s of the polyimide blocks, to allow for a significant processing window to minimize foam collapse.

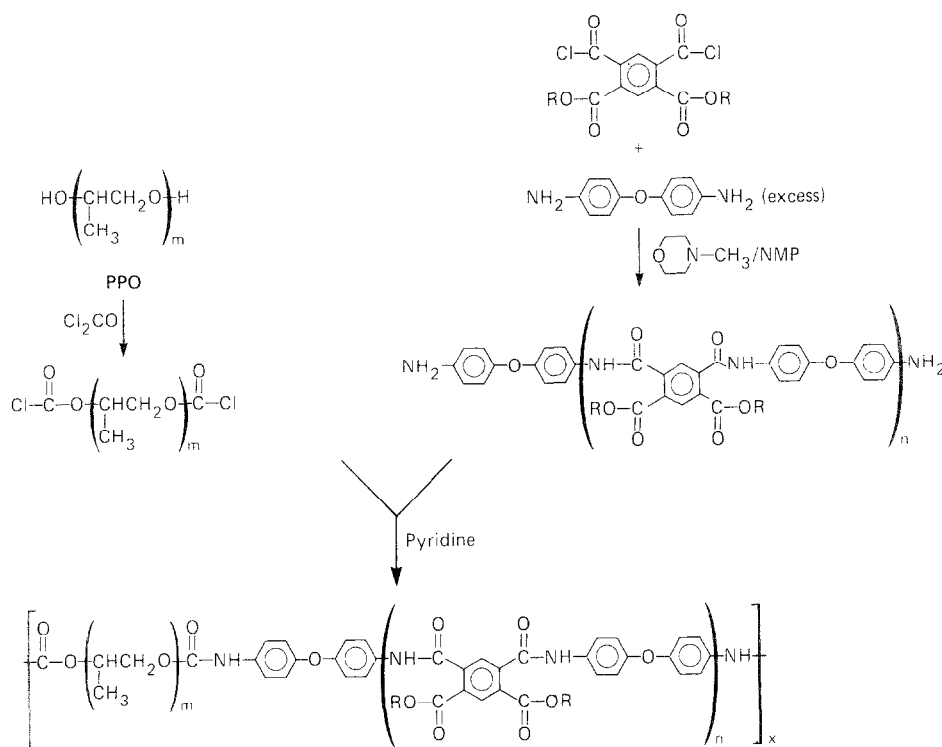
The morphology of the block copolymer before foam formation defines the final foam structure. Earlier results on the PPQ systems suggested that, in addition to the solubility parameter difference between blocks, control of block copolymer architecture and block molecular weights were important variables controlling the morphology. Systems with poor phase purity led to substantial collapse during foam formation and less than the theoretical porosity based on the PO incorporated into the copolymer. Furthermore, phase mixing served to further reduce the processing window for foam formation. Like poly(phenylquinoxaline), polyimide block copolymer schemes are limited to difunctional monomers for the polyimide precursor, and hence offer the possibility of generating only multiblock or triblock copolymers through the use of either difunctional or monofunctional thermally decomposable blocks, respectively. Two synthetic schemes were investigated for the polyimide block copolymers, i.e. oligomer–oligomer and monomer(s)–oligomer approaches. The poly(amic ester) polyimide precursor polymer was used in both approaches, either as an amine-functional oligomer to condense with a thermally labile oligomer or in an *in situ* polymerization from monomer with an amine-functional thermally decomposable block.

The first system studied was based on PMDA–ODA polyimide with PO as the thermally decomposable block using an oligomer–oligomer synthetic approach. The poly(amic ester) polyimide precursor was chosen due to the advantages this system has in polyimide block copolymer synthesis with regards to the aforementioned improvement in solubility, isolation, purification and characterization as compared with a poly(amic acid) precursor<sup>26</sup>. Well-controlled poly(amic ester) oligomers of PMDA–ODA were prepared by the polymerization of ODA with PMDA diethyl ester diacyl chloride in NMP containing base. An excess of ODA was employed, as dictated by the Carothers equation, to provide end group functionality and controlled molecular weight (*Scheme 1*). Oligomers with number-average molecular weights between 6000 and 16 000 g mol<sup>-1</sup> (oligomers **1a–c**) were prepared (*Table 1*). The molecular weight was obtained from <sup>1</sup>H n.m.r. spectroscopy of oligomers after functionalization with trimethylsilylpropionyl chloride<sup>27</sup>.

Chloroformate-functional propylene oxide oligomers were prepared by reaction of hydroxy-terminated oligomers with phosgene in toluene (*Scheme 1*). After removal of unreacted phosgene and the toluene *in vacuo*, the resulting chloroformate oligomers, **2**, were isolated as oils. This procedure was used to generate chloroformate difunctional oligomers with number-average

**Table 1** Characteristics of amic–ethyl ester oligomers

Sample	$\langle M_n \rangle$ (g mol <sup>-1</sup> )	$[\eta]_{\text{NMP}}^{30^\circ\text{C}}$
<b>1a</b>	6000	0.36
<b>1b</b>	12 000	0.42
<b>1c</b>	16 000	0.39



Scheme 1

molecular weights of 2000, 3000 and 4000 g mol<sup>-1</sup> (**2a–c**) and monofunctional oligomers with number-average molecular weights of 2300, 5000 and 10 000 g mol<sup>-1</sup> (**2d–f**) (Table 2). Conversion to the chloroformate was confirmed by infra-red spectroscopy, as evidenced by the appearance of the characteristic carbonyl stretch band at 1780 cm<sup>-1</sup> and the disappearance of the –OH stretch at 3500 cm<sup>-1</sup>.

Block copolymers derived from oligomers **1** and **2** were prepared by dissolving **1** and one equivalent of pyridine in NMP, cooling to 0°C, and adding a toluene solution of the functional PO oligomer **2** in THF (Scheme 1). The solution generally did not show a large increase in viscosity. After warming to room temperature and stirring for 18 h, the copolymers were isolated by precipitation in methanol/water and given selected washes to remove possible unreacted PO oligomers and salts. The compositions of the copolymers prepared by this procedure were characterized by <sup>1</sup>H n.m.r. Initially triethylamine was used as a base; however, problems were encountered in redissolving the polymer after isolation. I.r. spectroscopy indicated that

low levels of imidization had occurred, which has been reported to be catalysed by amines<sup>28</sup>. This problem could be circumvented by addition of a 20 mol% excess of the functional PO oligomer in either a multiblock or triblock synthesis. A more satisfactory solution to the problem was to use pyridine as the acid acceptor. This procedure was used to prepare multiblock and triblock copolymers based on **1b** with 2000, 3000 and 4000 g mol<sup>-1</sup> difunctional oligomers and a 2300 g mol<sup>-1</sup> monofunctional oligomer to afford copolymers **3a–d** (Table 3). The 16 000 g mol<sup>-1</sup> poly(amic ester) oligomer, **1c**, was copolymerized with 5000 and 10 000 g mol<sup>-1</sup> monofunctional PO, **2e** and **2f**, to afford copolymers **3e** and **3f**. The copolymers were obtained in yields of the order of 80% for PO compositions in the 20–30 wt% range, but were lower for higher PO compositions due to the solubility of the copolymers in the wash solvents. A manifestation of this synthetic approach and isolation procedure was that the PO compositions obtained were always lower than charged, particularly for copolymers **3e** and **3f**. The copolymers were obtained as fibrous white powders and all formed clear viscous solutions in NMP with no evidence of gel or phase separation. Solutions

Table 2 Characteristics of propylene oxide and methyl methacrylate oligomers

Sample	Oligomer type	$\langle M_n \rangle$ (g mol <sup>-1</sup> )	$T_g$ (°C)
<b>2a</b>	PO	2000 <sup>a</sup>	-54
<b>2b</b>	PO	3000 <sup>a</sup>	-54
<b>2c</b>	PO	4200 <sup>a</sup>	-42
<b>2d</b>	PO	2300 <sup>b</sup>	-46
<b>2e</b>	PO	5000 <sup>b</sup>	-52
<b>2f</b>	PO	10 000 <sup>b</sup>	-53
<b>2g</b>	PMMA	5000 <sup>b</sup>	116
<b>2h</b>	PMMA	15 000 <sup>b</sup>	123
<b>2i</b>	PMMA	25 000 <sup>b</sup>	128

<sup>a</sup> Potentiometric titration with HBr in acetic acid

<sup>b</sup> <sup>1</sup>H n.m.r.

Table 3 PMDA/ODA–poly(propylene oxide) block copolymers

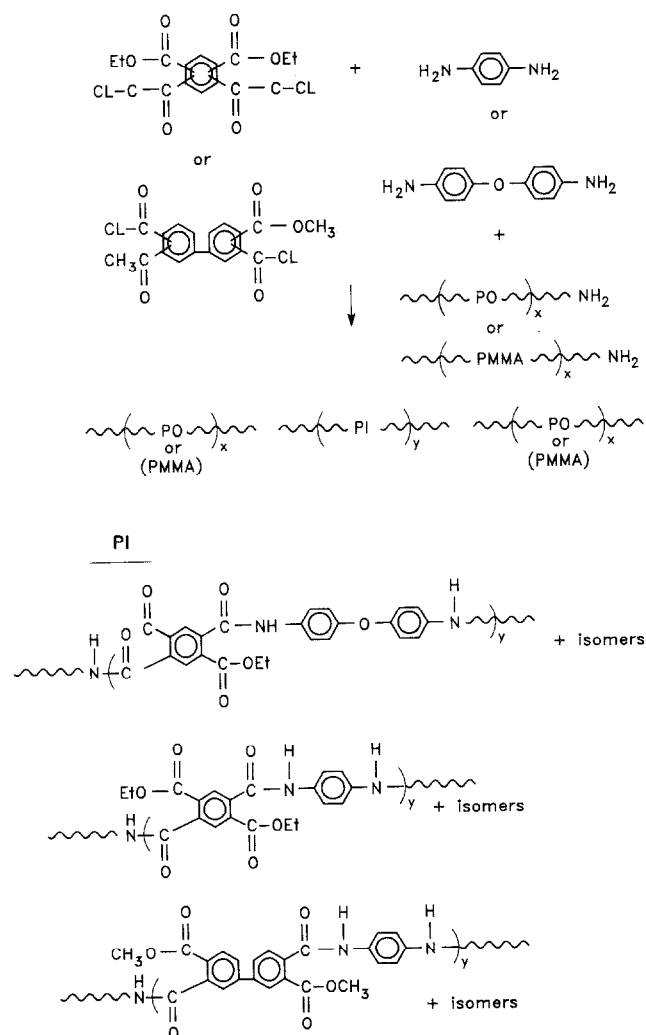
Polymer	$M_n$ (g mol <sup>-1</sup> )		Yield (%)	PO composition (wt%)	
	PO	Poly(amic ester)		Theo.	Expt <sup>a</sup>
<b>3a</b>	2000	12 000	84	17.2	14.6
<b>3b</b>	3000	12 000	79	23.8	19.1
<b>3c</b>	4000	12 000	80	29.4	23.1
<b>3d</b>	2300	12 000	75	27.7	21.7
<b>3e</b>	5000	16 000	61	38.5	23.8
<b>3f</b>	10 000	16 000	54	55.6	43.7

<sup>a</sup> Determined by <sup>1</sup>H n.m.r.

could be cast and cured (250°C) to give perfectly clear films, indicative of minimal homopolymer contamination.

The second synthetic procedure used was a monomer–oligomer approach to produce both ABA and (AB)<sub>n</sub> type molecular architectures. For this strategy, three imide blocks comprising either PMDA/ODA, PMDA/PDA or BPDA/PDA were investigated as the matrix of the copolymer. Thus, the imide blocks were derived from either semi-rigid or rigid chains which displayed liquid crystalline or crystalline type morphologies. As in the previous case, the imide intermediates were prepared via the poly(amic alkyl ester) route to facilitate solubility and subsequent copolymerization. The PMDA based polymers were derived from the ethyl ester, whereas the BPDA based copolymer was prepared from the methyl ester. Also for this monomers–oligomer approach, appropriately functionalized preformed oligomers of both propylene oxide and methyl methacrylate were investigated.

The copolymers derived from PMDA/ODA and PMDA/PDA were prepared from the incremental addition of PDMA diethyl ester diacyl chloride dissolved in methylene chloride to a solution of either PO (oligomers **2d–f**) or PMMA (**2g–i**) and either ODA or PDA in NMP in the presence of *N*-methylmorpholine (Scheme 2). The solids composition for the copolymerizations were maintained at 12–13 wt% for each of the



Scheme 2

polymerizations. *N*-methylmorpholine was used as the acid acceptor, since the subsequent salt precipitated from the reaction mixture and did not interfere with the solubility of the starting materials or subsequent polymer. Completion of the polymerization was taken as the point where the viscosity increased dramatically. The copolymers were isolated in a water/methanol mixture and rinsed with water to remove salts formed during the polymerization.

The BPDA/PDA based copolymers were prepared in an analogous fashion to the copolymers described above. The BPDA dimethyl ester was added to a solution of PO in the presence of base, followed by the addition of PDA. Near completion of the polymerization, the reaction turned somewhat turbid and, in some instances, a small precipitate was observed. The resulting polymer was isolated and rinsed with methanol to remove any homopolymer contamination.

Use of the monomer–oligomer approach permitted a study of both (AB)<sub>n</sub> and ABA molecular architectures. For the case where the difunctional aliphatic amine-terminated propylene oxide oligomer was employed in the copolymer synthesis, perfectly alternating sequence distributions of the imide and propylene oxide blocks were obtained. Conversely, use of the preformed monofunctional amine-terminated propylene oxide or methyl methacrylate oligomers with the polyimide monomers produced an ABA copolymer where the propylene oxide or methyl methacrylate components comprised the A blocks. The average molecular weight of the propylene oxide or methyl methacrylate block is identical to that of the preformed oligomers. The molecular weight of the imide block was controlled by the stoichiometric imbalance between the diamines and PMDA diethyl ester diacyl chloride, dictated by the PO or PMMA block length, functionality and composition.

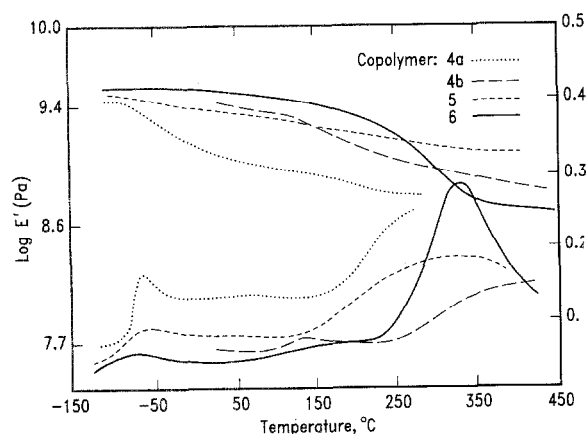
The characteristics of the imide–propylene oxide multiblock and triblock copolymers together with the imide–methyl methacrylate triblock copolymers are shown in Table 4. The propylene oxide based copolymers have imide blocks comprising either PMDA/ODA, PMDA/PDA or BPDA/PDA, denoted as **4–6**, respectively, in Table 4. The propylene oxide and methyl methacrylate compositions were deliberately maintained low to produce discrete phases of the labile polymer in the high temperature polymer matrix. The composition of the propylene oxide and methyl methacrylate components in the copolymer was determined using both <sup>1</sup>H n.m.r., by comparison of the integrated polyimide signal to that of either the PO or PMMA resonances, and by t.g.a., by measuring the weight retention after the decom-

Table 4 Characteristics of polyimide–propylene oxide triblock copolymers prepared via monomer–oligomer approach

Sample	Polyimide block type	Thermally decomposable block type <sup>a</sup>	PO composition (wt%)	
			Charge	Incorporation <sup>b</sup>
<b>4a</b>	PMDA/ODA	<b>2c</b> (4200)	15	9
<b>4b</b>	PMDA/ODA	<b>2e</b> (5000)	15	12
<b>4c</b>	PMDA/ODA	<b>2g</b> (5000)	15	11
<b>5</b>	PMDA/PDA	<b>2c</b> (4200)	20	14
<b>6</b>	BPDA/PDA	<b>2c</b> (4200)	15	9

<sup>a</sup> Values in parentheses are block length (g mol<sup>-1</sup>)

<sup>b</sup> <sup>1</sup>H n.m.r.

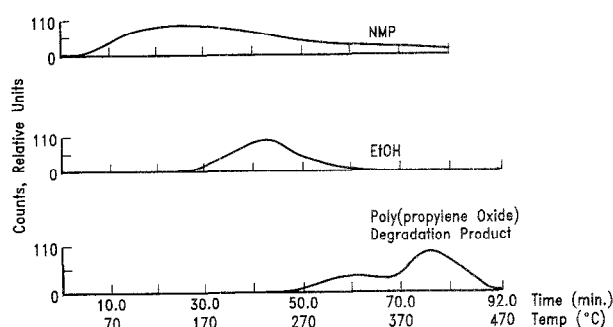


**Figure 1** Dynamic mechanical analysis of imide-propylene oxide and imide-methyl methacrylate copolymers

position of the thermally labile block. The composition of PO and PMMA in the copolymer was somewhat lower than that charged due, most likely, to the solvent rinses which removed PO- or PMMA-rich copolymer.

The dynamic mechanical results for the imide-propylene oxide multiblock and triblock copolymers and for the imide-methyl methacrylate triblock copolymer are shown in *Figure 1*. The imide-propylene oxide copolymers showed two transitions, which is characteristic of a microphase-separated morphology. The transition occurring near  $-60^{\circ}\text{C}$  is similar to that seen for the PO oligomer and, consequently, can be attributed to nearly pure microphases of PO in the copolymer films. In addition, the damping peak is rather sharp in most cases, which suggests that the amount of interfacial mixing is minimal, i.e. the phase boundaries are sharp. The transitions associated with the imide block for the PMDA/ODA and BPDA/PDA based copolymers were somewhat lower than that observed for the corresponding homopolymers. This can be attributed to either incomplete removal of solvent or to partial solubilization of PO in the polyimide microphase. It has been shown that the temperature at which this transition occurs is highly dependent on the final curing temperature at which this transition occurs is highly dependent on the final curing temperature. Not only does the transition shift to higher temperatures with increasing temperature, but the magnitude of the transition decreases as well. Curing these copolymers at more elevated temperatures was not possible due to the decomposition of PO. For the PMDA/PDA based copolymer no damping peaks were found, which is consistent with the parent homopolymer. The imide-methyl methacrylate copolymers exhibited two transitions indicative of a microphase-separated morphology (*Figure 1*). The PMMA transition occurred at nearly the same temperature as the PMMA oligomer, suggesting minimal phase mixing.

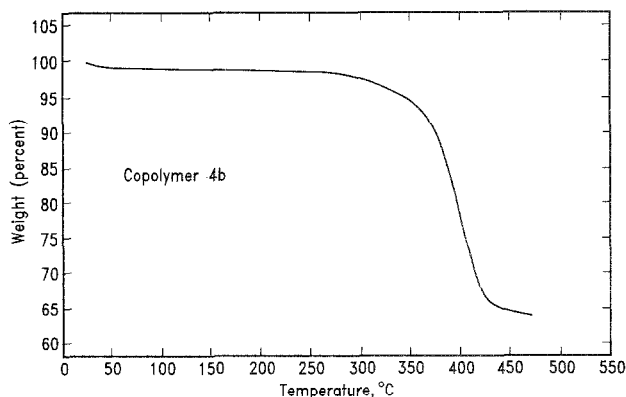
To generate a nanofoam successfully, decomposition of the labile block can only be done after complete removal of the solvent and by-products of the cyclimidization reaction (in this case, ethanol). Under an inert atmosphere both PMMA and PO decompose at relatively high temperatures. Shown in *Figure 2* are the variable temperature t.g.a./mass spectroscopy (m.s.) results for copolymer **3c**, where the evolution of NMP (casting solvent), ethanol (imidization by-product) and



**Figure 2** T.g.a./m.s. analysis of copolymer **3c**

propylene oxide (labile coblock by-product) are shown as a function of temperature. First NMP comes off, followed by ethanol. The evolution of propylene oxide degradation product occurred at substantially higher temperatures and is somewhat broader. Since the thermal degradation of poly(propylene oxide) involves a random chain cleavage and does not proceed via an unzipping mechanism as does PMMA, the evolution of low molecular weight by-products occurs over a broad time and temperature range. The mass spectroscopy data suggest that the vitrified polyimide matrix acts as an effective diffusion barrier, entrapping large mass degradation by-products. With time and increasing temperature these larger fragments undergo further degradation to low molecular weight species which then diffuse through the polyimide and out of the film. For our experiments, the copolymers were cast and cured to  $265^{\circ}\text{C}$  for 1.5 h under  $\text{N}_2$  to effect imidization. Both i.r. and isothermal gravimetric analysis showed that, under these conditions, imidization is complete without loss of the propylene oxide or methyl methacrylate coblocks.

Generation of the foam structure was accomplished by a subsequent heat treatment of the films in air to decompose the propylene oxide. For the case of the imide-propylene oxide copolymers, the films were heated to  $275^{\circ}\text{C}$  (air) to decompose the propylene oxide. Isothermal gravimetric analysis indicated that decomposition of the poly(propylene oxide) in the copolymer was complete after  $\sim 5$  h. The imide-methyl methacrylate copolymers required substantially higher temperatures to decompose the methyl methacrylate coblock. *Figure 3* shows a t.g.a. thermogram for copolymer **4b**, where the methyl methacrylate component is seen to decompose



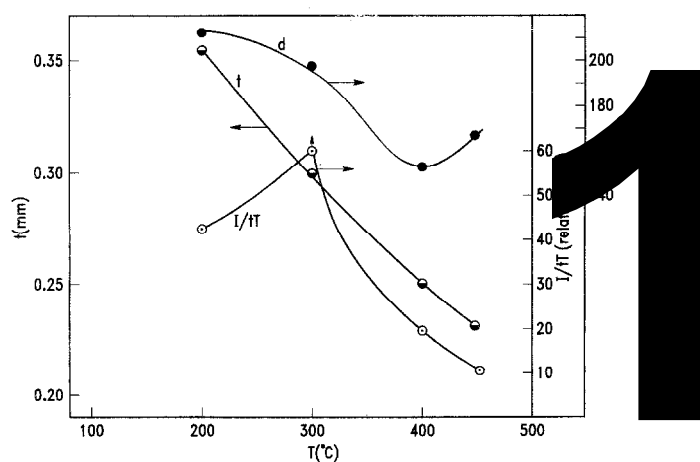
**Figure 3** Variable temperature t.g.a. thermogram of imide-methyl methacrylate copolymer **4b**



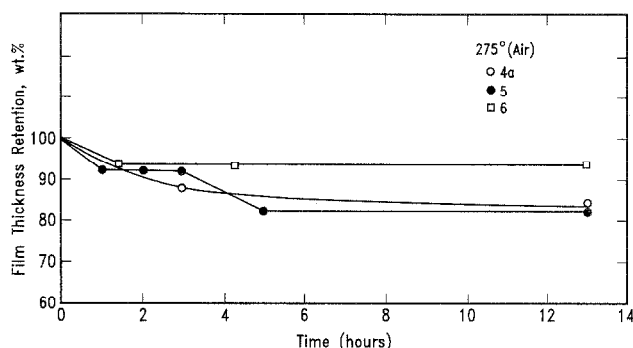
just above 340°C (under N<sub>2</sub>). Isothermal gravimetric analysis at temperatures below 340°C showed only partial degradation of the methyl methacrylate in the copolymer after 9 h. Complete decomposition of the methyl methacrylate in the copolymer was observed only for temperatures of 350°C or above in ~5 h. Thus, the *in situ* decomposition of the PO or PMMA coblock in the copolymer is quantitative with no evidence of side reactions and results in complete elimination of the labile component.

The imide-propylene oxide copolymer, **3c**, demonstrated many of the problems posed by the use of polyimides in this approach to foam formation. Foam formation in these samples was followed by small angle X-ray scattering; SAXS is ideally suited to this purpose since the size scale of the pores is ~100 Å and the total amount of scattering increases dramatically due to the enhanced contrast between the matrix polymer and the pores. Density measurements are also a direct means of measuring the formation of a foam and the volume fraction of pores. While sample thickness should not change with the production of a foam, it is also most sensitive to collapse of the foam at elevated temperature.

These techniques were combined to monitor foam formation in a block copolymer of PMDA-ODA and PO as a function of annealing temperature. Initial heating to 275°C produced a decrease in the film thickness along with a 50% increase in total X-ray scattering (Figure 4). This result is consistent with the formation of a nanofoam upon decomposition of the PO blocks. However, increasing the temperature further led to a reduction in the film thickness and total scattering so that, by 400°C, the foam which was present at 300°C was found to have collapsed. Likewise, the density of the foamed material was essentially identical to that of the parent homopolymer. It should be noted, however, that there is still evidence of a microphase-separated morphology as evidenced by the retention of an interference maximum that occurs at a Bragg spacing of 16 nm. These results suggest that the foam has not fully collapsed and that the amount of collapse perpendicular to the film



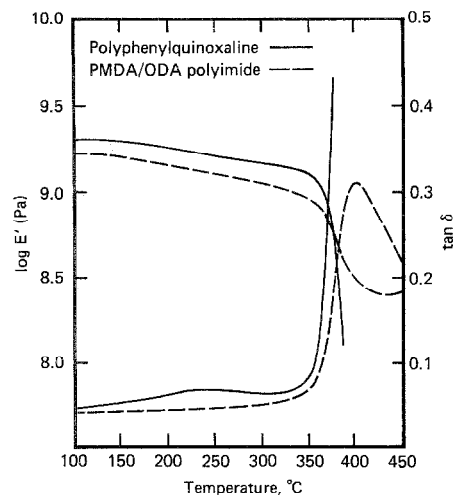
**Figure 4** Film thickness (○), Bragg spacing (●) and the peak intensity normalized by the film thickness and transmission coefficient (○), as a function of temperature.  $I/tT$  is indicative of the foam formation. Up to 300°C  $I/tT$  increases and, in fact, only a minimum value can be shown (indicated by the vertical arrow) due to saturation effects on the detector. The drops in  $I/tT$  and  $t$  are indicative of the collapse of the foam structure



**Figure 5** Film thickness as a function of time at 275°C in air for copolymers **4a**, **5** and **6**

plane is much greater than that in the plane of the film. Similar results were also observed from the triblock copolymers derived from PMDA/PDA and BPDA/PDA. Figure 5 shows the film thickness of the copolymers as a function of time. Clearly, a decrease in the film thickness is observed proportional to the initial PO composition, indicating a collapse in the foam structure. These results are rather unexpected given that the nominal  $T_g$ s of the polymers are greater than 400°C.

Many of the desirable properties of the rigid aromatic polyimides result from their liquid crystalline type ordering. However, due to the confinement of the film on the substrate and volume losses during curing, strong preferential orientation of the chain axis parallel to the surface of the film occurs. This has been shown to produce a high thermal expansion coefficient and low modulus normal to the film surface. Earlier studies on polyimide block copolymers have shown that both the ordering and orientation of the molecules are retained, independent of the coblock type or composition<sup>25</sup>. However, due to this orientation, the modulus in the film thickness direction may not be sufficient to stabilize the subsequent foam structure. Therefore, molecular ordering and orientation are critical in determining the foam structure and stability. Presumably, the low modulus normal to the film surface allows enhanced relaxation rates, particularly at elevated temperatures, leading to collapse of the foam well below its nominal  $T_g$ .



**Figure 6** Dynamic mechanical analysis of poly(phenylquinoxaline) and PMDA/ODA polyimide



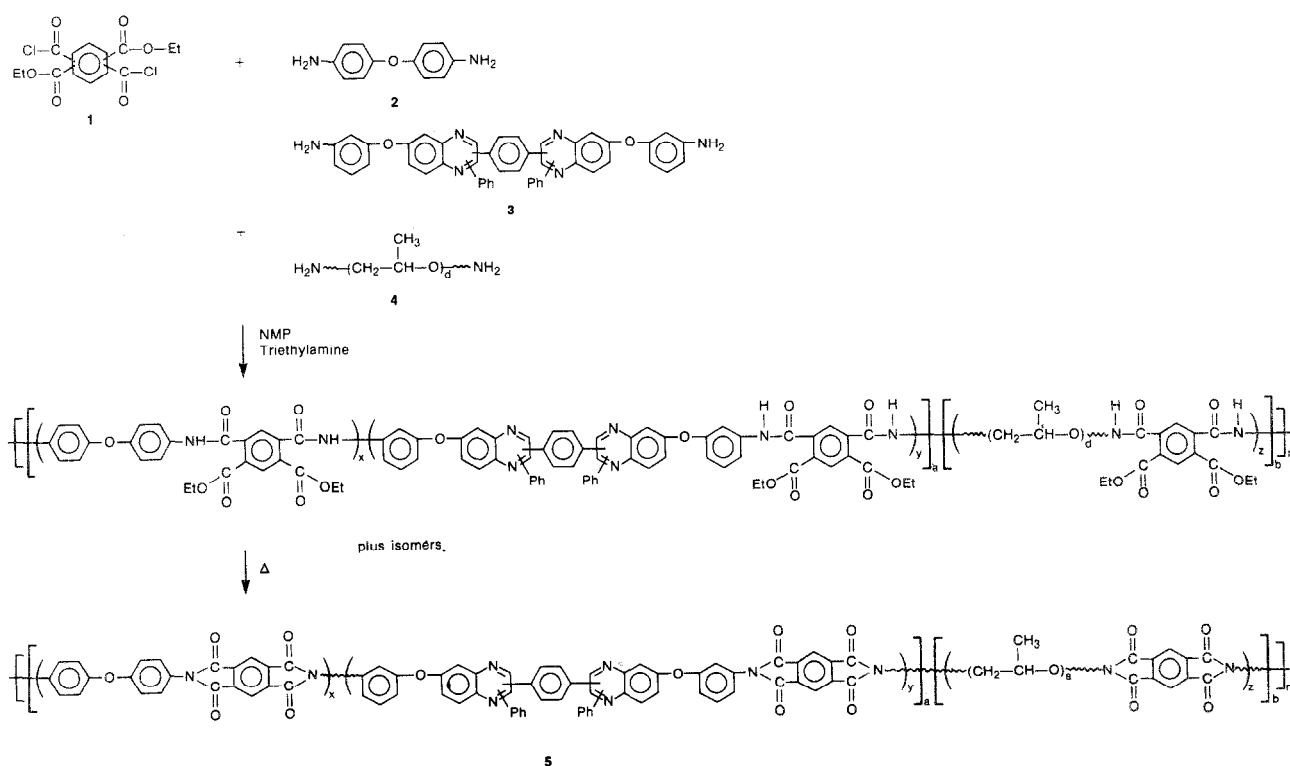
In contrast, PPQ is amorphous and isotropic, and stable foams were obtained up to the  $T_g$  of the PPQ matrix<sup>22</sup>. The polyimide and PPQ homopolymers can best be compared by their dynamic mechanical behaviour, as shown in Figure 6. The PMDA/ODA polyimide shows a retention of the ordered molecular structure and no evidence of a  $T_g$ , only a small drop in modulus is seen at  $\sim 350^\circ\text{C}$ . PPQ shows a modulus invariance up to  $T_g$ , at which point the modulus falls dramatically characteristic of an amorphous melt. The characteristics of each of these polymers were combined by the incorporation of an aryl ether phenylquinoxaline linkage into a semi-rigid polyimide backbone based on ODA and PMDA by the use of 1,4-bis[6-(3-aminophenoxy)-3-phenyl-2-quinoxaliny]benzene (DADQ) as a co-diamine. This monomer was prepared<sup>25</sup> by a novel nucleophilic aromatic substitution reaction of 1,4-(6-fluoro-3-phenyl-2-quinoxaliny) benzene with 3-aminophenol in the presence of  $\text{K}_2\text{CO}_3$ . Imide-aryl ether phenylquinoxaline copolymers have been reported and it was shown that copolymers with high phenylquinoxaline compositions sufficiently disrupted the ordering of the PMDA/ODA sequences to produce an amorphous and isotropic material<sup>25</sup>.

The copolymer synthesis was similar to that described before and involved the incremental addition of PMDA diethyl ester diacyl chloride dissolved in methylene chloride to a solution of the PO oligomer (2a-f), ODA and DADQ in NMP in the presence of *N*-methylmorpholine (Schemes 3 and 4). The solids content for the copolymerizations was maintained at 12–13 wt% for each of the polymerizations. *N*-methylmorpholine was used as the acid acceptor and the subsequent salt, *N*-methylmorpholium hydrochloride, precipitated from the reaction mixture. High molecular weight was readily achieved as judged by the dramatic increase in viscosity,

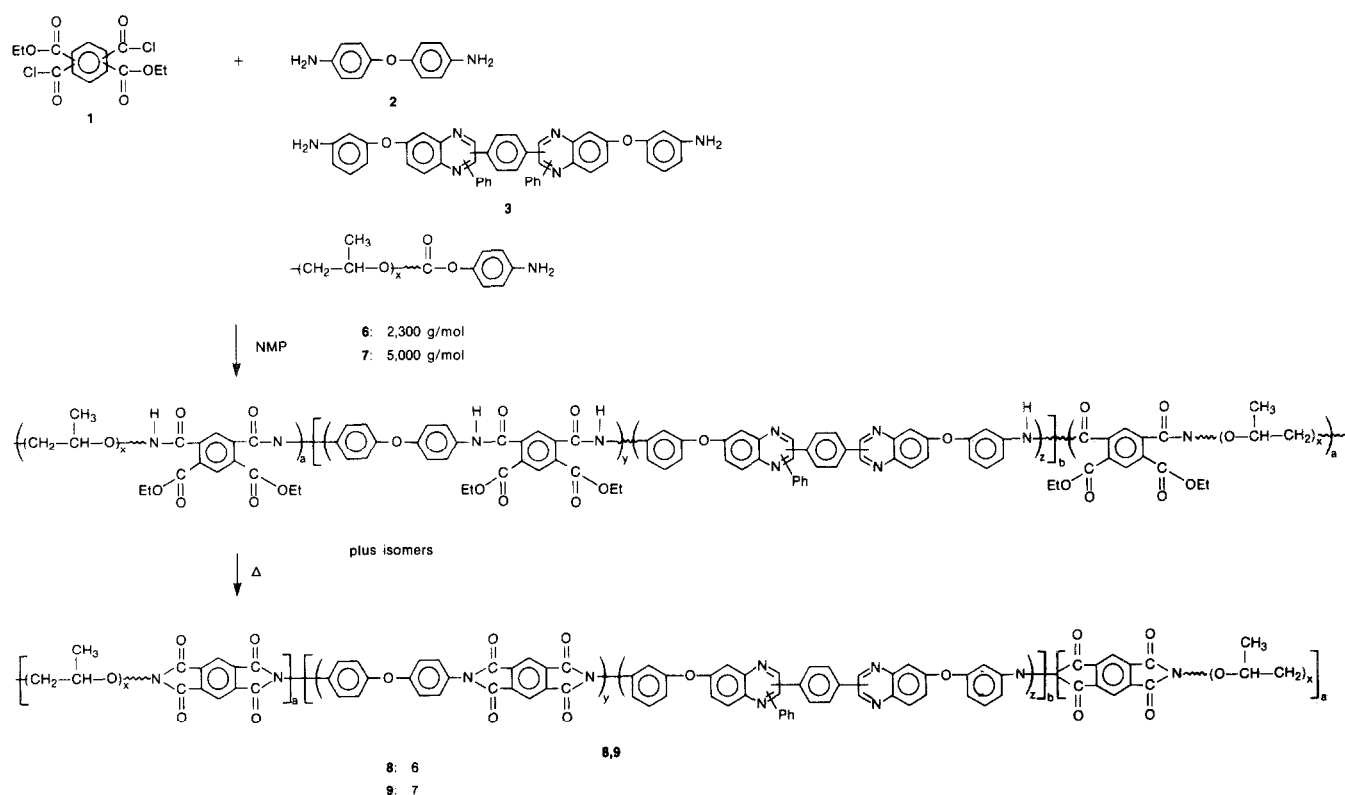
characteristic of most condensation polymerizations. The resulting copolymers were precipitated in a water/methanol mixture and rinsed with water to remove salts formed during polymerization. Finally, the copolymers were subjected to a methanol wash to remove possible PO homopolymer contamination. The copolymers were once again dissolved (NMP, 10% solids) and films were cast and cured to  $265^\circ\text{C}$  (1.5 h) to effect imidization.

The characteristics of the imide-propylene oxide multiblock and triblock copolymers (7–9, respectively) are shown in Table 5. Both the multiblock and triblock imide-propylene oxide copolymers have imide segments containing various compositions of the DADQ. The amount of DADQ was varied relative to the total weight of ODA and PMDA from 0 to  $\sim 70$  wt% (as shown in Table 5). The propylene oxide compositions were deliberately maintained low so as to maximize the possibility of having discrete, non-continuous domains of PO in the high temperature polymer matrix. This was done to facilitate the formation of a stable foam upon decomposition of the thermally labile block. The copolymer composition was determined as described previously. The composition of PO incorporated into the copolymer agreed with the amount charged.

The dynamic mechanical results for these polymers are shown in Figures 7 and 8. Two transitions were observed, indicative of a microphase-separated morphology: that at  $\sim -65^\circ\text{C}$  corresponds to the  $T_g$  of the PO phase and the second between 200 and  $350^\circ\text{C}$  is attributable to the imide coblock. The temperature of the PO transition was nearly identical to that of the preformed oligomer regardless of the block length or copolymer microstructure, and suggests that there is little, if any, mixing with the alternate block. The transition associated with the imide or imide-aryl ether phenylquinoxaline block was substantially depressed, particularly for the multiblock



Scheme 3



Scheme 4

copolymers. This may be due to the limited cure temperature required to prevent PO degradation or disruption of the ordered morphology by incorporation of the less polar PPQ. The copolymers with high imide compositions showed only a minimal drop in modulus at high temperatures, indicating both the absence of a  $T_g$  and retention of the morphology of the parent polyimide. However, the copolymers containing ~50 wt% phenylquinoxaline compositions (**8b** and **9b**) showed significantly different behaviour. A large, broad drop in modulus is observed at lower temperatures. The copoly-

mers with the highest phenylquinoxaline compositions (**8c** and **9c**) showed  $T_g$  values near 200°C.

Generation of the nanofoam structure was accomplished by subsequent heat treatment of the triblock polymers to decompose the thermally labile block. Samples were cast and then cured to 265°C in nitrogen to effect imidization. Due to the substantial depression in the  $T_g$  of the high temperature polymer matrix, mild conditions were required to decompose the PO. In a nitrogen atmosphere, PO is thermally stable up to ~300°C which allows for imidization of the

Table 5 Characteristics of imide-propylene oxide copolymers

Sample	PO block <sup>a</sup>	PPQ composition (wt%)	PO composition (wt%)		
			Charge	Incorporation ( <sup>1</sup> H n.m.r.)	Incorporation (t.g.a.)
<b>7a</b>	<b>2c</b> (4200)	0	15	12	12
<b>7b</b>	<b>2c</b> (4200)	10	15	9.0	9.0
<b>7c</b>	<b>2c</b> (4200)	25	15	14.3	16.0
<b>7d</b>	<b>2c</b> (4200)	50	15	14.2	14.5
<b>7e</b>	<b>2c</b> (4200)	70	15	14.4	13.5
<b>8a</b>	<b>2d</b> (2300)	25	15	11.0	15.0
<b>8b</b>	<b>2d</b> (2300)	50	15	9.4	12.0
<b>8c</b>	<b>2d</b> (2300)	70	15	8.0	12.0
<b>9a</b>	<b>2e</b> (5000)	25	15	6.4	—
<b>9b</b>	<b>2e</b> (5000)	50	15	9.3	9.0
<b>9c</b>	<b>2e</b> (5000)	75	15	9.45	—

<sup>a</sup> Values in parentheses are block length (g mol<sup>-1</sup>)

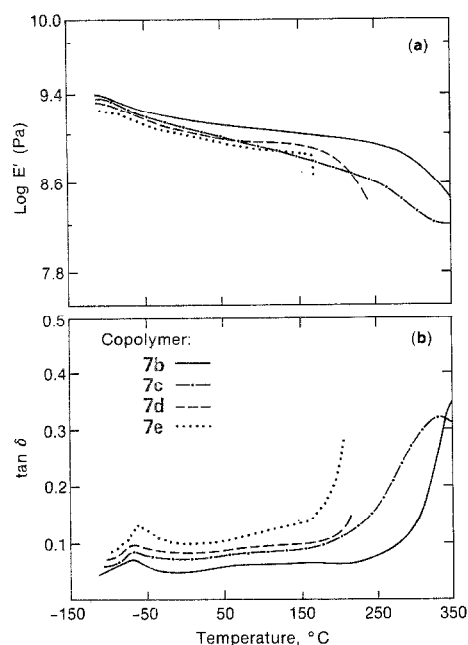


Figure 7 Dynamic mechanical analysis of copolymer series 7

copolymer. However, when exposed to an air or oxygen environment, the decomposition temperature drops substantially. Shown in Figure 9 is the decomposition of the PO component in copolymer 9b. These data indicate that the *in situ* decomposition of PO was quantitative at 225°C, with no evidence of side reactions.

Incorporation of the phenylquinoxaline-containing comonomer into the high temperature polymer component of the copolymer produced markedly different behaviour. The formation and stability of the foam structure was followed by SAXS and film thickness. reduction with decomposition of the PO block, indicative of an unstable foam structure (Figure 10). These materials were shown to be anisotropic and behave similarly to the polyimide based copolymers. The foam collapse was observed for both the multiblock and triblock architectures for all decomposition temperatures investigated.

Copolymers 7e, 8c and 9c, containing approximately 70% phenylquinoxaline composition in the high temperature polymer matrix, also showed a decrease in film thickness with thermal degradation of the PO

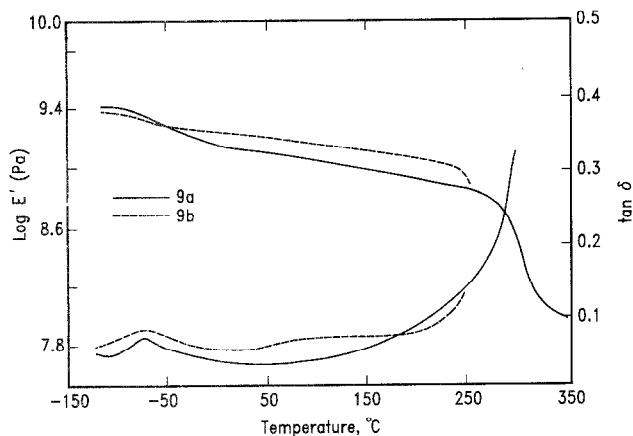


Figure 8 Dynamic mechanical analysis of copolymer series 9

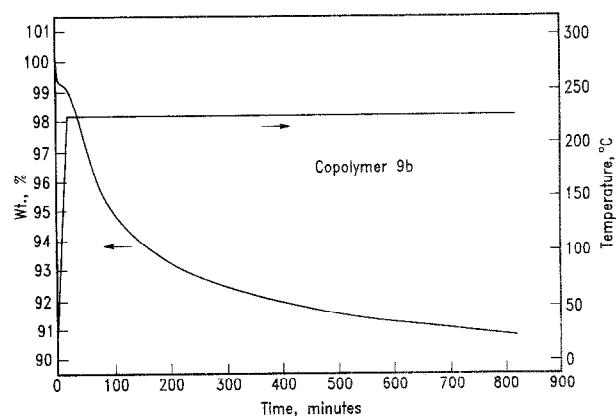


Figure 9 T.g.a. thermogram of copolymer 9b

component (Figure 11). Although these copolymers were both amorphous and isotropic, the poor phase purity and associated depression in  $T_g$  of the matrix polymer did not allow a sufficient processing window. In fact, in some cases, the  $T_g$  was below the decomposition temperature of the PO block. Conversely, copolymers 7d, 8b and 9b, containing approximately 50% phenylquinoxaline in the imide block, were isotropic and also had a sufficient, yet narrow, window between the decomposition temperature of the PO block and  $T_g$  of the matrix. Upon decomposition of the PO component (225°C, air atmosphere) a stable foam structure developed, as judged by the retention in film thickness. Temperatures above 250°C resulted in collapse due to the proximity to the  $T_g$ .

The SAXS profiles for copolymer 9b are shown in Figure 12 as a function of the scattering vector  $q$  ( $= (4\pi/\lambda) \sin \theta$ , where  $\lambda$  is the wavelength and  $\theta$  is the scattering angle). Scattering profiles for the uncured (heated to 80°C) copolymer show a weak maximum at  $q = 0.0243 \text{ \AA}^{-1}$  which corresponds to a Bragg spacing of 258 Å. Consequently, the copolymer is microphase-separated into an ordered array with a repeat period of ~258 Å. The structure is fairly disordered, as would be expected for a multiblock copolymer, as evidenced by the absence of higher-order reflections. Upon annealing at 265°C under  $N_2$ , the intensity of the scattering increases and the maximum shifts to  $q = 0.0201 \text{ \AA}^{-1}$  corresponding to a period of 312 Å. The increase in intensity can be attributed to the increase in electron density by conversion of the amic ester to the corresponding polyimide. However, this alone cannot account for the

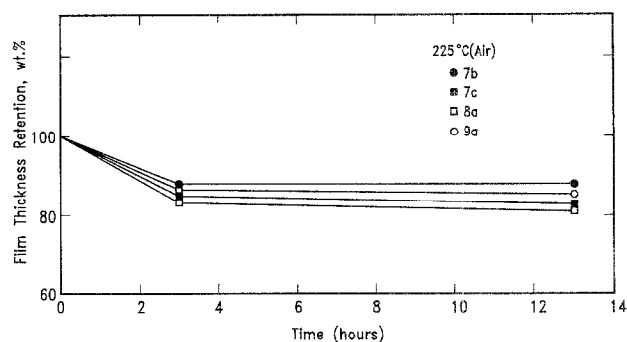
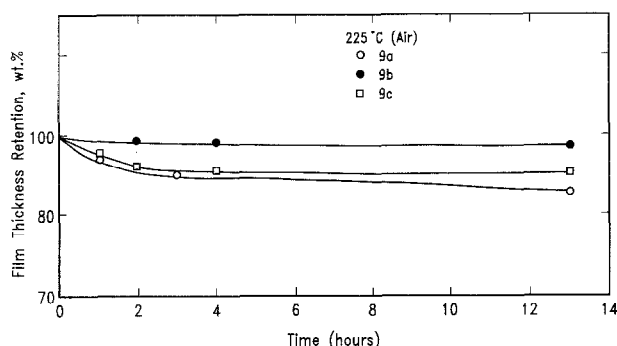


Figure 10 Film thickness as a function of time at temperature for copolymers 7b, 7c, 8a and 9a



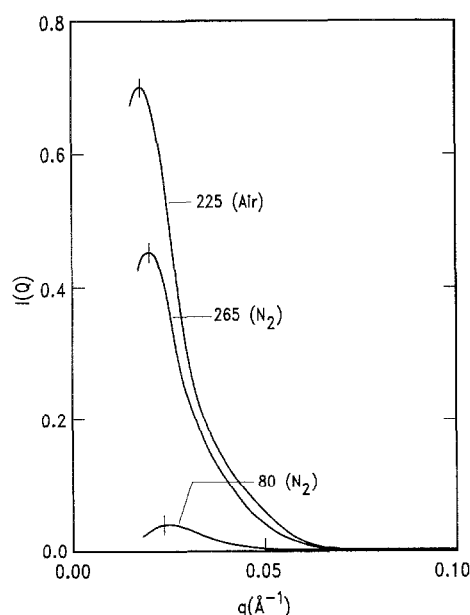
**Figure 11** Film thickness as a function of time at temperature for copolymer series 9

increase in the scattering observed since the change in the density is at most 10% and a greater than eightfold increase in the total scattering is observed. Consequently, the scattering suggests that some of the PO must have decomposed, thereby reducing the electron density of the PO phase. In addition to the loss of PO, the decomposition of PO occurs with the formation of gaseous monomers which would tend to increase the size of the PO microdomains and, consequently, increase the period as observed. Heating to 225°C in air results in a further increase of the scattering by  $\sim 50\%$  and a shift of the maximum to even smaller scattering vectors. The maximum is found at  $q = 0.018 \text{ \AA}^{-1}$  which corresponds to a period of  $\sim 350 \text{ \AA}$ . In keeping with the previous arguments, these data indicate a further decomposition of the PO, reducing the electron density of the PO microphase further and increasing the size of the PO microdomains.

The total integrated scattering or the invariant,  $Q$ , is given by

$$Q = K \int_0^\infty I(q) q^2 dq = \phi_1 \phi_2 (\rho_1 - \rho_2)^2$$

where  $K$  is a calibration constant and  $\phi_i$  is the volume fraction of phase  $i$  with electron density  $\rho_i$ . The



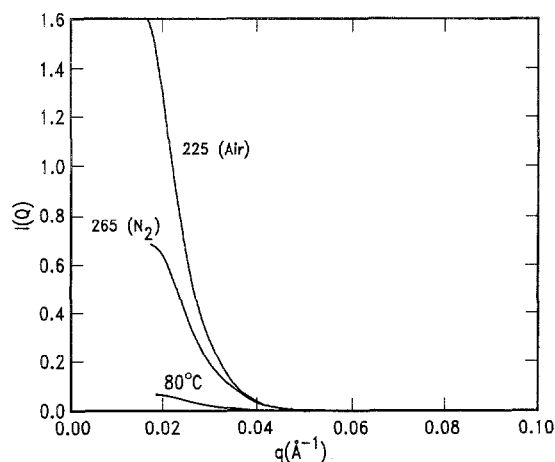
**Figure 12** SAXS profiles for copolymer 9b as a function of the scattering vector after heating to 80°C (N<sub>2</sub>), 225°C (air)

electron density of the imide phase is  $\sim 0.728 \text{ mole}^{-1} \text{ cm}^{-3}$  whereas that for the PO is  $\sim 0.122 \text{ mole}^{-1} \text{ cm}^{-3}$ . If the decomposition of the PO was quantitative and assuming that the volume fractions of the phases were unchanged with decomposition of the PO, then the ratio of the invariant of the foamed polymer,  $Q_F$ , to that of the initial material,  $Q_i$ , is simply

$$R = \frac{Q_F}{Q_i} = \frac{\rho_{\text{imide}}}{(\rho_{\text{imide}} - \rho_{\text{PO}})^2} = 35$$

This ratio sets a minimum value since a change in the size of the PO domain is observed which would increase the product of volume fractions and, consequently, increase  $R$ . From the data both  $Q_i$  and  $Q_F$  were determined and  $R$  was found to be 13.9. This is only 40% of the ideal value and suggests that partial collapse of the void structure has occurred. However, care must be exerted in the interpretation of this result since, as indicated, the scattering measurements indicate that some of the PO had decomposed during the heating to 265°C under N<sub>2</sub>. Consequently,  $Q_i$  will be larger than the ideal value, forcing the ratio to be low. In addition, a low value of  $R$  cannot be viewed as surprising since the energy required to support very small pores will be quite large and one would expect that the average size of the PO or microvoid domains would increase by removal of the smaller domains by a collapse of the foam. Nonetheless, from  $Q_F$  an estimated  $9 \pm 3\%$  of the material comprises microvoids with a size of  $\sim 30\text{--}60 \text{ \AA}$  based on the position of the scattering maximum. This value is comparable to the initial incorporation of PO in the copolymer, these data indicating that a nanofoam structure has been produced.

Experiments were also performed on a multiblock copolymer, 7d. The scattering data as a function of  $q$  are shown in Figure 13 for the different thermal treatments. For the unimodified polymer, a weak, monotonically decreasing profile is seen. For this multiblock copolymer, the morphology of the triblock appears to be much less ordered, as indicated by the absence of a scattering maximum. Nearly a tenfold increase in the scattering is seen by heating the material to 265°C under N<sub>2</sub>. Again, solvent loss and imidization account for some of the increase in intensity, but some decomposition of the PO,



**Figure 13** SAXS profiles for copolymer 7d as a function of the scattering vector after heating to 80°C (N<sub>2</sub>), 265°C (N<sub>2</sub>) and foaming at 225°C (air)

however small, must have occurred to account for the substantial increase in the scattering. Heating to 225°C in air causes a further increase in the scattering which can be attributed to the decomposition of PO forming microvoids in the polymer matrix. However, comparing the invariants of the foamed copolymer with that of the copolymer heated to 265°C under N<sub>2</sub>, yields  $R = 3.5$ . This is only 10% of the ideal value and strongly suggests that substantial collapse of the voids has occurred. Based on  $Q_F$ ,  $5 \pm 3\%$  of the film comprises voids, which is much less than the PO charged in the copolymer. Consequently, the spatially more organized structure achieved with the triblock copolymer appears to give a more stable foam structure.

## SUMMARY

A new approach to low dielectric, high temperature polymers has been demonstrated based on the generation of a foam with pore dimensions on the scale of tens of nanometres. These foams were prepared from microphase-separated block copolymers where the dispersed phase comprised a thermally labile material. Upon heating, the thermally unstable block decomposed, leaving pores of a size and shape dictated by the copolymer morphology. Several high temperature coblocks were investigated including rigid polyimides (PMDA/PDA and BPDA/PDA), semi-rigid (PMDA/ODA) and flexible polyimides (imide-phenylquinoxaline copolymers). Two types of thermally decomposable block were studied, poly(propylene oxide) and poly(methyl methacrylate). Both of these materials decomposed significantly below the  $T_g$  of the polyimide block. The copolymer synthesis detailed the use of the poly(amic alkyl ester) as a soluble precursor to the polyimide block, since this scheme can be applied to rigid polyimides and allows for isolation and characterization prior to imidization. Two synthetic schemes were investigated for the polyimide block copolymers, a monomer(s)-oligomer and an oligomer-oligomer approach, yielding triblock and multiblock architectures, respectively. The propylene oxide and methyl methacrylate compositions were deliberately maintained low to produce discrete phases of the labile polymer in the high temperature polymer matrix. Microphase-separated morphologies were observed for each of the copolymers, irrespective of block type or composition, by dynamic mechanical and SAXS measurements. The processing conditions required to effect imidization and subsequent thermolysis of the labile block were established by i.r., t.g.a. and t.g.a./m.s. measurements. Upon thermal degradation of the propylene oxide or methyl methacrylate in copolymers derived from rigid or semi-rigid polyimides, collapse of the foam structure was observed well below the nominal  $T_g$  of the polyimide block. The foam collapse was believed to

result from the strong orientation of the polymer chains normal to the surface producing anisotropic mechanical properties (i.e. a low modulus in the film thickness direction normal to the surface). The semi-rigid polyimide copolymer derived from PMDA/ODA with propylene oxide was modified with various compositions of a flexible phenylquinoxaline-containing diamine. Phenylquinoxaline composition of 50 wt% or greater yielded amorphous isotropic materials. Upon decomposition of the thermally labile propylene oxide coblock, stable foams were obtained only within those copolymers with high phenylquinoxaline compositions.

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