Polyimide Nanofoams from Aliphatic Polyester-Based Copolymers

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High-temperature polymeric foams were prepared using compositionally asymmetric microphase-separated block copolymers where the major component is thermally stable and the minor component is thermally labile. Upon thermal treatment, the dispersed phase undergoes thermolysis leaving pores the size and shape of which are dictated by the initial copolymer morphology. The driving force behind the survey of aliphatic polyesters as possible labile blocks stems from their quantitative degradation into low-boiling, polar degradation products. Poly(lactones), as a general class of materials, degrade by a backbiting process producing, primarily, monomer and cyclic oligomers. A ring-opening synthetic route to poly(lactones) affords oligomers of predictable molecular weight, narrow molecular weight distribution, and controlled end-group functionality. Block copolymers were prepared using monofunctional caprolactone and valerolactone oligomers and a high-T_g polyimide. Microphase separation was observed in all cases, and the lactone blocks did not crystallize. Thermal decomposition of the caprolactone block was accomplished by heating the copolymer to 370 °C for 5 h. Significant density reductions were found with pores sizes in the 60−70 Å range.

Introduction

Organic polymers have found use in the microelectronics industry primarily either as structural components or in other low-performance systems such as cards, cables, or circuit boards.[1] The use of polymers as insulating layers in semiconductor devices or in multichip modules has been less pervasive, with inorganic oxides being the dominant materials. Organic polymers are being examined for potential use in future applications due to their intrinsically low dielectric constants. To that end, a number of polymeric materials have been studied as low dielectric insulators, with polyimides looking the most promising due to their high-temperature stability.[2−15]

A means of further reducing the dielectric constant of polyimides is by the generation of a foam where the size of the pores are submicron.[15,16] The reduction in the dielectric constant is simply achieved by replacing polymer with air, which has a dielectric constant of 1. However, the size of the voids must be much smaller than either the film thickness and any microelectronic features for the gain in the dielectric constant to be realized. Suitable foams can be prepared from block copolymers comprised of a thermally stable and thermally labile material, where the latter constitutes the dispersed phase.[16,17] Using a specified heat treatment, the thermally unstable block decomposes, leaving a

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porous structure of a size that is commensurate with the copolymer morphology, i.e., on the tens of nanometer size scale. Hence, such foams are called nanofoams. Nanofoams have been made using poly(propylene oxide) as the labile coblock with either a polyimide or a poly(phenylquinoxaline) as the matrix polymer.[16] The degradation of the propylene oxide component occurs by 250−300 °C in an aerobic atmosphere via a thermooxidative degradative mechanism.

It was of interest to see if a non-oxidative route toward the generation of nanofoams could be developed, since processing steps that require high-temperature oxidative conditions may be unacceptable in microelectronic device fabrication. To this end, nanofoams derived from monodispersed oligomers of poly(ϵ-caprolactone) (PCL), poly(valerolactone) (PVL), and PCL/PVL copolymers of controlled molecular weight and end group functionality were studied. Such aliphatic polyesters degrade quantitatively in an inert atmosphere by unzipping.[19−22] The major thermal degradation products are cyclic monomers or a combination of monomers and oligomers. The decomposition temperatures of PCL and PVL are sufficiently high to allow films of block copolymers to be cast and cured to remove solvent and imidized, all with minimum decomposition of the labile block. In addition, the decomposition temperature is much lower than the glass transition temperature, T_g, of many polyimides. This should provide an ample temperature window in which the lactone can be degraded without causing a flow of the matrix.

Experimental Section

Materials. *N*-Methyl-2-pyrrolidone (NMP), pyridine, and acetic anhydride were purchased from Aldrich and used without further purification. Diethyl pyromellitate diacyl chloride was prepared according to a procedure described by Volksen et al.[8] The ϵ-caprolactone (Aldrich), denoted ϵ-CL, and δ-valerlactone (Aldrich), denoted δ-VL, were distilled under reduced pressure (10^{-2} Torr of Hg) from CaH_2. Aluminum triisopropoxide (Aldrich) was purified by distillation under reduced pressure and dissolved in dry toluene.

Monomer Synthesis. *Preparation of 1,1-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA).*[23,24] To a 1 L three-necked round-bottomed flask equipped with a stir bar, thermocouple, Ar inlet and Dean−Stark condenser was added 54.6 g (0.287 mol) p-toluene sulfonic acid monohydrate and 325 mL of freshly distilled aniline and the mixture refluxed to a constant head temperature (184 °C) with separation of water. The Dean−Stark trap was replaced by a regular reflux condenser, while the pot temperature was reduced to 130 °C under positive Ar pressure. At this point, 50.0 g (0.287 mol) of 2′,2′,2′-trifluoroacetophenone was added in one portion, and the mixture heated at 145 °C with stirring for 48 h. The reaction mixture was then cooled to 90 °C and 500 mL of 1 N NaOH added in one portion with vigorous stirring. After cooling to room temperature, 1 L of CH_2Cl_2 was added with stirring and the layers separated. The aqueous layer was extracted with 150 mL of CH_2Cl_2 and the combined organic layers washed sequentially with 4 × 250 mL of saturated $NaHCO_3$, 4 × 250 mL of water, and 200 mL of brine. The dark solution was dried over $MgSO_2$, evaporated to approximately 300 mL, and added slowly to 4 L of stirring hexane. The hexane was decanted and the resulting dark semisolid dissolved in about 500 mL of CH_2Cl_2, which was then evaporated to approximately 300 mL and added slowly to 4 L of stirring hexane. The suspension was filtered to yield 78 g of a purple-red solid which was, in turn, dissolved in 2 L of $(Et)_2O$ and treated with 500 g of silica gel (60−230 mesh) and 100 g of Norit and stirred overnight. The mixture was filtered over Celite, the filtrate concentrated to approximately 125 mL, and the product slowly precipitated with stirring into 2 L of hexane. This procedure (resuspension of the original silica gel/Norit, stirring for 1 h, filtration, and precipitation) was repeated a total of four times resulting in a total of 68 g of a beige powder. This material was dissolved in 1 L of $(Et)_2O$ and treated with 50 g of silica gel and 5 g of Norit. Processed as described above with precipitation into 1 L of hexane ultimately resulted in 63 g of white powder, mp 215−218 °C. Yield 64%. ^1H NMR δ ($CDCl_3$) (ppm) 7.26 (m, 3H, phenyl), 7.2 (m, 2H, phenyl), 6.92 (d, 4H, aniline), 6.61 (d, 4H, aniline), 3.70 (s, 4H, NH_2).

Preparation of 1,1-Bis(4-aminophenyl)-1-(4-ethynyl phenyl)-2,2,2-trifluoroethane 4-Bromotrifluoroacetophenone.[25] A 500 mL round-bottomed flask equipped with a thermometer adapter, a dropping funnel charged with *n*-butyllithium (*n*-BuLi, 55 mL of 1.6 M in hexane, 88 mmol, Aldrich), a second dropping funnel charged with ethyl trifluoroacetate (13.47 g, 95 mmol, Aldrich) nitrogen inlet and magnetic stirrer was charged with 1,4-dibromobenzene (20.04 g, 85.00 mmol, Aldrich) and 150 mL of anhydrous ether (EM Science). After the 1,4-dibromobenzene dissolved, the solution was cooled to −78 °C in a dry ice/acetone bath. The *n*-BuLi was added dropwise over a period of 30 min, and the reaction was allowed to stir at −78 °C before the ethyl trifluoroacetate was added dropwise. The mixture was allowed to warm to room temperature overnight. The mixture was then cooled to −25 °C, and 40 mL of saturated aqueous ammonium chloride (EM Science) was added dropwise, followed by 40 mL of 1 N hydrochloric acid. The mixture was allowed to warm to room temperature. The reaction mixture was transferred to a separatory funnel and the aqueous layer was removed. The ether layer was washed with 100 mL of saturated aqueous sodium bicarbonate ($NaHCO_3$), dried over anhydrous magnesium sulfate ($MgSO_4$), and filtered, and the solvent evaporated. The resulting oil was vacuum distilled yielding a water white liquid which distilled at 45 °C (0.09 Torr). This liquid solidified to yield 19.21 g of 4-bromotrifluoroacetophenone, a white solid (89% yield). The ^1H NMR in deuterated chloroform shows only an AB quartet centered at 7.83 ppm.

1,1-Bis(4-aminophenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane. 4-Bromotrifluoroacetophenone (19.14 g, 75.65 mmol), aniline hydrochloride (13.18 g, 101.7 mmol), and aniline (53.3 mL, 62.87 mmol) were placed in a 250 mL round-bottomed flask and refluxed (120−133 °C) under nitrogen for 24 h. After this cooled to room temperature, $NaHCO_3$ (17.2 g) and water were added, and the aniline and the aniline/water azeotrope were distilled off under nitrogen until no further aniline was observed in the distillate. After cooling again, the water was decanted off, and the purple solid was dissolved in chloroform (200 mL). The solution was dried over anhydrous $MgSO_4$ and then filtered through silica gel using acetone and methylene chloride to wash the silica gel. The solvent was evaporated to yield a purple oil that was dried further at 60 °C in a vacuum oven to yield 31.5 g of purple semisolid (99% yield). The ^1H NMR in deuterated chloroform shows two AB quartets centered at 7.25 ppm (4H) and 6.75 ppm (8H) and a broad singlet at 3.72 ppm (4H).

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Table 1. Characteristics of Aliphatic Polyester Oligomers

sample entry	polyester type	δ	M_n (g/mol) hydroxyl end-capped[a]	M_n (g/mol) amino end-capped[b]	T_g (°C)	T_d (°C)	TGA T_d (°C)
1a	poly(caprolactone)	1.12	10 000	17 000	−60	66	
1b	poly(caprolactone)	1.12	12 000	18 000	−58	66	
1c	poly(valerolactone)	1.12	12 000	17 000	−60	69	
1d	copoly(valerolactone−caprolactone), FVL = 0.5	1.13	13 000	17 000	−57	28	
1e	copoly(valerolactone−caprolactone), FVL = 0.65	1.1	14 000		−61	27	
1f	copoly(valerolactone−caprolactone), FVL = 0.8	1.1	14 000		−58	40	

[a] By GPC using polystyrene standards. [b] By titration on the assumption of one amino end per chain. [c] Thermal decomposition temperature measured at the maximum of the TGA curve.

1,1-Bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane. 1,1-Bis(4-aminophenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane (31.5 g, 74.77 mmol) was dissolved in a mixture of triethylamine (125 mL, distilled) and *N*-methylpyrrolidinone (NMP) under an atmosphere of argon. Copper(I) iodide (0.33 g, 1.73 mmol, Aldrich), tetrakis(triphenylphosphine)palladium-(0) (2.08 g, 1.80 mmol, Aldrich) and trimethylsilylacetylene (14.56 g, 148.24 mmol, Farachan) were then added. The flask was sealed with a septum and stirred with a magnetic stirrer and heated in a 90 °C oil bath for 24 h. After cooling to room temperature, the solvents were removed on a rotary evaporator. The solids were triturated with ether and filtered off. The ether solution was washed with water (3 × 250 mL), dried over $MgSO_4$, and filtered, and the solvent evaporated to yield a brown solid. Ethanol (250 mL) and 1 N sodium hydroxide (50 mL) were added, and the mixture was stirred at room temperature overnight. The mixture was transferred to a separatory funnel, ether was added (500 mL), and the mixture was washed twice with water. After drying over $MgSO_4$, the mixture was filtered, the solvent removed, and the resulting solid dried at 60 °C in a vacuum oven to yield 16.8 g of a light brown foamy solid (60% yield). ^1H NMR in deuterated chloroform shows two AB quartets at δ 7.35 (4H) and 6.8 (8H), a broad singlet at 3.76 (4H), and a broad singlet at 1.67 (1H).

Polymerizations. *Synthesis of Hydroxyl-Terminated Poly-ϵ-caprolactone and Poly-δ-valerolactone Oligomers.* ϵ-CL and δ-VL were polymerized in toluene at 0 °C using $Al(OPr)_3$ as the initiator. Polymerization was carried out under dry nitrogen, in a previously flamed-treated glass reactor equipped with rubber septums. Solvent, monomer, and initiator were added successively through rubber septums using either stainless steel cannulas or syringes. The polymerization was terminated by adding an excess (with respect to the initiator) of 0.1 N HCl solution. Polymers were recovered by precipitation in heptane and finally dried to constant weight under reduced pressure at 25 °C.

Synthesis of Aminophenyl-Terminated Poly-ϵ-caprolactone and Poly-δ-valerolactone Oligomers. A 250 mL three-necked round-bottomed flask equipped with a stir bar, thermocouple, and Ar inlet was charged with 19.5 g (1.95 mmol) of 10K poly-(ϵ-caprolactone), 100 mL of anhydrous THF, and 0.232 g (2.925 mmol) of pyridine. The mixture was cooled to 5 °C under Ar, and 0.59 g (2.925 mmol) of 4-nitrophenylchloroformate dissolved in 10 mL of THF was added dropwise. The temperature was allowed to reach ambient and the mixture stirred for 48 h. The resulting suspension was filtered, and the filtrate was evaporated. The residue was dissolved in a minimum amount of CH_2Cl_2 and precipitated into 500 mL of stirred methanol. The solid was filtered, washed with methanol, and air-dried. The resulting white powder (17.5 g) was taken up in 100 mL of anhydrous THF and charged into a Parr hydrogenation bottle containing 750 mg of $Pd(OH)_2$ (Pearlman's catalyst) and hydrogenated at 40 psi for 48 h. The reaction mixture was filtered twice through a Celite pad, evaporated, redissolved in 300 mL of CH_2C1_2, and washed first with 2 × 100 mL of saturated $NaHCO_3$ followed by 2 × 100 mL of water. The volume of the organic layer was reduced to ≈65 mL and added slowly to 500 mL of methanol with vigorous stirring. The resulting solid was collected and dried for 48 h at 40 °C under reduced pressure to yield 13.5 g of the desired product as a white powder. Titration of the amine end group yielded a molecular weight of 10 500 g/mol.

Alternative Synthesis of Nitrophenyl-Terminated Polycaprolactone. Weighing and measurement of reagents were performed in a moisture-free drybox. To a 100 mL three-necked round-bottomed flask, fitted with an overhead stirrer, was added 0.65 mL (1.25 mmol) of a 1.9 M solution of $Al(Et)_3$ in toluene and 6.5 mL of tetrachloroethane (TCE). To this stirred mixture was slowly added a solution of β-phenethyl alcohol, 0.42 g (2.5 mmoI), in TCE. When the addition of the coinitiator was complete, ϵ-caprolactone (10.0 g, 87.6 mmol) and 10 mL of TCE were added. The resulting clear yellow mixture was stirred and heated to 85 °C for 3 h. A dramatic increase in viscosity was noted. The polymer was first precipitated into methanol, dissolved in CH_2Cl_2, and then reprecipitated several times, giving 7.8 g of a white powder (77% yield), **1b**.

Alternative Synthesis of Aminophenyl-Terminated Polycaprolactone. A Parr hydrogenation bottle was charged with 7.6 g of **I** (**1b**), 0.7 g of 10% Pd/C, and 50 mL of dry THF. The mixture was hydrogenated at 40 psi (H_2) for 24 h. The reaction mixture was centrifuged and decanted from the solids. The solution was then filtered (0.5 μm), the solvent evaporated, and the residue redissolved in CH_2Cl_2. The polymer was reprecipitated into methanol/water (1:1), filtered, and dried to constant weight in a vacuum oven, yielding 7.2 g of an off-white polymer.

Block Copolymer Synthesis. The amic ester−α-caprolactone triblock copolymers were prepared by the co-reaction of the amino-terminated caprolactone oligomers with 3FDA, 3FET, and PMDA diethyl ester diacyl chloride in NMP in the presence of *N*-methylmorpholine. A detailed procedure for the preparation of an amic ester/caprolactone copolymer, with a caprolactone content of 25 wt %, using a caprolactone oligomer of 10 000 g/mol molecular weight is provided (copolymer 3, Table 1). A three-necked flask equipped with an overhead stirrer and addition funnel was charged with caprolactone oligomer (1.0000 g, 0.000 095 2 mol), 3FDA (0.913 27 g, 0.000 266 7 mol), and 3FET (0.6515 g, 0.001 778 mol), and carefully rinsed in with 15 mL of NMP. The solution was then cooled to −5 °C, and pyridine (0.71 g, 0.0089 mol) was added to the solution. The PMDA diethyl ester diacyl chloride (0.727 g, 2.095 mmol) was dissolved in ca. 25 mL of methylene chloride and added in increments over a 2 h period so as to slowly approach the stoichiometric end point. The polymerization was allowed to proceed overnight. The polymer was precipitated into methanol/water, rinsed first 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 or cyclohexanone at a concentration of 9−15% solids. Coatings of 25 μm in thickness were obtained by spin coating at 2000 rpm^{-1} on 2.54 cm diameter Si wafers or by doctor blading. The removal of the solvent and imidization, if required for the caprolactone-based copolymers, were accomplished by heating the polymer films to 300 °C at 5 °C min^{-1} and maintaining them at 300 °C for 1.0 h in a nitrogen atmosphere. The films were then heated to 370 °C over a 6 h period and held for 3 h to decompose the caprolactone block. The valerolactone-based copolymers were imidized at 240 °C for 6 h followed by a slow temperature ramp (6 h), to 310 °C, and held at this temperature to decompose the valerolactone coblock. The copolymers containing the (valerolactone-*co*-caprolactone) labile block were heated to 240 °C to effect imidization and solvent removal, followed by a slow ramp (6 h) to 340 °C (3 h) to effect the decomposition of the labile coblock.

Characterization. Glass transition temperatures, taken as the midpoint of the change in the slope of the baseline, were measured on a DuPont 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 assess the dynamic mechanical properties. Isothermal and variable temperature (5 °C min^{-1} heating rate) thermal gravimetric analysis (TGA) measurements were performed on a Perkin-Elmer Model TGA-7 instrument 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.

Small-angle X-ray scattering studies were performed on Beamline I-4 at the Stanford Synchrotron Radiation Laboratory. Details of the beamline optics are described elsewhere. In these experiments, X-rays of wavelength 1.29 Å were passed through a Mettler FP85 hot stage where the sample was mounted. X-ray scattering profiles were obtained either as the sample temperature was ramped at 10 °C min^{-1} or at a specific temperature as a function of time. Experiments were performed under a steady flow of N_2 or in air. Samples of ~0.25 mm in thickness were prepared by placing stacks of thinner films in a sample cell with Kapton windows. Standard procedures were used to correct the scattering profiles for parasitic scattering, electronic noise and sample absorption. Scattering profiles will be presented as a function of the scattering vector, $\mathbf{Q}$, which is given by $(4\pi/\lambda)\sin\theta$, where λ is the wavelength and 2θ is the scattering angle.

Results and Discussion

The successful implementation of the block copolymer approach to the high-temperature polymer nanofoam requires the judicious combination of a high-temperature polymer with the thermally labile coblock. The material requirements for the high-temperature polymer matrix are stringent and include thermal stability, chemical stability, and solubility in common organic solvents to allow copolymerization with the thermally labile coblock. Polyimides were selected as the matrix high-temperature polymer, because of their high T_g, thermal stability, and solubility, at least, in the polyimide precursor form. This article deals with polyimide nanofoams derived from pyromellitic dianhydride (PMDA) with 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA).[23,24,26] This polyimide has a T_g of 440 °C, thermal decomposition temperature of 500 °C, and a low dielectric constant (2.8) and is soluble in the fully imidized form. The 3FDA/PMDA polyimide is prepared from the condensation of PMDA with 3FDA in NMP to form a soluble poly(amic acid) solution. Imidization can be accomplished thermally or chemically (acetic anhydride−pyridine) by dehydration to yield the polyimide. Alternatively, the poly(amic alkyl ester) precursor of the polyimide can be employed as a versatile intermediate. Pyromellitic dianhydride reacts with ethanol to yield a mixture of diesters (i.e., para and meta isomers). The isomers may be separated by fractional recrystallization and converted to the respective acid chlorides.[22] Reaction with 3FDA affords the poly(amic acid ethyl ester) which is hydrolytically stable and may be isolated and characterized prior to imidization. Furthermore, by using the meta isomer the solubility is significantly enhanced in a wide variety of solvents. The onset of thermal imidization at ~250 °C is significantly higher than for the poly(amic acid) analogue, which permits the microphase separation of the copolymer to progress further than the para isomer prior to vitrification or imidization. Another advantage of using the meta isomer of the poly(amic alkyl ester) is the observed T_g or softening at ~120 °C prior to imidization (~250 °C).[27,28] Thus, other transformations, e.g., cross-linking, are possible prior to the onset of imidization and well below the decomposition temperature of the lactone coblock. Cross-linking the matrix polyimide can in principle improve the stability of the resulting nanofoam by providing "solvent resistance" to the degradation products upon thermolysis of the labile coblock.

The "softening" or T_g observed with the poly(amic acid ethyl ester) precursor allows sufficient mobility for the cross-linking reaction to occur at a temperature well below the T_g of the polyimide. The ethynyl functionality has been shown to cross-link thermally in the temperature regime of 180−300 °C, and the resulting networks possess the requisite thermal stability.[29] Poly(amic ethyl ester)s have been prepared with several ethynyl compositions, and swelling measurements of the networks showed substantially less solvent uptake with increasing ethynyl content than the corresponding non-cross-linked material.[27] The minimized interaction of the degradation products with the cross-linked polyimide is anticipated to result in nanofoams with controlled pore size and minimal interconnectivity. In this study, copolymers were prepared in either the fully imidized form via chemical imidization, from the poly(amic ethyl ester) and the poly(amic ethyl ester) with additional ethynyl functionality by thermal imidization.

One of the most important requirements of the thermally labile blocks is the availability of well-defined oligomers having controlled molecular weight, molecular weight distribution, and end group functionality amenable to copolymerization with the polyimide. This block must also decompose quantitatively into unreactive species that can diffuse easily through a glassy polyimide matrix. The temperature at which thermal decomposition of the labile block occurs is critical. It must be sufficiently high to permit standard film preparation and solvent removal but much less than the T_g of the polyimide block to avoid foam collapse. Aliphatic polyesters, in particular polylactones, are ideally suited as the thermally labile component, since oligomers of controlled molecular weight, molecular weight distribution and end-group functionality can be prepared, and moreover they thermally degrade via a backbiting or unzipping process in an inert atmosphere,

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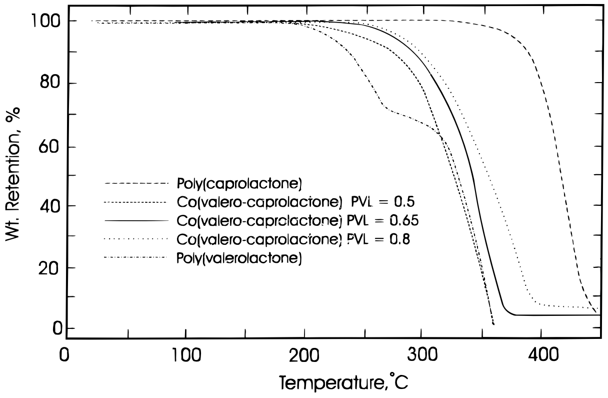

Figure 1. Thermogravimetric analysis of polylactones.

to cyclic monomers or oligomers, depending on the structure of the polylactone.[18−21] Thermogravimetric analyses of polycaprolactone, polyvalerolactone, and caprolactone−valerolactone copolymers are shown in Figure 1. In each case, quantitative degradation is found. The onset degradation temperature of the polycaprolactone is higher than that of either polyvalerolactone or the copolymers. Furthermore, the temperature range over which degradation occurs is significantly broader for the polycaprolactone than polyvalerolactone, which suggests an unzipping mechanism accompanied by transesterification reactions.

Several synthetic approaches were examined for the preparation of poly(lactone) oligomers with a single aryl−amine functionality, which is amenable toward polyimide copolymerization. Aluminum isopropoxide has proven to be a very effective initiator for the polymerization of caprolactone and valerolactone in toluene at 0 °C.[30] The ring-opening proceeds through a "coordination−insertion" mechanism that involves the insertion of the monomer into the "Al−O" bond of the initiator. The acyl−oxygen bond of the cyclic monomer is cleaved in a way that maintains the growing chain attached to aluminum through an alkoxide bond. Hydrolysis of the active aluminum alkoxide bond leads to the formation of a hydroxyl end group. The second chain extremity is terminated with an ester carrying the isopropoxy group of the initiator (Scheme 1). The monofunctional hydroxy-terminated oligomers were reacted with 4-nitrophenyl chloroformate to form a nitrophenyl carbonate end group.[15] Hydrogenation over Pearlman's catalyst gave the corresponding amine in a manner similar to that reported previously.[15]

Jérôme et al.[31−35] and Kricheldorf et al.[36,37] have reported the synthesis of end-functional aliphatic polyesters by ring-opening polymerization (ROP) of ϵ-caprolactone (ϵ-CL) and lactides (LA). Polymerization initiated with any of the functional aluminum alkoxides of the general structure $Et_{(3-p)}Al(OR)$, where $p = 1$ and 3, proceeds via a living "coordination insertion" mechanism, under suitable conditions (temperature, concentration, and solvent), with the formation of α-functional chains of a predictable molecular weight. The use of nitrophenethyl alcohol as the co-initiator allows direct introduction of a single nitrophenyl end functionality (Scheme 1). However, when using nitrophenyl ethyl alcohol as the co-initiator, the alcohol/$Al(Et)_3$ ratio must be 2:1 in order to achieve the desired molecular weight control. The nitro group of the polymer chains could be reduced by standard analytic methods (Pd/C and H_2) to yield the desired amino-terminated polymers.

The characteristics of the hydroxyl end-capped oligomers (**1a** and **1c**−**f**) synthesized using aluminum isopropoxide are shown in Table 1 together with the oligomer prepared from the reactive functionalized initiator (**1b**). The molecular weights of the oligomers were determined by GPC and, for the amino end-capped polymers, by end-group titration methods. Upon conversion of the hydroxyl end group to the amino functionality, the apparent molecular weight of each of the oligomers increased. This is the result of fractionation of low molecular weight chains during the repeated polymer precipitation and isolation steps, leading to an enrichment of higher molecular weight oligomer. However, comparison of molecular weights of the crude amino-terminated oligomers, determined by GPC and titration of the amino group confirmed the introduction of a single amine end group. Furthermore, no evidence of exchange reactions were observed by GPC measurements during the reaction of the amine and polyester. As expected, the molecular weight distributions were narrow. The thermal characteristics of the oligomers are also shown in Table 1. In the case of the copolymers, a depression in the melting point can be observed, which is consistent with a random distribution of comonomers.

Two synthetic approaches were examined for the preparation of the block copolymers. In the first approach, the 3FDA/PMDA based copolymers were prepared via the poly(amic acid) precursor route followed by chemical imidization (Scheme 2). The synthesis involved the addition of solid PMDA to a solution of the polylactone oligomer and 3FDA in NMP to yield the corresponding poly(amic acids) with a solids content of ~10% (w/v). Imidization of the poly(amic acid) solutions was accomplished chemically with excess acetic anhydride and pyridine in 6−8 h at 100 °C.

The copolymers were also prepared via the poly(amic ethyl ester) route. This synthesis involved the incremental addition of PMDA diethyl ester diacyl chloride in methylene chloride to a solution of the oligomer and 3FDA. In cases where crosslinking was desired, 3FDA together with 3FET in NMP containing pyridine as the acid acceptor were used (Scheme 3). In our experiments, 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 copolymers were isolated by precipitation from a methanol/water mixture, rinsed with water to remove remaining salts, then rinsed with methanol and toluene and dried at 50 °C (24 h) under vacuum. The use of

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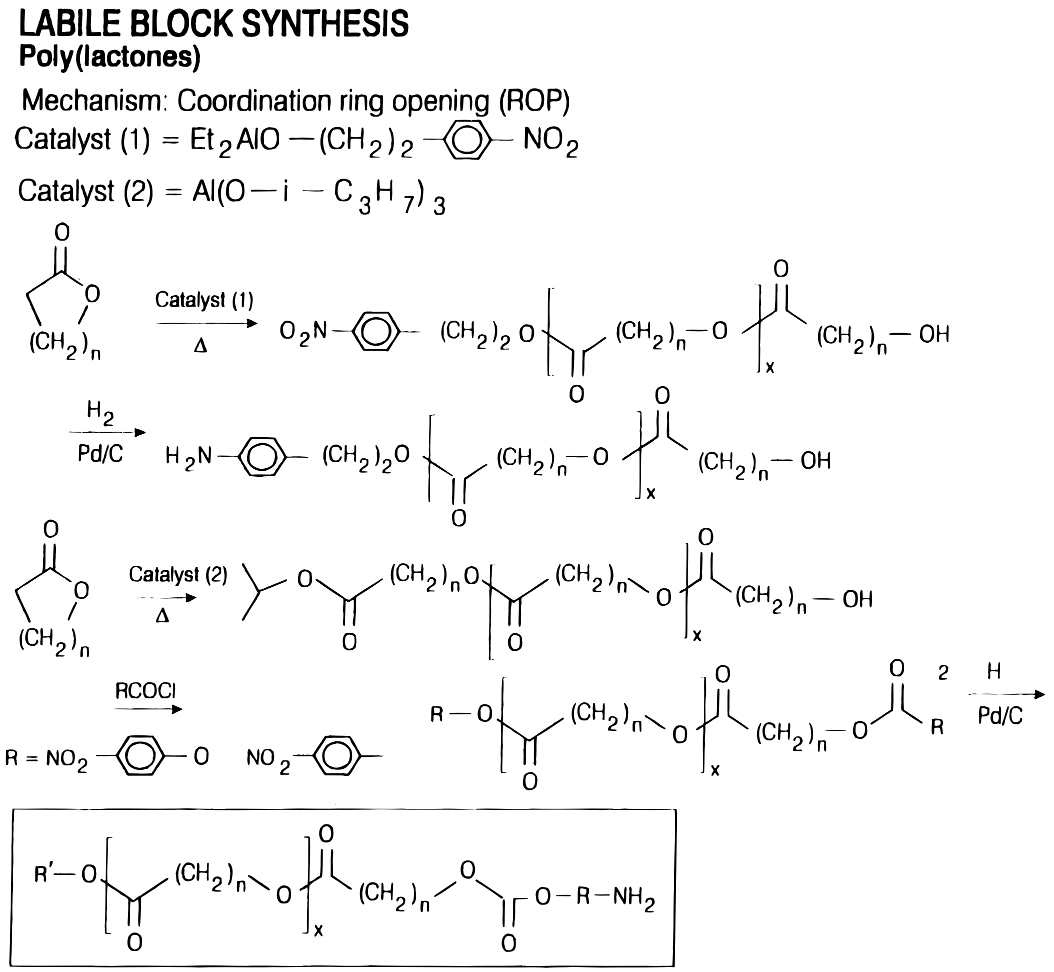
Scheme 1



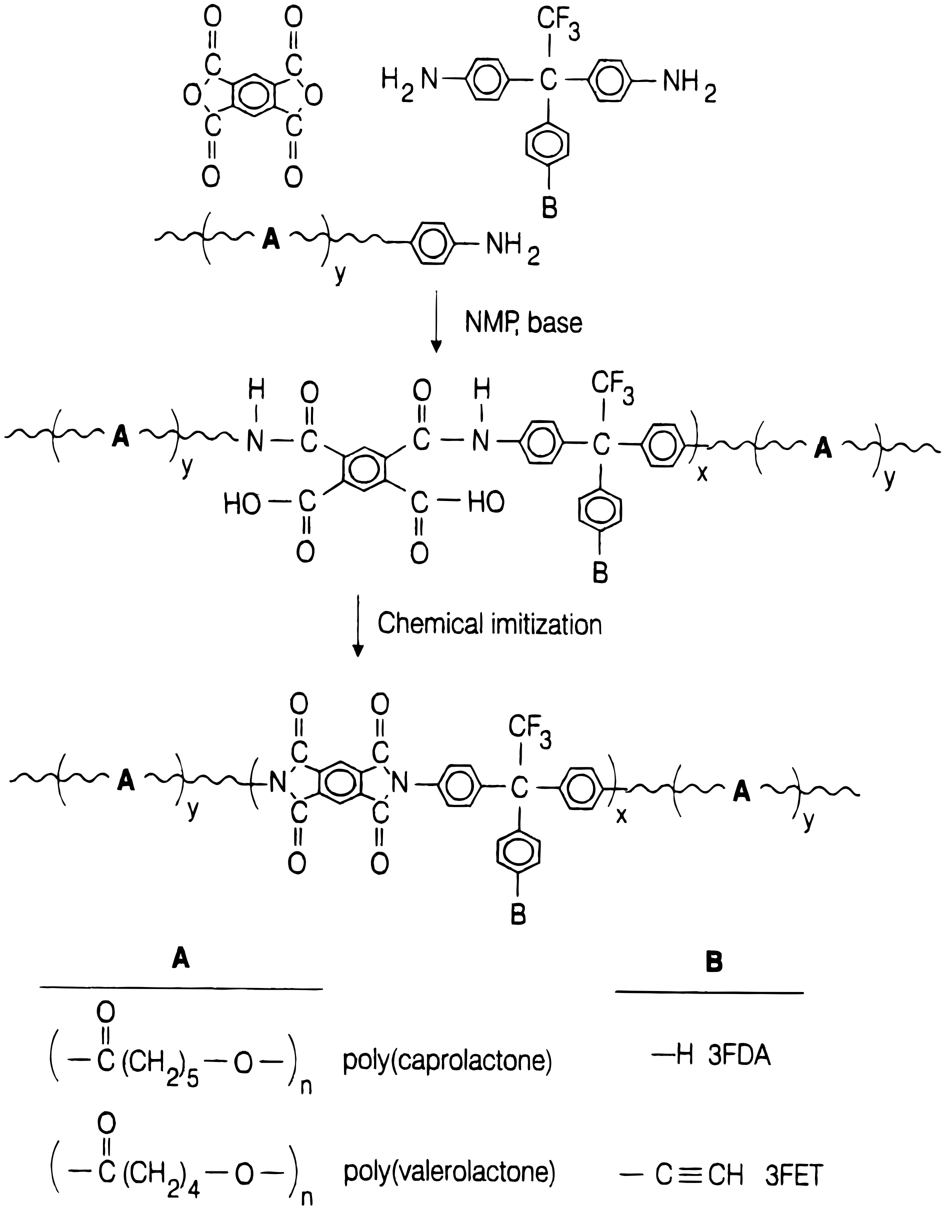
the monofunctional amino terminated oligomers in the polyimide syntheses described above affords an ABA triblock copolymer architecture, where the thermally labile component comprised the terminal A blocks.

A number of imide-lactone copolymers were prepared in both the fully imidized form (copolymers **3a**,**b**, **4a**,**b**, and **5a**) and in the poly(amic alkyl ester) precursor form (copolymers **2a**–**c**, **3c**–**i**, and **4c**–**e**). The characteristics of the copolymers are shown in Table 2. It is important to note that there are two isomeric forms of PMDA diethyl ester that can be separated and isolated at the monomer stage and subsequently polymerized (Scheme 3). Copolymers from each individual isomer were prepared as denoted in Table 3. In addition, several copolymers prepared contained 3FET as a codiamine introduced at 40 mol % to provide a means of crosslinking the polyimide matrix. For this study, three polylactone coblocks were investigated including valerolactone, valerolactone–caprolactone copolymers, and caprolactones with compositions of 15 and 25 wt % and, in one instance, 35 wt %. The labile coblock compositions in the copolymer were maintained at a low level in order to produce discrete domains of the lactone embedded in the polyimide matrix. The morphology of the copolymers with a higher lactone volume fraction would, in principle, result in cylindrical or more interconnected structures. The composition of lactone incorporation into the copolymer was determined gravimetrically from the weight retention after decomposition of the thermally labile block (Table 2). For most copolymers, the composition of lactone incorporated agreed closely with that charged.

A key component in generating a nanofoam is the ability to process the block copolymer by conventional methods in order to remove solvent and effect imidization. The polycaprolactone decomposition temperature is high enough to allow removal of solvents prior to void formation. The polycaprolactone-based block copolymers were dissolved in either NMP or cyclohexanone, cast, and cured to 300 °C for 1.5 h to effect imidization and to remove the solvent in the case of the poly(amic alkyl ester) precursor. ^{1}H NMR and IR measurements showed no loss in caprolactone content with quantitative imidization. Furthermore, the 300 °C cure is sufficient to effect the cross-linking of the pendant ethynyl functionalities.[30] For the valerolactone-based copolymers, the processing temperature was restricted by the temperature of the polyvalerolactone decomposition. Here the onset of decomposition occurs at ~265 °C, limiting the extent of imidization of the poly(amic alkyl ester). This, in turn, limited the attainment of a high T_g of the resulting polyimide matrix and consequently narrowed the processing window (i.e., temperature difference between the apparent polyimide T_g and the decomposition temperature).

The dynamic mechanical spectra for the copolymers are shown in Figures 2–4. In the case of the caprolactone-based copolymers (Figure 2), two transitions were

Scheme 2



observed, indicative of microphase separated morphologies. The transition occurring near −50 °C is somewhat higher than the known T_g of polycaprolactone and is broad and weak. These features suggest that there is some intermixing and the phase boundaries are diffuse. No evidence of crystallization of the caprolactone block was observed either by the dynamic mechanical or X-ray diffraction measurements. The transition of the imide block is significantly lower than that of the parent homopolymer. Since the imidization is quantitative, this suggests some incorporation of caprolactone in the imide domain. Figure 6 shows the variable-temperature thermograms of the poly(caprolactone) oligomer **1b** and copolymer **3**. Clearly, the evolution of poly(caprolactone) degradation products for the copolymer occurs at a significantly higher temperature than for the homopolymer, even though the degradation rates are comparable. This suggests that the long residence time of the degradation products of poly(caprolactone) in the polyimide matrix leads to plasticization of the matrix with a substantial reduction in the T_g. Crosslinking of the polyimide (Figure 2) appears to provide the requisite "solvent resistance" to minimize plasticization as evidenced by the retention of modulus.

Similar spectra are observed for the valerolactone- and valerolactone/caprolactone-based copolymers as shown in Figures 4 and 5, respectively. The transition associated with the valerolactone T_g is clearly seen at ∼−50 °C (Figure 3), and the transition is also observed with the introduction of caprolactone (Figure 4). No evidence of crystallization was observed for the valerolactone derived copolymers. For these examples, the transition associated with the imide block is substantially lower than that of the parent polyimide (∼440 °C). The modulus drop associated with the imide transition in the films prepared from the poly(amic alkyl ester) precursor was significantly more pronounced than that observed for the copolymers that were chemically imidized. This results, most likely, from the incomplete imidization of the valerolactone-based copolymers. The copolymers that were chemically imidized or crosslinked showed modulus recovery upon evolution of the

Scheme 3

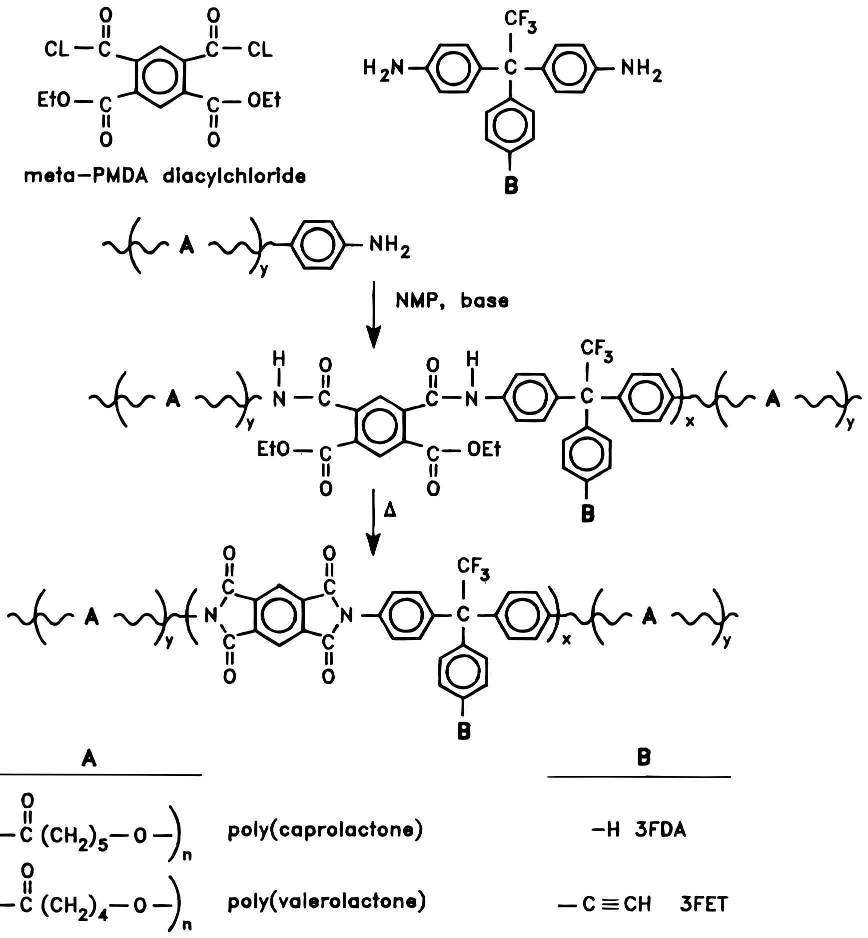


Table 2. Characteristics of Imide–Lactone Copolymers

sample entry	copolymer form	lactone coblock	copolymer composition, wt %	
			charge	TGA
2a	poly(amic alkyl ester) (meta isomer)	1a	15	14
2b	poly(amic alkyl ester) (meta isomer)	1a	25	25
2c	poly(amic alkyl ester) (ethynyl functional)	1a	25	26
3a	polyimide	1b	15	12
3b	polyimide	1b	25	21
3c	poly(amic alkyl ester) (para isomer)	1b	15	1S
3d	poly(amic alkyl ester) (para isomer)	1b	25	26
3e	poly(amic alkyl ester) (para isomer)	1b	35	38
3f	poly(amic alkyl ester) (meta isomer)	1b	15	16
3g	poly(amic alkyl ester) (meta isomer)	1b	25	23
3h	poly(amic alkyl ester) (meta isomer, ethynyl functional)	1b	15	15
3i	poly(amic alkyl ester) (meta isomer, ethynyl functional)	1b	35	23
4a	polyimide	1c	25	23
4b	polyimide (ethynyl functional)	1c	25	24
4c	poly(amic alkyl ester) (meta isomer)	1c	15	12
4d	poly(amic alkyl ester) (meta isomer)	1c	25	23
4e	poly(amic alkyl ester) (para isomer)	1c	25	24
5a	polyimide	1d	25	25

polyvalerolactone degradation products. The plasticization of the polyimide by the valerolactone can be evident in the data shown in Figure 6, where the modulus versus temperature profile and thermogravimetric analysis for copolymer **4c** and polyvalerolactone (**1c**) are plotted together. Upon degradation of the polyvalerolactone, a decrease in the modulus is observed. The recovery in modulus can be observed when the degradation products diffuse out of the copolymer. While the 3FDA/PMDA polyimide is swollen by caprolactone (~20%), it can actually dissolve in valerolactone. Retention of the foam structure depends upon a delicate balance between the rate of decomposition of the lactone coblock, the solubility of the lactone in the imide matrix and the rate at which the degradation product(s) diffuse out of the matrix. If the rate of decomposition is much higher than the diffusion of the degradation products, the processing window narrows. If the reverse holds, then the chance of developing a nanofoam is much improved.

Small-angle X-ray scattering (SAXS) experiments were performed on the parent copolymers and on the

Table 3. Porosity and Density Measurements of Polyimide Foams

	porosity, %	
sample entry	flotation	IR
2a	3	11
2b	13	
2c	20	18
3a		0
3b	6	17
3c	0	
3d	15	19
3e	17	13
3f		13
3g	13	16
3h	15	
3i		20
4a	0	0
4b	0	0
4c	0	
4d	0	0
4e	0	
5a	0	0

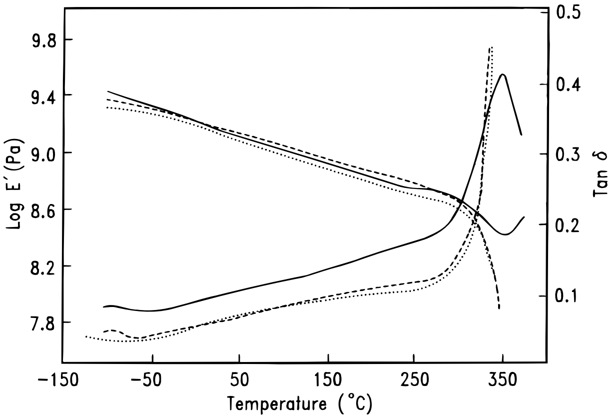


Figure 2. Dynamic mechanical analysis of copolymers **2c** (—), **2b** (···), and **3b** (- - -).

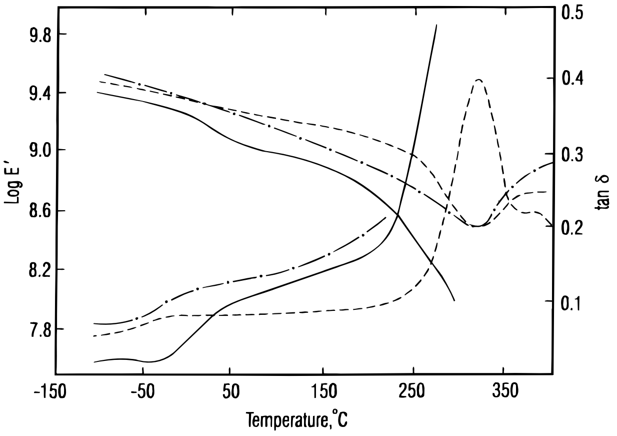


Figure 3. Dynamic mechanical analysis of copolymers **4a** (- - -), **4b** (-·-), and **4c** (—).

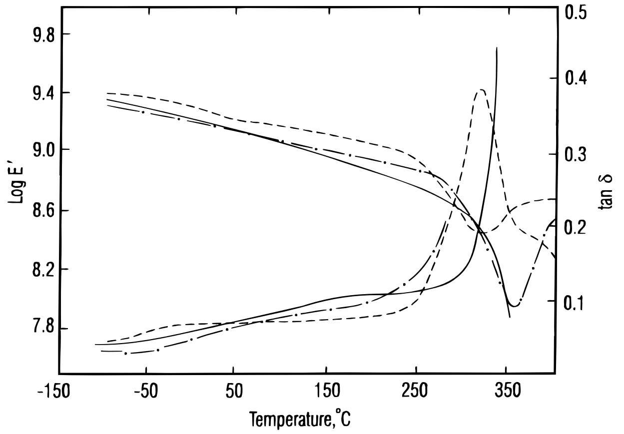


Figure 4. Dynamic mechanical analysis of copolymers **3b** (—), **4a** (- - -), and **5a** (-·-).

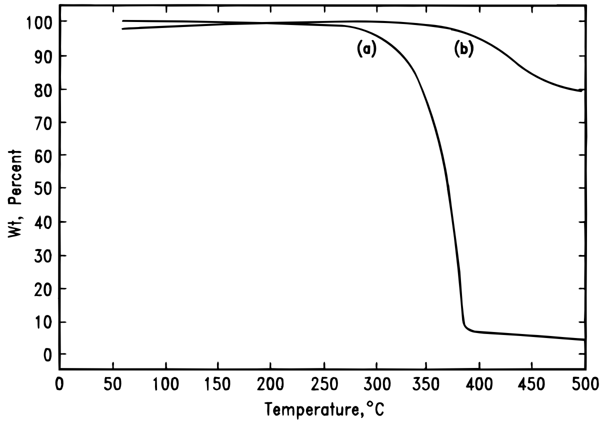


Figure 5. Thermogravimetric analysis of (a) polycaprolactone **1b** and (b) copolymer **3g**.

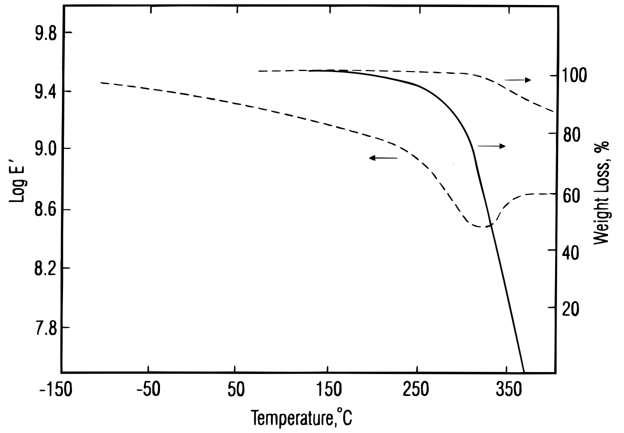


Figure 6. Dynamic mechanical and thermogravimetric analysis of copolymer **4c** (- - -) and thermogravimetric analysis of polyvalerolactone (—).

polycaprolactone copolymers after the decomposition of the caprolactone block. A typical scattering profile for the parent copolymers is shown in Figure 7. Here the scattering from a 3FDA/PMDA alkyl ester copolymer containing 15 wt % caprolactone is shown as a function of the scattering vector $\mathbf{Q} = (2\pi/\lambda)\sin\theta$, where λ is the wavelength (1.492 Å) and 2θ is the scattering angle. For all the copolymers, the SAXS profile shows a monotonic decrease in the scattering as a function of **Q**. While there is a substantial amount of excess scattering, the absence of a scattering maximum shows that a well-defined, spatially periodic morphology has not formed. This is not surprising when one considers the conditions under which the sample has been prepared. It is evident that the copolymer has been trapped in a highly nonequilibrium state. However, there is no question that the copolymer has microphase separated. Using a Debye–Beuche analysis, a correlation length can be determined that, knowing the volume fraction of the phases, will yield an average domain size. Assuming that the volume fraction of the phases is given by the

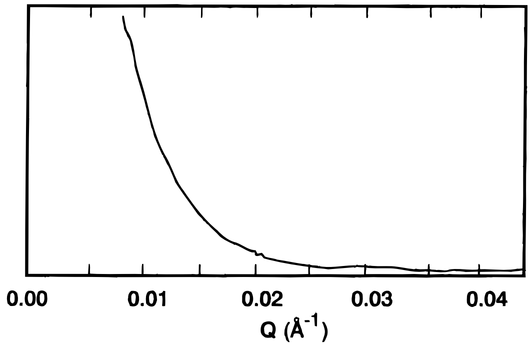


Figure 7. Small-angle X-ray scattering profile of a 3FDA/PMDA alkyl ester copolymer containing 15% caprolactone.

volume fraction of the components in the copolymer, an average size of the polycaprolactone domains of ~100 Å is obtained for both the 15% and 25% copolymers. Defining the size of the polycaprolactone domains with any greater precision is not reasonable given the assumptions. The more important observation is that a microphase-separated morphology is obtained under the processing conditions used. The slight differences in the domain sizes for the 15% and 25% copolymers is of secondary importance.

As mentioned, 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 rate at which the degradation products diffuse out of the sample, then degradation products will be trapped within the matrix, reducing its T_g. This may lead to a blowing effect that coarsens the void structure. Previous studies also have shown that both the heating rate and residence time at final temperature are crucial variables in minimizing plasticization and optimizing foam content.[38] The optimum cure schedule for the caprolactone-based copolymers, as determined by density measurements, was found to be 300 °C for 2 h to remove solvent and imidize the matrix, followed by a slow heating to 370 °C over a 5 h period and holding at this temperature for 3 h. Isothermal gravimetric analysis showed a quantitative degradation of the caprolactone coblock at 370 °C in nitrogen. This is also consistent with the IR spectra shown in Figure 8 of copolymer 3 at the cure temperature of 300, and foaming temperatures of 345 and 370 °C. As evidenced by the absorption band at 2947 cm $^{-1}$, characteristic of the CH_2 group stretching, temperatures of 370 °C are required to effect the quantitative degradation of the caprolactone coblock. In the case of the valerolactone-based copolymers, the decomposition of the valerolactone coblock occurs at lower temperatures. Isothermal gravimetric analysis showed quantitative degradation of the valerolactone coblock at 320 °C in nitrogen. The optimum cure schedule in this case was found to be 265 °C to remove solvent and effect partial imidization followed by a slow ramp (4 h) to 320 °C and holding at this temperature for 2 h to effect the complete degradation of the valerolactone coblock.

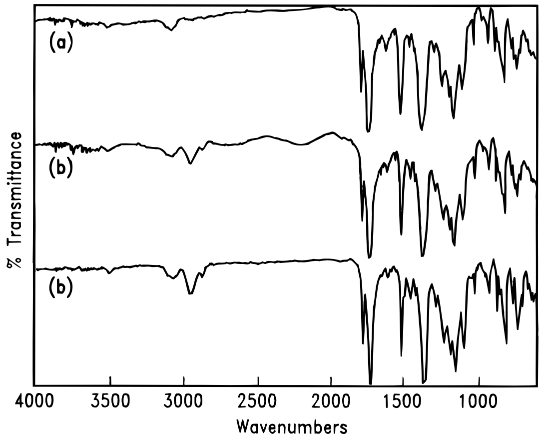


Figure 8. FT-IR spectra of copolymer **2b** at (a) 300 °C (1.5 h), (b) 345 °C (4 h), and (c) 370 °C (4 h).

The formation of the foam was assessed by both density and IR measurements. The densities for the foamed 3FDA/PMDA-based copolymers are shown in Table 3. The density of the pure 3FDA/PMDA polyimide is 1.34 g/cm^3. Foam densities range from 1.34 to 1.08, which are consistent with void contents from 0 to 20%, respectively. However, the porosity obtained in some cases appears considerably lower than expected from the chemical composition of the copolymer. Consequently, the foaming efficiency, i.e., the actual porosity relative to that expected, would appear to be low. However, the density results must be interpreted carefully. In particular, if the pores are not closed cell, then the flotation fluid can easily fill the pores giving rise to an arbitrarily high density and, consequently, low porosity. To circumvent this problem, infrared spectroscopy was used to augment the density measurements.[39] The values of the film porosities as measured by IR are uniformly greater than those measured by density, suggesting that the foaming efficiency was, in fact, much better than that determined by density measurements. In the case of the caprolactone-based copolymers containing the high volume fractions of caprolactone, foams were successfully generated. As expected, cross-linking of the polyimide matrix increased the foaming efficiency. Minimal differences in porosity were observed between the different synthetic routes employed (i.e., polyimide vs poly(amic alkyl ester) and meta vs para isomers of the latter). Conversely, the films obtained from the valerolactone-based copolymers showed no drop in density after the heat treatment to remove the labile block. Likewise, the films derived from the valerolactone/caprolactone labile blocks showed only minimal density drop upon decomposition of the labile coblock.

Shown in Figure 9 are the scattering profiles for the 15% and 25% copolymers after the PCL has been removed. As with the parent copolymers, the scattering from the nanofoams decreases monotonically with q. It is seen that the scattering from the 15% copolymer decreases more rapidly than that of the 25% copolymer. From the scattering profiles, the average void size in the foam is calculated to be ~125 Å for the 15%

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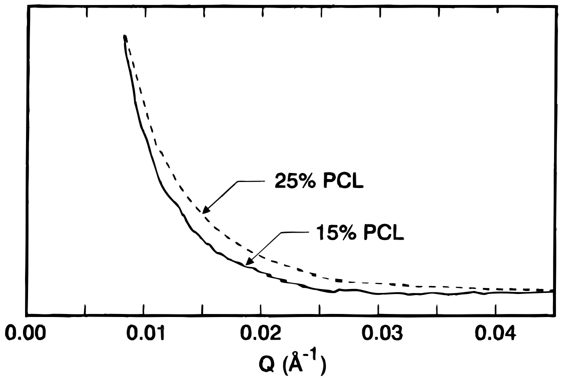

Figure 9. Small-angle X-ray scattering profiles for polyimide foams made from 3FDA/PMDA with 15% caprolactone and 25% caprolactone.

copolymer and ~100 Å for the 25% copolymer. From the magnitude of the scattering, it is evident that the volume fraction of voids is somewhat greater in the 25% copolymer than that of the 15% copolymer (~10%). However, from the integrated scattering, the total void content for the 25% copolymer is estimated only 13%, which indicates that a partial collapse of the foam has occurred. These porosity values are consistent with those measured by the other techniques.

Conclusion

The use of polycaprolactone as the thermally labile coblock was a successful route to polyimide nanofoams, although the polyvalerolactone- and poly(valerolactone–caprolactone)-based copolymers did not show the expected nanopore formation. The polycaprolactone in the copolymer required high temperatures in an inert atmosphere. Although the foam efficiency was high, especially for the cross-linked polyimide matrix, a partial collapse of the foam structure occurred. Since the average size of the pores increased slightly from that expected from the copolymer, it is reasonable to conclude that the smaller pores collapsed as a result of the local mobility imparted to the matrix by the solubilization of the decomposition products. This collapse occurred even when the matrix was cross-linked. The rapid collapse of the valerolactone-based copolymer presumably resulted from plasticization of the matrix by the degradation products. The dielectric constant of these nanofoams were not measured due to the fact that the porous structures tended to collapse at higher temperatures, thus precluding these materials from being considered as low-*k* materials in microelectronic applications. The study did show that a non-oxidative route toward generating nanofoams could be developed.

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