Polyimide Nanofoams from Caprolactone-Based Copolymers

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Polyimides are currently used as interlayer dielectrics in microelectronic packaging, since they have the requisite properties to survive the thermal, chemical, and mechanical stress of manufacturing and operation. The main advantage realized by the use of polyimides over inorganic alternatives is the lower dielectric constant. A reduction in the dielectric constant of the medium reduces pulse propagation delay, allowing for faster machine time, and minimizes the noise between lines.[1] One approach to reducing the dielectric constant is to use a polyimide foam where the size of the pores are submicron. The reduction in the dielectric constant is simply achieved by replacing the polymer with air, which has a dielectric constant of 1. Foams can be prepared from block copolymers comprised of a thermally stable and thermally labile material, where the latter constitutes the dispersed phase.[2−4] Upon thermal treatment, the thermally unstable block undergoes thermolysis, leaving a structure that is commensurate with the initial copolymer morphology, i.e., on the 10's of nanometer size scale, hence, nanofoams. Nanofoams have been demonstrated using poly(propylene oxide) as the labile coblock with both polyimide and poly(phenylquinoxaline) as the matrix polymer.[2] The degradation of the propylene oxide component can be achieved at 300 °C in an oxygen or air environment via thermooxidative degradative mechanism, which is, however, unacceptable in microelectronic fabrication. To this end, monodispersed oligomers of poly(ϵ-caprolactone), PCL, having controlled molecular weight and end group functionality were studied. Poly(caprolactone) and related aliphatic polyesters degrade quantitatively in an inert atmosphere by a stepwise process to produce cyclic compounds.[5−7] The major thermal degradation products are cyclic monomers and oligomers. The decomposition temperature of PCL is sufficiently high to allow films of block copolymers to be cured to remove solvent and to have the poly(amic alkyl ester) matrix imidized without decomposing the PCL. In addition, the decomposition temperature is sufficiently below the glass transition temperature, T_g, of many polyimides to provide an ample temperature interval where the PCL can be degraded. In this study, block copolymers of poly(ϵ-caprolactone) with a high T_g polyimide were investigated as a route to polyimide nanofoam formation.

Materials and Methods

The polyimide examined as the thermally stable block, derived from 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA)[8] and pyromellitic dianhydride (PMDA), has a T_g of 440 °C and a decomposition temperature of 500 °C.[9,10] Cross-linking of the imide block was accomplished by the incorporation of 1,1-bis(4-aminophenyl)-1-(4-ethylphenyl)-2,2,2-trifluoroethane, 3FET, as a comonomer.[11,12] The monofunctional hydroxy-terminated PCL (Poly Sciences), with a nominal molecular weight of 10 000 g/mol, was reacted with 4-nitrophenyl chloroformate to form a nitrophenyl carbonate end group.[13] Hydrogenation over Pearlman's catalyst gave the corresponding amine in a manner similar to that reported previously.[2−5] Comparison of molecular weights, determined by SEC and titration of the amino group (i.e., 10 500 g/mol), confirmed the introduction of a single amine end group. Furthermore, no evidence of exchange reactions was observed during the transformation between the amine and polyester by SEC measurements.

The block copolymers were prepared via a poly(amic alkyl ester) precursor since this intermediate may be isolated and characterized prior to imidization. The poly(amine alkyl ester) is less likely to exchange with the polyester than the corresponding poly(amic acid).[14] The synthesis involved the incremental addition of PMDA diethyl ester diacyl chloride in methylene chloride to a solution of the oligomer and 3FDA or, in one case, 3FDA together with 3FET in NMP containing pyridine as the acid acceptor (Scheme 1).[15] 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 in a methanol/water mixture, rinsed with water to remove remaining salts, and then rinsed with methanol and toluene followed by drying at 50 °C (24 h) under vacuum. The use of monofunctional oligomers in the polyimide syntheses described above affords an ABA triblock copolymer architecture, where the thermally labile component comprised the terminal A blocks and the stable polyimide is the B block.

The 3FDA/PMDA alkyl ester-based copolymers prepared are shown in Table 1. The weight percentage, or loading, of the labile block in the copolymers was intentionally maintained low to enhance the formation of discrete domains of the minor component. The concentration of the labile block in the copolymer was assessed by the thermal gravimetric analysis (TGA). The composition agreed closely with that expected from the feed ratios. Copolymer **3** contains 40 mol % of 3FET as a comonomer.

Thin films of the copolymer were prepared by solution casting from NMP followed by a slow temperature ramp of 4°C/min to 300 °C where the films were held for 1.5 h. This process removed the residual NMP, converted the poly(amic alkyl ester) block to the corresponding polyimide, and, for copolymer **3**, cross-linked the matrix without decomposing the labile block. ^{1}H NMR studies of copolymers **1** and **2** show no residual casting solvent, quantitative imidization, and retention of the labile block. The cured films of each copolymer were transparent with no evidence of large scale phase separation, characteristic of homopolymer contamination.

Results and Discussion

The dynamic mechanical spectra of the copolymers are shown in Figure 1. Two transitions were observed in each case, indicative of microphase-separated morphologies. The transition occurring near −50 °C is somewhat higher than that observed for the poly(caprolactone) T_g and is broad, suggesting diffuse phase boundaries. No evidence of crystallization of the caprolactone block was observed by either dynamic mechanical or X-ray diffraction measurements. The transition of the imide block is significantly lower than that of the parent homopolymer. Figure 2 shows the variable temperature thermograms of the poly(caprolactone) and copolymer **2**.[16] Clearly, the evolution of PCL degradation products in the copolymer occurs at a significantly higher temperature than the homopolymer, even though the degradation rates are comparable. This suggests that the long resonance time of the degradation products of poly(caprolactone) in the polyimide matrix leads to plasticization of the matrix with

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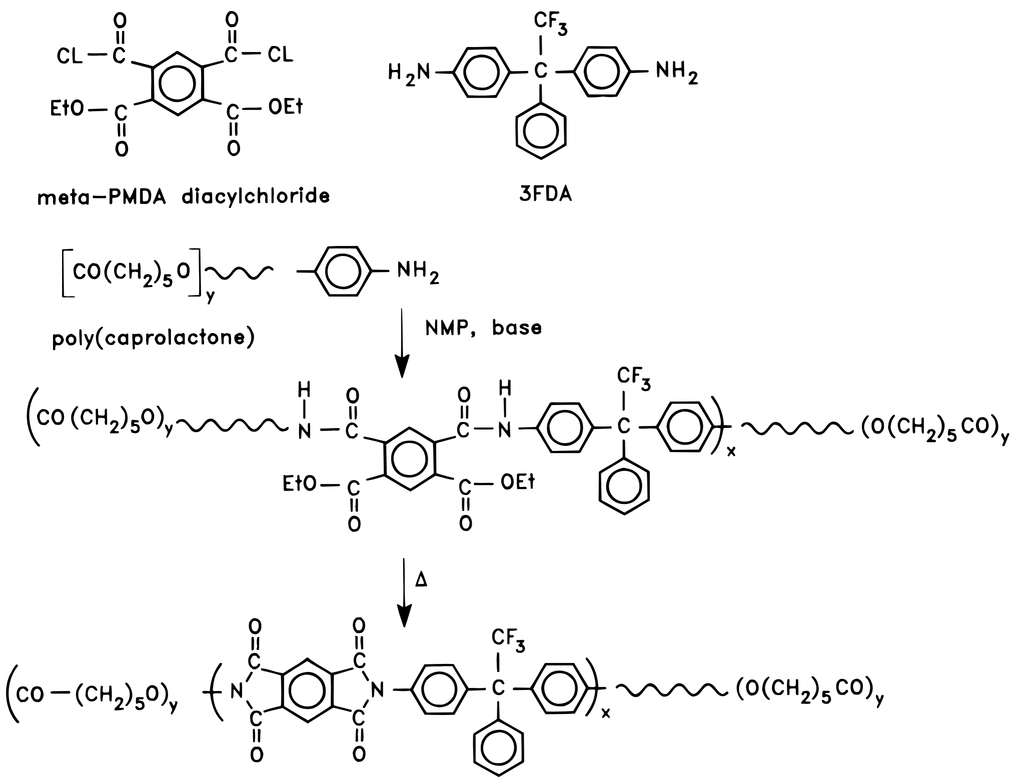
Scheme 1



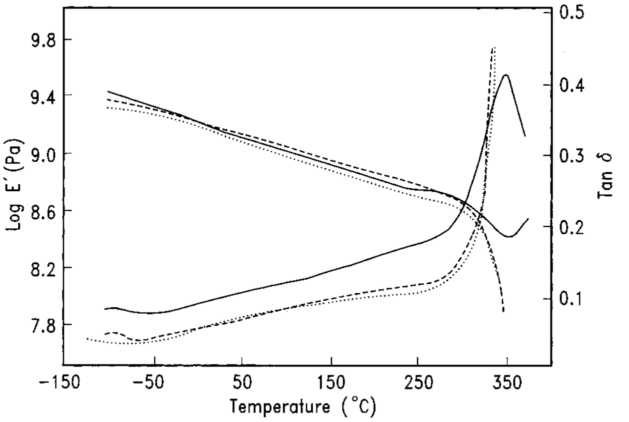


Figure 1. Dynamic mechanical spectra of copolymer **1** (— — —), copolymer **2** (· · ·), and copolymer **3** (—).

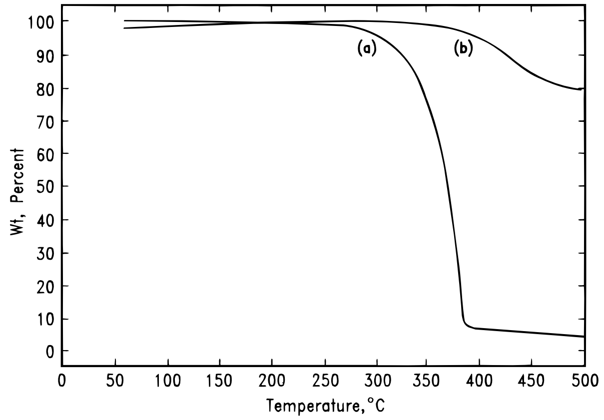


Figure 2. Variable temperature thermograms of (a) poly(caprolactone) and (b) copolymer **2**.

a substantial reduction in the T_g. Cross-linking of the polyimide (copolymer **3**) appears to provide the requisite "solvent resistance" to minimize plasticization of the polyimide block, as evidenced by the retention in modulus over the appropriate temperature regime in the dynamic mechanical spectra (Figure 1).

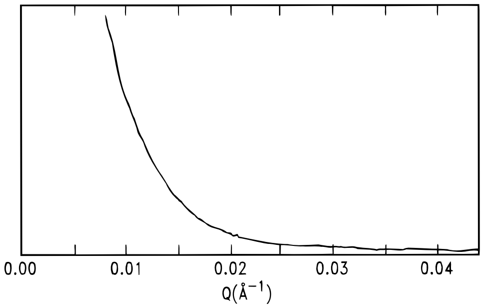


Figure 3. Small angle X-ray scattering profile of a 3FDA/PMDA alkyl ester copolymer containing 15% caprolactone.

Small angle X-ray scattering (SAXS) experiments were performed on the parent copolymers and on the copolymers after the decomposition of the caprolactone block. A typical scattering profile for the parent copolymers is shown in Figure 3. Here the scattering from a 3FDA/PMDA alkyl ester copolymer containing 15% caprolactone is shown as a function of the scattering vector $Q = (2\pi/\lambda) \sin \theta$, 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 which, knowing the volume fraction of the phases, will yield an average domain size. Assuming that the

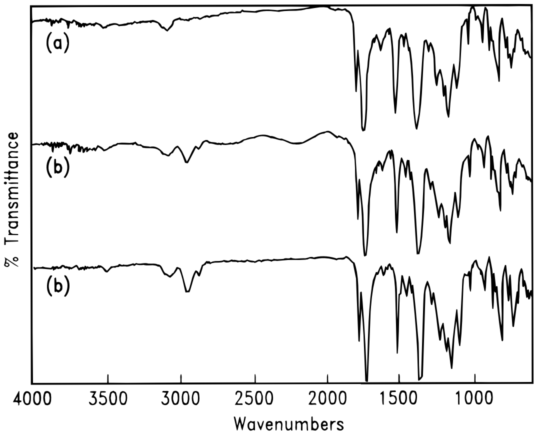


Figure 4. FT-IR spectra of copolymer **2** at (a) 300 °C (1.5 h), (b) 345 °C (4 h), and (c) 370 °C (4 h).

Table 1. Characteristics of 3FDA/PMDA Alkyl Ester−Caprolactone Copolymers and Subsequent Foams

sample entry	ethynyl comp, wt %	caprolactone comp, wt % charge	caprolactone comp, wt % incorporated	porosity, % flotation	porosity, % IR
1	0	15	14	3	11
2	0	25	25	13	
3	40	25	26	20	18

volume fraction of the phases is given by the volume fraction of the components in the copolymer, an average size of the PCL domains of ∼100 Å is obtained for both the 15% and 25% copolymers. Defining the size of the PCL domains with any greater precision is not reasonable given the assumptions used to obtain this value. It is more important to note that a microphase-separated morphology is obtained under the preparation conditions used. The slight differences between the domain sizes for the 15% and 25% copolymers is of secondary importance.

Previous studies have shown that the retention of the foam structure depends upon a balance between the rate of decomposition of the labile coblock, the solubility of the degradation products in the imide matrix, and the rate at which these products diffuse out of the matrix.[2−4] If the rate of decomposition is significantly higher than the rate at which the degradation products diffuse out of the sample, then they are trapped within a matrix having a reduced T_g. This leads to a blowing effect which coarsens the void structure. Previous studies have shown that both the heating rate and the residence time at final temperature are crucial variables in minimizing plasticization and optimizing foam content. The optimum cure schedule, 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 4 h. Isothermal gravimetric analysis showed a quantitative degradation of the caprolactone coblock at 370 °C in nitrogen. This is in keeping with the IR spectra shown in Figure 4 of copolymer **3** at the cure temperature at 300 °C and foaming temperatures of 345 and 370 °C. As evidenced by the absorption band at 2947 cm^{-1}, characteristic of the CH_2 group, temperatures of 370 °C are required to effect the quantitative degradation of the caprolactone coblock.

The formation of the foam was assessed by density and IR measurements.[17] The density of the pure 3FDA/PMDA polyimide is 1.34 $\mathrm{g/cm}^3$. Foam densities range from 1.08 to 1.25, which is consistent with void content from 3% to 20%, as shown in Table 1. However, the porosity obtained is considerably less than that expected from the chemical composition of the copolymer. Consequently, the foaming efficiency, the actual porosity relative to that expected, would appear to be low. However, caution must be exerted in the interpretation of the density results. In particular, as discussed previously,[4] the flotation fluid can fill the porous structure giving rise to an arbitrarily high density and, therefore, low porosity. To circumvent this problem, infrared spectroscopy was used to augment the density measurements. The values of the porosity as measured by IR are uniformly greater than that measured by density, indicating that the foaming efficiency was, in fact, much better.

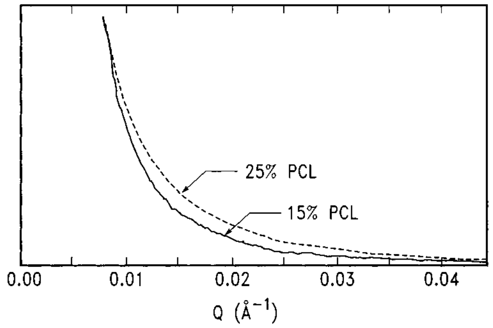


Figure 5. Small angle X-ray scattering profiles for polyimide foams made from 3FDA/PMDA with 15% caprolactone and 25% caprolactone.

Shown in Figure 5 are the scattering profiles for the 15% and 25% copolymers after the PCL has been removed. As with the profiles of the parent copolymers, the SAXS 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 ∼125 Å for the 15% copolymer and ∼100 Å for the 25% copolymer. From the magnitude of the scattering, it is evident that the volume fraction of voids is greater in the 25% copolymer than in the 15% copolymer by ∼10%. However, from the integrated scattering, the total void content for the 25% copolymer is only 13%, which indicates that a partial collapse of the foam has occurred. These porosity values are comparable to those measured by the other techniques.

Conclusion

The use of PCL as the thermally labile coblock was a successful route to polyimide nanofoams. Although the decomposition of the PCL in the copolymer required high temperatures, the decomposition was effected quantitatively 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.

References and Notes

(1) Tummala, R. R.; Rymaszewski, E. J. *Microelectronics Packaging Handbook*; Van Nostrand Reinhold: New York, 1989; Chapter 1.

(2) Hedrick, J. L.; Labadie, J. W.; Russell, T.; Wakharkar, V. *Polymer* **1993**, *34*, 22.

(3) Hedrick, J. L.; Russell, T. P.; Lucas, M.; Labadie, J.; Swanson, S. *Polymer* **1993**.

(4) Charlier, Y.; Hedrick, J. L.; Russell, T. P.; Volksen, W. *Polymer* **1995**, *36*, 987.

(5) Iwabuchi, S.; Jaacks, V.; Werner, K. *Makromol. Chem.* **1976**, *177*, 2675.

(6) Garozzo, D.; Giuffrida, M.; Montaudo, G. *Macromolecules* **1986**, *19*, 1643.

(7) Plage, B.; Schulter, H. *Macromolecules* **1990**, *23*, 2642.

(8) Preparation of 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA). To a 1 L 3-necked round-bottomed flask equipped with a stir bar, thermocouple, Ar inlet, and Dean−Stark condenser were added 54.6 g (0.287 mol) of *p*-toluenesulfonic acid monohydrate and 325 mL of freshly distilled amine, and the mixture was refluxed to a constant head temprature (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 were separated. The aqueous layer was extracted with 150 mL of CH_2Cl_2, and the combined organic layers were washed sequentially with 4 × 250 mL of saturated $NaHCO_3$, 4 × 250 mL of water, and 200 mL of brine. The dark solution was $MgSO_4$, evaporated to ca. 300 mL, and added slowly to 4 L of stirring hexane. The hexane was decanted and the resulting dark semisolid taken up in about 500 mL of CH_2Cl_2 which was again evaporated to ca. 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 with stirring overnight. The mixture was filtered over Celite, the filtrate concentrated to ca. 125 mL, and the product slowly precipitatd with stirring into 2 L of hexane. This procedure (resuspension of the original SiO_2/Norit, stirring for 1 h, filtration, and precipitation) was repeated a total of four times resulting in a total of 68 g of beige powder (subsequent treatments provide exceedingly small amounts of material). This material was taken up in 1 L of $(Et)_2O$ and treated with 50 g of silica gel and 5 g of Norit. Processing as above with precipitation into 1 L of hexane ultimately resulted in 63 g of white powder: mp 215−218 °C; yield, 64%; NMR (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).

(9) Rogers, M. E.; Mog, T. M.; Kim, Y. S.; McGrath, J. E. *Mater. Plast. Soc. Symp.* **1992**, *164*, 13.

(10) Rogers, M. E.; Brink, M. H.; McGrath, J. E. *Polymer* **1993**, *34*, 849.

(11) Jensen, B. J.; Hegenrother, P. M.; Ninokogu, G. *Polymer* **1993**, *34*, 639.

(12) Preparation of 1,1-bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane 4-bromotrifluoroacetophenone. A 500 mL round-bottomed flask equipped with a thermometer adapter, a dropping funnel chargeed with *n*-butyllithium (*n*-BuLi) (44 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 an internal temperature of −78 °C in a dry ice/acetone bath. The *n*-BuLi was added dropwise over a period of 30 min, and the reaction mixture was allowed to stir at −78 °C for 2 h. The mixture was then allowed to warm to 0 °C and then recooled to −78 6C before the ethyl trifluoroacetate was added dropwise. Then 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 ($MgSO_4$), filtered, and rotary evaporated to remove the solvent. The oil was vacuum distilled and a water white liquid was distilled over a 45 °C at 900 μmHg. This liquid solidified to 19.21 g of 4-bromotrifluoroacetophenone, a white solid (89% yield). Proton NMR in deuterated chloroform shows an AB quartet centered at 7.83 ppm. Preparation of 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, recrystallized; Aldrich), and aniline (53.3 mL, 62.87 mmol, distilled, Aldrich) were placed in a 250 mL round-bottomed flask and refluxed (120−133 °C) under nitrogen for 24 h. After cooling to room temperature, $NaHCO_3$ (17.2 g) and water were added, and the aniline and water were codistilled off molar 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 rotary evaporated to yield a purple oil which was dried further in a 60 °C vacuum oven to yield 31.5 g of a purple semisolid (99% yield). Proton NMR in deuterated chloroform shows two AB quartets centered at 7.25 (4H) and 6.75 (8H) ppm and a broad singlet at 3.72 ppm (4H). Preparation of 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, 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 (trimethylsilyl)acetylene (14.56 g, 148.24 mmol; Farchan) were then added. The flask was sealed with a septum, 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 $MgSO_4$, filtered, and rotary evaporated to a brown solid. Ethanol (250 mL) and 1 N sodium hydroxide (50 mL) were added, and the mixture was stirred at room temperature overnight, transferred to a separatory funnel, added to ether (500 mL), and washed twice with water. It was then dried over $MgSO_4$ and filtered, and the solvent was rotary evaporated off. The sample dried in a 60 °C vacuum oven to yield 16.8 g of a light brown foamy solid (61% yield). Proton NMR in deuterated chloroform shows two AB quarters at 7.35 (4H) and 6.8 (8H) ppm and broad singlets at 3.76 (4H) and 1.67 (1H) ppm.

(13) To a 250 mL 3-necked round-bottomed flask equipped with a stir bar, thermocouple, and Ar inlet were added 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-nitrophenyl chloroformate dissolved in 10 mL of THF was added dropwise. The temperature was allowed to each 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 stirring 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, charged into a Paar hydrogenation bottle containing 750 mg of $Pd(OH)_2$ (Pearlman's catalyst), and hydrogenated at 40 psi for 48 h. The reaction mixture was filterd twice through a Celite pad, evaporated, redissolved in 300 mL of CH_2Cl_2, and washed with 2 × 100 mL of saturated $NaHCO_3$ followed by 2 × 100 mL of water. 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.

(14) Volksen, W.; Yoon, D. Y.; Hedrick, J. L.; Hofer, D. *Mater. Res. Soc. Symp. Proc.* **1991**, *227*, 23.

(15) The amic ester−α-caprolactone triblock copolymers were prepared by the coreaction 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 designed to prepare an amic ester−α-methylstyrene copolymer, having a caprolactone content of 25 wt %, using a caprolactone olgiomer of 10 000 g/mol molecular weight is provided (copolymer **3**, Table 1). A 3-necked flask equipped with an overhead

stirrer and addition funnel was charged with caprolactone olgiomer (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 (0.710 00 g, 0.008 90 mol) was added to the solution. The PMDA diethyl ester diacyl chloride (1.5600 g, 6.004 490 mol) 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 and the mixture isolated by precipitation in methanol/water, rinsed with water (to remove excess salts) and cyclohexene (to remove possible homopolymer contamination), and dried in a vacuum oven.

(16) 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.

(17) Sanchez, M. I.; Hedrick, J. L.; Russell, T. P. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 253.

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