

Two-Sided Comb Poly(amic ester)–Poly(propylene oxide) Graft Copolymers as Porous Polyimide Precursors

ELENA LEBEDEVVA,¹ BRENDA S. KESLER,¹ KENNETH R. CARTER²

¹Department of Chemistry, San Jose State University, San Jose, California 95192-0101

²Polymer Science and Engineering Department, University of Massachusetts Amherst, Conte Center for Polymer Research, 120 Governors Drive, Amherst, Massachusetts 01003

Received 10 December 2004; accepted 11 December 2004

DOI: 10.1002/pola.20698

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: New step-growth graft block copolymers were synthesized. These two-sided comb copolymers consisted of a poly(amic ester) (PAE) backbone and pendant poly(propylene oxide) (PPO) grafts. The copolymers were made via a macromonomer approach, in which the 4,6-bis(chlorocarbonyl) isophthalic acid bis[poly(propylene oxide)] ester macromonomer was synthesized through the reaction of hydroxyl-terminated PPO oligomers with pyromellitic dianhydride and oxalyl chloride. This macromonomer was subsequently used in step-growth polymerization with comonomers 4,6-bis(chlorocarbonyl) isophthalic acid diethyl ester, 2,5-bis(chlorocarbonyl) terephthalic acid diethyl ester, and 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane, and this yielded PPO-co-PAE graft copolymers. Accordingly, we report the synthesis and characterization of the PPO oligomer, the PPO macromonomer, and their corresponding PPO-co-PAE graft copolymers. Graft copolymers with PPO concentrations of 3–26 wt % were synthesized. These polymers were thermally cured to produce polyimide/PPO composites. The thermolysis of these polyimide/PPO composites yielded porous polyimide films with porosities ranging of 4–22.5%. © 2005 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 43: 2266–2275, 2005

Keywords: graft copolymers; phase separation; polyamides; step-growth polymerization; macromonomers

INTRODUCTION

Polyimides (PIs), high-performance polymers with superior thermal (stability up to 500 °C), mechanical, and electrical properties, are used in many applications, from aerospace to fuel cells to microelectronics.¹ Because of their very low electrical leakage in surface or bulk, PIs form excellent interlayer dielectric insulators and are used in multilayer integrated circuit (IC) structures.² Additionally, aromatic PIs are generally solvent-

resistant and easy to process from soluble polymeric precursors. They can be easily prepared in the form of PI films by spin-on or flow-coating solutions of PI precursors, such as poly(amic acid)s and poly(amic ester)s (PAEs), followed by thermal or chemical imidization.³

Creating heterogeneous hybrid materials through the reaction of block copolymer precursors can lead to polymer films with new properties. We have reported the synthesis of ABA triblock copolymers that, upon spin coating and heating, spontaneously form films consisting of a thermally stable matrix, PI, with a thermally labile oligomer, poly(propylene oxide) (PPO), as a dispersed phase. These block copolymers have shown utility in the formation of nanoporous PI

Correspondence to: K. R. Carter (E-mail: krcarter@polysci.umass.edu)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 43, 2266–2275 (2005)
© 2005 Wiley Periodicals, Inc.

films after selective thermolysis of the PPO phase.⁴

AB and ABA block copolymers are commonly synthesized by various living polymerization techniques, in contrast to the aforementioned polycondensation block copolymer route. In these polycondensation systems, stoichiometric amounts of diamine and diester dichloride are reacted in a step-growth polymerization. The preparation of the ABA block copolymer via condensation polymerization is complicated by the statistical nature of this stoichiometrically controlled reaction. These syntheses require properly monofunctionalized A blocks that effectively act as end-capping units during the polycondensation reaction. For example, one end of the PPO oligomer chains is functionalized with an aromatic amine. The functionalized PPO (A block) is reacted with aromatic diamines and 4,6-bis(chloro-carbonyl isophthalic acid diethyl ester (m-DCDE) or 2,5-bis(chloro-carbonyl terephthalic acid diethyl ester (p-DCDE) in stoichiometric ratios, and this results in the corresponding PPO/PAE/PPO ABA triblock copolymers. Although ABA block copolymers have been shown to act as appropriate precursors for PI nanofoams, we have sought new graft-type⁵ step-growth copolymer architectures that could also be useful for such approaches, and we have tried to simplify the synthetic route toward useful PPO-containing block copolymers. For these block copolymers, we have sought to exploit a new macromonomer approach in which the PPO oligomer block is attached to a bis(chloro-carbonyl isophthalic acid diester monomer unit, and this macromonomer is subsequently used in polycondensation reactions with an aromatic diamine and

either m-DCDE or p-DCDE to produce new two-sided comb PAE/PPO graft copolymers (Fig. 1). The results of this synthetic study are presented along with an initial evaluation of these polymers for the formation of porous PI thin films.

EXPERIMENTAL

Materials

Diethylaluminum chloride (1 M in heptane; Aldrich), oxalyl chloride (98%; Aldrich), 5,10,15,20-tetraphenylporphyrin (Midcentury), and 1-methyl-2-pyrrolidone (99.5% anhydrous; Aldrich) were used as received. Pyromellitic dianhydride (PMDA; Criskev) and 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (4-BDAF; Criskev) were sublimed before use. Propylene oxide (Aldrich) was distilled over calcium hydride. m-DCDE and p-DCDE were prepared as described in our previous work.⁶ All other solvents and reagents were commercially available and were used as received.

Characterization

NMR spectra [in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) or CDCl₃] were recorded on an IBM WP 250 spectrometer operating at 250.1 (¹H) or 62.9 MHz (¹³C), with chemical shifts reported in parts per million downfield from tetramethylsilane. Intrinsic viscosity ([η]) measurements were conducted with a Cannon-Ubbelohde dilution viscometer in 1-methyl-2-pyrrolidinone (NMP) at 30 °C. The polymer molecular weights were determined with a Waters 150-C gel permeation chromatography (GPC) instrument calibrated with polystyrene standards with tetrahydrofuran as the elution solvent.

Polymer films for mechanical and thermal analysis were cast from NMP and heated to remove the solvent and anneal the polymer. Glass-transition temperatures, taken as the midpoint of the change in the slope of the baseline, were measured on a DuPont DSC 1090 instrument at a heating rate of 10 °C/min (N₂). Thermogravimetric analyses (TGAs; N₂ and air) of the polymer films were conducted on a PerkinElmer TGA-7 at a heating rate of 10 °C/min, or the isothermal weight loss was measured at different temperatures over a 4–10-h period. Dynamic mechanical measurements were performed with a Polymer Laboratories dynamic mechanical thermal ana-

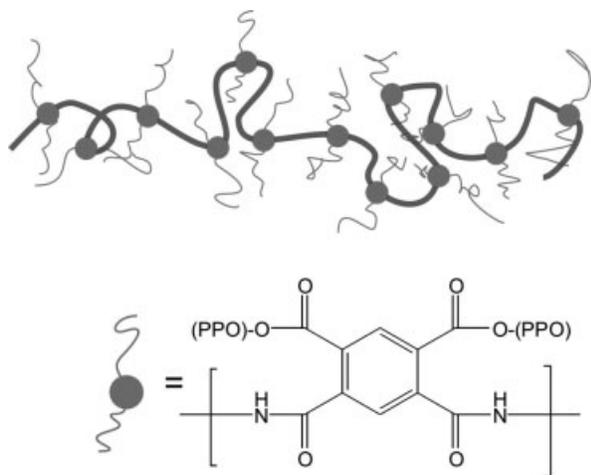


Figure 1. Two-sided comb graft copolymers. The PAE backbone is red, and the PPO blocks are blue.

lyzer in the tension mode at a heating rate of 10 °C/min (10 Hz). The 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 (Scientific Glass & Instruments, Inc.) and maintained at 25 °C (density = 1.07–1.45). At least two specimens were used for each density measurement. Macromonomer end-group titrations were performed with a Metrohm 736 GP Titrino unit with a standardized tetrabutylammonium hydroxide solution in methanol, and averages were taken of five duplicate measurements.

Monomer and Polymer Preparation

Catalyst Solution Preparation: 5,10,15,20-Tetraphenylporphyrato Aluminum Chloride (1)

In a drybox, a 500-mL, round-bottom flask was charged with tetraphenyl porphyrin (4.72 g, 7.67 mmol, 1 equiv) dissolved in 200 mL of methylene chloride. Diethylaluminum chloride (9.2 mL, 9.2 mmol, 1.2 equiv) was added slowly with stirring. After the addition was complete, the catalyst solution was left to stir for 4 h before use.

Preparation of Hydroxy-Terminated Poly(propylene oxide) Oligomer (PPO-OH or 2)

A solution of freshly prepared catalyst (1) was cooled to 0 °C, and freshly distilled propylene oxide (23 g, 396 mmol, 52 equiv) was added via a needle. The reaction was left to stir overnight under a nitrogen flow at room temperature. After the workup, the mixture was shaken well with concentrated HCl (3 mL) and CH₃OH (10 mL), and methylene chloride was removed *in vacuo*. The semisolid, purple residue was dissolved in diethyl ether and filtered through Celite. The filtrate was washed with 20 mL of concentrated HCl, and the ether layer was filtered through Celite to remove the residual insoluble catalyst. The solution was then further subjected to a water wash, a base wash (a solution of 10 mL of 50% NaOH in 300 mL of water), a sodium bicarbonate wash (10% NaHCO₃), and a water wash again. After each washing step, the ether layer was filtered through Celite. The resulting light pink ether solution was stirred for 12 h over charcoal and anhydrous MgSO₄. Filtration through Celite and concentration *in vacuo* afforded PPO as a light yellow, viscous liquid. Traces of water in PPO were removed as an azeotropic mixture (wa-

ter/toluene) by distillation with toluene. Dry and pure monohydroxy-terminated PPO (14.2 g) was collected (66%). The oligomer had a molecular weight of 2700 g/mol, as determined by GPC.

¹H NMR (acetone-*d*₆, δ): 1.10 (d, 3H, CH₃), 3.31 (m, 1H, CH), 3.40 (d, 2H, CH₂).

Preparation of Macromonomer Precursor Benzene 1,2,4,5-Tetracarboxylic Acid 2,4-Bis[poly(propylene oxide)] Ester (3)

2 (8.32 g, 3.2 mmol, 2 equiv) was dissolved in ethyl acetate (100 mL), and PMDA (0.35 g, 1.6 mmol, 1 equiv) was added. The reaction was allowed to reflux for 48 h. The product was transferred to a clean flask and concentrated *in vacuo*; this yielded 8.3 g of **3** as a very viscous, yellow fluid. NMR analysis revealed that the reaction was nearly quantitative, and it was used in the next step with no further purification.

¹H NMR (acetone-*d*₆, δ): 1.11 (d, 264H, CH₃), 3.38 (m, 88H, CH), 3.54 (m, 176H, CH₂), 8.31 (s, 1H, aromatic H), 8.39 (s, 1H, aromatic H), 12.1 (s, 2H, COOH).

Preparation of Macromonomer 4,6-Bischlorocarbonyl Isophthalic Acid Bis[poly(propylene oxide)] Ester (4)

Macromonomer **3** (10 g, 1.6 mmol, 1 equiv) was heated in ethyl acetate to 55 °C and slowly treated (dropwise) with oxalyl chloride (4 g, 32 mmol, 20 equiv). The materials were allowed to react at 55 °C for 24 h, and the mixture turned brown-red. The ethyl acetate and excess oxalyl chloride were removed *in vacuo*, and several subsequent ethyl acetate additions and distillations were performed to ensure complete oxalyl chloride removal. Finally, the product (**4**) was concentrated *in vacuo* as a viscous, brown liquid with an isolated yield of 10.2 g (100%). The molecular weight of macromonomer **4** was 6380 g/mol, as determined by titration with tetrabutylammonium hydroxide.

¹H NMR (acetone-*d*₆, δ): 1.1 (d, 282 H, CH₃), 3.38 (m, 94H, CH), 3.47 (m, 188H, CH₂), 8.54 (s, 1H, aromatic H), 8.57 (s, 1H, aromatic H).

10% PPO-co-PAE Graft Copolymer (Typical Procedure)

All reaction setups and the addition of the reagents and reaction vials were performed in a nitrogen-atmosphere drybox. In a 15-mL vial, macromonomer **4** (0.3500 g, 0.0612 mmol) was

dissolved in 5 mL of NMP. p-DCDE (1.2505 g, 3.602 mmol) was added, and the mixture was stirred. The diamine, 4-BDAF, (1.8995 g, 3.6636 mmol), was dissolved in 5 mL of NMP and added to the vial with stirring. Finally, pyridine (0.83 mL, 0.81 g, 10.25 mmol) was added, and the flask was sealed. The mixture was placed on a mechanical stirrer for 12 h. The resulting viscous polymer solution was precipitated into a blender with a mixture of 75% water and 25% methanol and was stirred for 30 min. The precipitated copolymer was filtered and washed with H₂O/methanol and was rinsed with pure methanol to remove any unreacted PPO oligomer; it was then filtered and dried overnight *in vacuo* at 50 °C. This afforded a creamy-white solid (3.01 g, 86%).

¹H NMR (DMSO-*d*₆, δ): 1.00 (d, 3.3H, CH₃CH(O)CH₂O), 1.18 (t, 6H, CH₃), 4.25 (q, 4H, CH₂), 7.05 (d, 4H, Ar—H), 7.14 (d, 4H, Ar—H), 7.33 (d, 4H, Ar—H), 7.76 (d, 4H, Ar—H), 8.04 (s, 2H, Ar—H).

RESULTS AND DISCUSSION

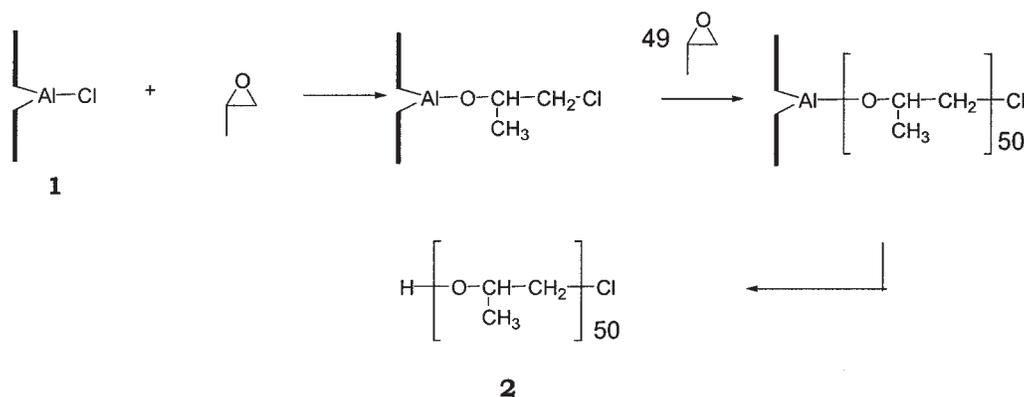
When PPO/PAE block copolymers are designed, a graft copolymer approach can be used as an alternative to previously reported linear block copolymer preparations. We chose to prepare PAE/PPO copolymers via macromonomer graft polycondensation. Our macromonomer, a derivative of PMDA, has two PPO blocks of the same length attached to the center of the macromonomer. The macromonomer contains two carboxylic acid groups at the core. These acid groups are activated toward polymerization by their conversion into the more reactive acyl chloride. When added

to the polycondensation reaction with the diamine, the diacylchlorides react, forming a PAE graft copolymer that resembles a two-sided comb structure (Fig. 1).

PPO was chosen as a graft oligomer for the preparation of the new graft copolymers for several reasons. First, we have been able to exploit the aluminum porphyrin initiated synthesis of PPO, which allows the control of both the molecular weight and the end-group functionality.^{7–9} PPO oligomers can be prepared with controllable, prescribed molecular weights and low polydispersities, and this allows for the uniformity of the graft lengths. Second, linear ABA block copolymers consisting of PPO (A block) and PAE (B block) have been previously prepared and can be compared with the current systems.^{3,5} Lastly, we wanted to prepare graft block copolymers that could be used as precursors to PI nanofoams.¹⁰

The classical two-step synthesis of aromatic polyamides and PAEs includes a polycondensation reaction between an aromatic diamine and an appropriate diacid, which can be in the chemically activated form of the acid chloride. We chose to use a fluorinated aromatic diamine, 4-BDAF.

First, we developed a synthetic route to the PPO-containing macromonomer (**4**). This required the preparation of hydroxy-terminated PPO of a controlled molecular weight (**2**). We chose a procedure developed by Aida et al.⁷ in which an aluminum porphyrin complex initiates the living polymerization of propylene oxide. Using this procedure, we were able to produce hydroxy-terminated PPO of a controlled molecular weight (Scheme 1). We targeted PPO of a relatively low molecular weight to use as the arms of our graft copolymers, and after the synthesis, the



Scheme 1. Synthesis of the PPO oligomer.

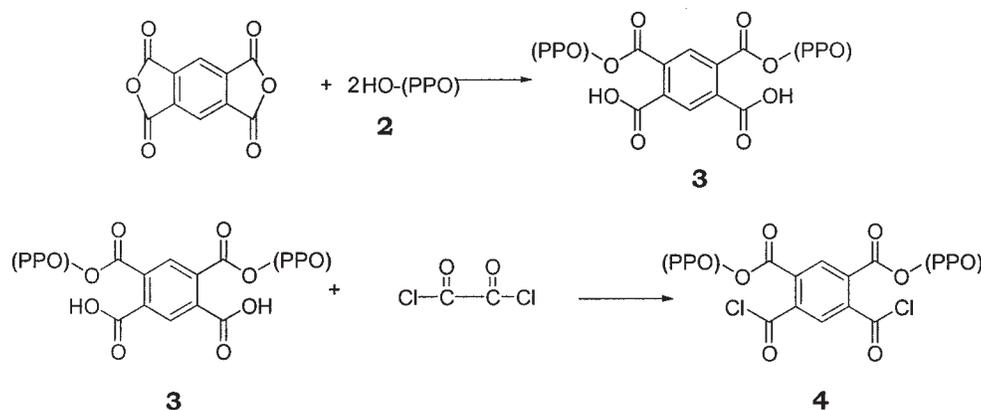


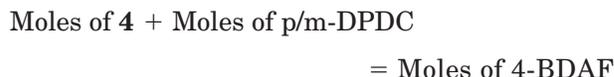
Figure 2. Synthesis of macromonomer 4.

obtained oligomer was analyzed by GPC, which showed a very narrow molecular weight distribution, with a polydispersity of 1.13 and a molecular weight of 3000. This molecular weight was confirmed by ^1H NMR and end-group titration.

Next, we heated the hydroxy-terminated PPO with PMDA in ethyl acetate. The hydroxy group of PPO reacted in a ring-opening reaction with PMDA to produce the expected bisesterified product (3). ^1H NMR confirmed quantitative conversion to the desired product. Finally, macromonomer 4 was prepared by the reaction of the PPO diester diacid with an excess of oxalyl chloride in ethyl acetate (see Fig. 2). The molecular weight of macromonomer 4 was 6380 g/mol, as determined by titration with tetrabutylammonium hydroxide. This value is in excellent agreement with the expected structure consisting of two PPO blocks attached to a single 2,5-dicarbethoxyterephthalic acid center.

Macromonomer 4 was used as a comonomer in a classical step-growth polymerization with an aromatic diamine to yield new two-sided comb PAE/PPO graft copolymers. We were able to control the level of incorporation of 4 with various amounts of other diacyldichloride comonomers in the polymerizations with diamines. Both m-DPDC and p-DPDC were used to effectively dilute the amount of 4 used in the synthesis of the graft copolymers. We chose two different PAE series for our study, both based on the aromatic diamine 4-BDAF. The first series of copolymers (5a–5d) were prepared with the comonomer that resulted in predominately meta linkages in the PAE backbone, m-DPDC (Fig. 3). The second series of copolymers (6a–6e) were similar but used the para comonomer, p-DPDC.

The starting materials for copolymers 5a–5d were m-DPDC, PPO macromonomer 4, and 4-BDAF (see Fig. 3). Five copolymers were prepared with PPO concentrations of 3.5, 7.5, 12, and 15 wt %. The procedure for the synthesis of copolymers 6a–6e was identical to that used for 5a–5d, with p-DPDC used in place of the meta isomer (6e was 27% PPO). To ensure the formation of a high-molecular-weight polymer, we ensured that each reaction had a balanced stoichiometry conforming to the following equation:



The monomers were reacted together at room temperature in NMP with approximately 30% solids. Pyridine was added as an HCl acceptor. After 12 h of stirring, the success of the polymerizations was evidenced by the resulting viscous reaction solutions. These types of condensation polymerizations are very sensitive to stoichiometry, and any impurities, nonreactive monomers, or contamination can result in low-molecular-weight, low-viscosity solutions. The graft copolymers were precipitated into a water/methanol mixture. Each precipitated polymer was washed repeatedly with water and methanol to remove salts and any unreacted PPO. The polymer was filtered and dried *in vacuo*. Because of the statistical nature of the polymerization and the high solubility of the lower molecular weight fraction of the PPO-containing copolymer, a slight amount of fractionation was observed with a loss of low-molecular-weight fractions, and the final isolated yield was approximately 85%. This type of fractionation is

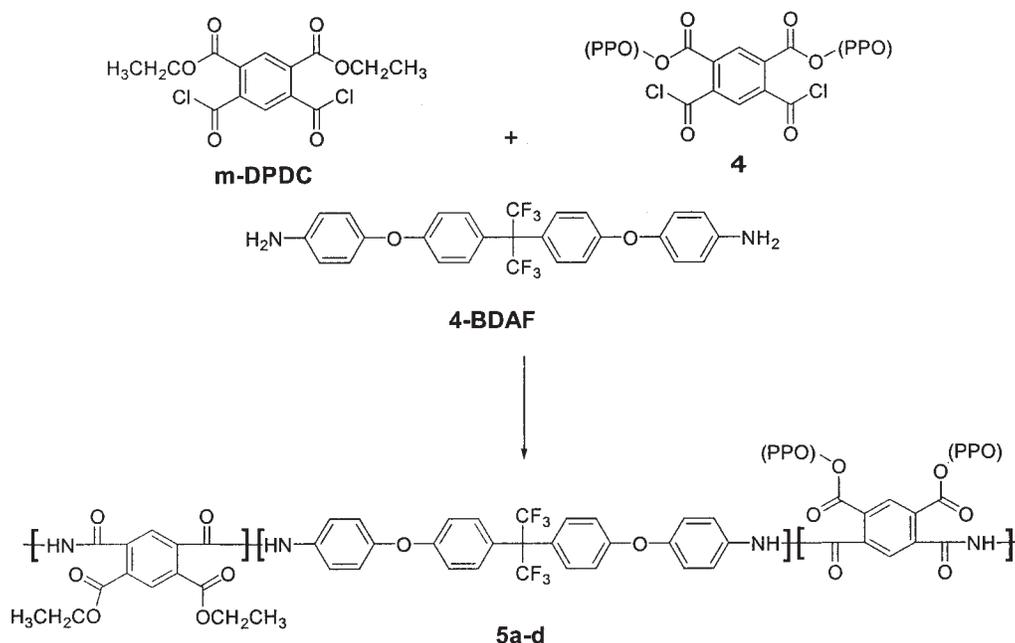


Figure 3. Synthesis of two-sided comb graft copolymers.

not unusual and was expected for these copolymers because of previously published findings.³

The graft copolymers were analyzed for the PPO content and $[\eta]$, and the results are shown in Table 1. There was good agreement between the amount of PPO that was added during the polymerization reaction and the amount found in the copolymers by ^1H NMR analysis. The PPO concentration was controllable from 3 to 27 wt %. The absolute molecular weight characterization of these types of graft copolymers proved to be challenging. Because GPC was cal-

ibrated with polystyrene standards, the values obtained for the various PAE/PPO block copolymers were not absolute values. We used these relative values to compare the prepared graft copolymers. We believe that the GPC values greatly underestimate the true molecular weights and that both GPC results and $[\eta]$ results can be used as good relative measurements. Similar underestimations are not uncommon for aromatic backbone polymers.^{11,12} In the end, it is only important that these materials have a high enough molecular weight to

Table 1. Analysis of the Copolymers

Sample	Acid Chloride	PPO in the Reaction (wt %)	$[\eta]$ by GPC (dL/g) ^a	PPO by ^1H NMR (wt %)
5a	Meta	3.5	0.28 (12,400)	2.9
5b	Meta	7.5	0.42 (11,900)	9.1
5c	Meta	12	0.25 (15,100)	13.6
5d	Meta	15	0.23 (6,400)	16.7
6a	Para	3.5	0.32 (28,500)	3.4
6b	Para	7.5	0.31 (28,600)	7.1
6c	Para	12	0.28 (22,900)	9
6d	Para	15	0.32 (26,000)	13
6e	Para	27	0.27 (19,200)	26

^a GPC was performed with respect to polystyrene standards; the values in parentheses are M_w 's.

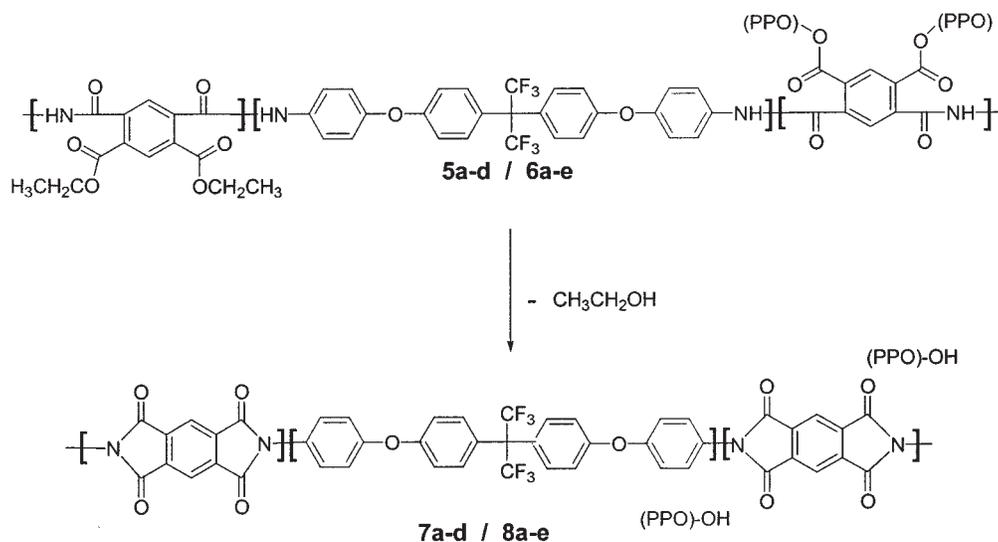


Figure 4. Imidization of the PAE/PPO copolymer leading to the formation of the PI/PPO composite.

enable chain entanglement and the formation of robust, freestanding thin films.

Some interesting trends can be noticed. Copolymers based on *m*-DPDC (**5a–5d**) appeared to have a lower molecular weight than analogous copolymers derived from *p*-DPDC polymers (**6a–6e**). *para*-PMDA-based PAEs (**6a–6e**) were rod-like, whereas *meta*-PMDA-based PAEs (**5a–5d**) were kinked and possessed more degrees of freedom. Therefore, the hydrodynamic volumes of the two systems were very different. This explains why the GPC results showed higher molecular weights for *para*-PMDA-based PAEs, the hydrodynamic volume of which was presumably higher than that for *meta*-PMDA-based polymers.

The viscosities of dilute solutions of all the copolymers were measured with a Cannon-Fenske capillary viscometer at 30.0 °C, and $[\eta]$ values were calculated in each case. $[\eta]$ can be related to the weight-average molecular weight (M_w) by the Mark–Houwink–Sakurada equation:¹³ $[\eta] = KM_w^a$, where K and a are coefficients whose values depend on the nature of the polymer, the temperature, and the solvent. K and a for these polymers were unknown, but we were able to use the measured values of $[\eta]$ for a relative comparison of the copolymers. All of the materials in Table 1 formed good, freestanding thin films from solution. Attempts to synthesize materials with PPO concentrations greater than 40% tended to yield very low-molecular-weight oligomers with $[\eta]$ values of 0.15 or less. These materials did not yield freestanding films; rather, they gave friable,

brick-dust powders upon solvent removal. These results indicated that copolymers with measured $[\eta]$ values greater than 2.5 dL/g had sufficiently high molecular weights to enable film formation.

The PAE/PPO graft copolymers were thermally imidized as thick films (10–40 μm) via casting from solutions on glass slides and or via spinning from solutions onto glass, quartz, and silicon wafers as thin films (0.5–2.5 μm). For the thick-film casting, the copolymers were dissolved in NMP at approximately 30 wt %. A solvent mixture of 1:1 cellosolve acetate and DMF was used for spinning the copolymers on quartz and silicon surfaces.

After the appropriate substrates were coated, the PAE/PPO films were heated, and the solvent was evaporated. As the heating continued, thermal imidization of the amic ester groups in the PAE/PPO copolymers occurred. The ethyl ester and PPO—O— ester bonds were broken during cycloimidization with the concurrent evolution of ethanol and the formation of free PPO within the curing PI matrix. Although gaseous ethanol permeated to the surface of the films and evaporated, PPO remained confined inside the PI structure, and this yielded a PI/PPO composite. PAE/PPO copolymers **5a–5d** and **6a–6e** were transformed into corresponding PI/PPO composites **7a–7d** and **8a–8e**, respectively (see Fig. 4).

The thermal curing process was conducted in an argon atmosphere with precise temperature control to ensure that the solvent was removed and imidization occurred, but at the same time, PPO degradation was avoided. The thermal cur-

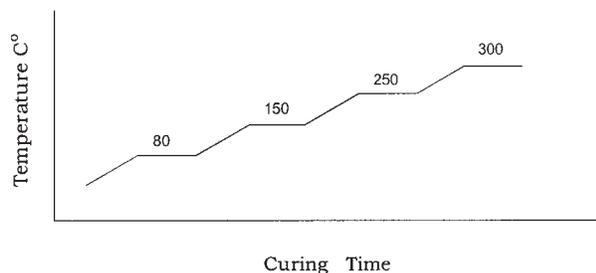


Figure 5. Thermal curing profile.

ing profile used is shown in Figure 5. A thermally controlled hotplate was regulated in a ramp and soak mode, with the ramp rate being 5 °C/min, and was held for an hour at each designated temperature:

Imidization occurred between 200 and 300 °C although PPO is known to be stable at these temperatures in the absence of oxygen.⁴ The PI/PPO composite films were cooled and examined by TGA and dynamic mechanical thermal analysis (DMTA). Isothermal TGA was performed in air at 300 °C for 1 h to observe the thermolysis of the PPO oligomer trapped within the cured PI matrix. We have previously demonstrated that PPO undergoes oxidative degradation into low-molecular-weight gaseous byproducts that diffuse from the PI matrix.³ The results of the TGA experiments are shown in Table 2.

An excellent agreement between the amounts of PPO incorporated into the original PAE/PPO copolymer and the final PI/PPO composite was observed. These data also confirm that the PPO oligomer was not destroyed during the argon-atmosphere cure.

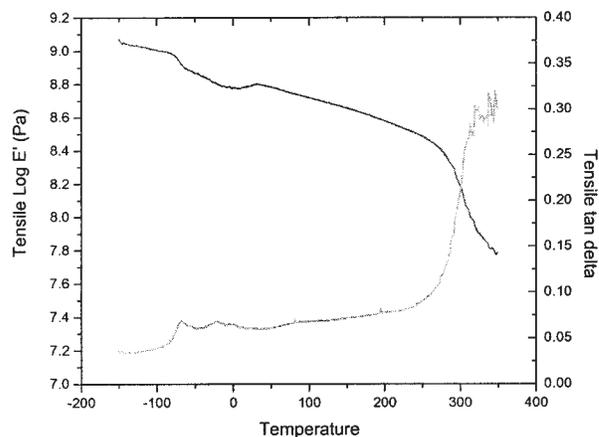


Figure 6. DMTA of composite **7b**.

The dynamic mechanical thermal behavior was also examined with DMTA. A film of PI/PPO composite **7b** was mounted in the tensile mode, and the mechanical response from –150 to 400 °C was measured. Plots of the tensile modulus (E') and loss tangent ($\tan \delta$) are shown in Figure 6. A slight drop in the modulus and an increase in the loss tangent was observed at –80 °C and was due to the glass-transition temperature for PPO. The presence of this transition confirmed that the PPO oligomer existed as a pure, unmixed phase within the PI matrix. A second high temperature transition, at approximately 300 °C, represented the glass-transition temperature of the matrix PI, 4-BDAF/PMDA.

To demonstrate the potential of these copolymers for creating porous PIs for possible use in low-dielectric-constant insulator applications, we examined the porosity of PI/PPO composites after

Table 2. Results from Isothermal TGA for Composites **7** and **8** and ^1H NMR Spectral Data for Original PAE/PPO Graft Copolymers **5** and **6**

Sample	PMDA (OEt) Isomer	PPO in the Reaction (%)	PPO by ^1H NMR (wt %)	PPO by TGA (wt %)
7a	Meta	3.5	2.9	3.4
7b	Meta	7.5	9.1	9.1
7c	Meta	12	13.6	13.5
7d	Meta	15	16.7	17.5
8a	Para	3.5	3.4	4
8b	Para	7.5	7.1	11.1
8c	Para	12	9	10.2
8d	Para	15	13	13.8
8e	Para	27	26	27

Table 3. Density Measurements for Porous PIs and Calculations of the Porosity

Sample	Density	PPO Incorporated (vol %)		Volume Fraction of Voids (Porosity; %)
		¹ H NMR	TGA	
PMDA/4BDAF	1.47			—
9a	1.41	4.2	4.6	4.1
9b	1.27	12.4	12.0	13.6
9c	1.21	18.3	17.6	17.7
9d	1.14	22.2	22.5	22.5

the thermolysis of the PPO block. Previous studies of PI nanofoams have shown that density measurements of PI films directly track their porosity and dielectric constant.^{3,5,9} Films of **5a–5d** were cured under argon as described previously, and this yielded the corresponding PI/PPO composites. Then, PPO was removed by thermolysis via the heating of the composite films to 250 °C in air for 30 min, and this yielded porous samples **9a–9d**.

The porous PI samples were isolated as free-standing thin films. The densities of the porous foamed PIs (**9a–9d**) were measured with a gradient density column calibrated with standard glass floats in the density range of 1.07–1.41 g/cm³. The measured densities are shown in Table 3 and were observed to track the amount of PPO present in the original films. The volume fractions of voids present in the porous samples were calculated from the densities of the samples and the known value of 1.47 g/cm³ for the homopolymer PMDA/4-BDAF.⁵ Porosities ranging from 4.1 to 22.5% were calculated. We found an excellent correlation with the volume percentage (calculated from the weight percentage) of PPO that was present in the copolymer films. These new graft copolymer film precursors have porosities comparable to those of previously studied linear ABA block copolymers also based on PMDA/4-BDAF PI.⁷

CONCLUSIONS

In the pursuit of routes to porous dielectric materials, we have studied porous PIs derived from PPO-containing precursor block copolymers. Previous studies have shown that ABA triblock copolymers, in which the A block is PPO and the B block is a PI or PI precursor, can undergo

nanophase separation and form discreet domains of PPO embedded within a PI matrix. Subsequent thermolysis of PPO yields porous PIs with pores that have the size and shape of the original phase-separated morphology. In this study, we sought to determine if new graft copolymers, also consisting of PPO and a PI precursor, could also be exploited to produce porous materials. New PAE/PPO two-sided comb graft copolymers were made via a clever macromonomer route. We synthesized and characterized these new graft copolymers, demonstrating a novel route to copolymers via step-growth polymerization. These polymers had sufficient molecular weight to form freestanding thin PI/PPO composite films upon imidization. The PPO phase could be selectively removed by thermolysis, and this yielded porous PI films. Future studies will examine the utility of these porous polymers in low-dielectric insulating applications and their potential use as gas-separation membranes.

The authors thank IBM Corp. for its support as most of the work described in this article was performed at the IBM Almaden Research Center in San Jose, CA.

REFERENCES AND NOTES

- (a) Liu, H.; Simone, C. D.; Scola, D. A. *J Polym Sci Part A: Polym Chem* 2003, 41, 2630; (b) Miyagawa, T.; Fukushima, T.; Oyama, T.; Iijim, T.; Tomoi, M. *J Polym Sci Part A: Polym Chem* 2003, 41, 861; (c) Fan, H.; Gu, Y.; Xie, M. *J Polym Sci Part A: Polym Chem* 2003, 41, 554; (d) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem Rev* 2004, 104, 4587.
- Polymers for Electronic Applications*; Lai, J. H., Ed.; CRC: Boca Raton, FL, 1989.
- Volkens, W.; Diller, R.; Yoon, D. Y. *Proceedings of the 2nd Technical Conference on Polyimides*; Sach-

- dev, H. S.; Khojasteh, M. M.; Feeger, C., Eds.; Society of Plastic Engineers: Hopewell Junction, NY, 1985; p 102.
4. Carter, K. R.; DiPietro, R. A.; Sanchez, M. I.; Swanson, S. A. *Chem Mater* 2001, 13, 213.
 5. (a) Kashiwa, N.; Matsugi, T.; Kojoh, S.-L.; Kaneko, H.; Kawahara, N.; Matsuo, S.; Nobori, T.; Imuta, J.-I. *J Polym Sci Part A: Polym Chem* 2003, 41, 3657; (b) Muehlebach, A.; Rime, F. *J Polym Sci Part A: Polym Chem* 2003, 41, 3425.
 6. Carter, K. R.; DiPietro, R. A.; Russell, T. P.; Sanchez, M. I.; Lakshmanan, P.; McGrath, J. E. *Chem Mater* 1997, 9, 105.
 7. Aida, T.; Mizuta, R.; Yoshida, Y.; Inoue, S. *Makromol Chem* 1981, 182, 1073.
 8. Carter, K. R.; DiPietro, R. A.; Hedrick, J. L.; Miller, R. D.; Furuta, P. T. *Polym Prepr* 1997, 38(1), 987.
 9. Carter, K. R.; Richter, R.; Kricheldorf, H. R.; Hedrick, J. L. *Macromolecules* 1997, 30, 6074.
 10. Hedrick, J. L.; Carter, K. R.; Labadie, J. W.; Miller, R. D.; Volksen, W.; Hawker, C. J.; Yoon, D. Y.; Russell, T. P.; McGrath, J. E.; Briber, R. M. *Adv Polym Sci* 1999, 141.
 11. Carter, K. R.; Furuta, P. T.; Gong, V. *Macromolecules* 1998, 31, 208.
 12. Havelka-Rivard, P. A.; Nagai, K.; Freeman, B. D.; Sheares, V. V. *Macromolecules* 1999, 32, 6418.
 13. Stevens, M. P. *Polymer Chemistry*; Oxford University Press: New York, 1990.