Preparation of Porous Thin Films of a Partially Aliphatic Polyimide

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ABSTRACT: A thermally labile polymer, poly(propylene glycol), was modified to obtain PPG having an amino end group. PPG was incorporated into a partially aliphatic polyimide based on an alicyclic dianhydride, and this afforded triblock copolymers containing various amounts of PPG blocks. The thermal properties of the copolymers were investigated by thermogravimetric analysis and differential scanning calorimetry. The thermal decomposition of the PPG block in the copolymers was carried out at 240°C under various pressures to obtain porous polyimide films. The pores remained during the thermolysis under a reduced pressure of 710 mmHg, whereas they collapsed under (near) atmospheric pressure. The pore size increased as the amount of the PPG block in the copolymers increased. The dielectric constants of the porous polyimides varied from 2.60 to 2.42 with the original copolymer composition. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 532–538, 2006

Key words: block copolymers; dielectric properties; foams; polyimides

INTRODUCTION

Polyimides have attracted much attention as insulating materials in the microelectronics industry because of their low dielectric constants, high thermal stability, and excellent mechanical properties.[1] The properties of polyimides, such as the dielectric constant, have been improved by various approaches for their use in the new generation of high-density integrated circuits.

The common approaches to reducing the dielectric constants of polyimides include the modification of their chemical structure and the generation of air-filled pores in a polyimide film.[2,3] Typical methods for the chemical modification of polyimides involve the incorporation of fluorine substituents or alicyclic structures. Fluorinated polyimides have been prepared to achieve reduced dielectric constants and enhanced solubility.[3,4] Alicyclic structures have also been incorporated into polyimide backbones to obtain partially or fully aliphatic polyimides with reduced dielectric constants and enhanced solubility/transparency.[5–18] As an alternative approach, the introduction of nanopores into a polyimide film is an effective way of lowering its dielectric constant.[2,3] On the other hand, as a combination of these methods, the introduction of pores into a fluorinated polyimide results in further reduction of the dielectric constant.[19,20]

Although the incorporation of pores in (partially) aliphatic polyimides is expected to provide several advantages, including reduced dielectric constants, there has been no report on this approach. In this article, the first example of the preparation of porous thin films of a partially aliphatic polyimide is described. The porous polyimide was prepared from triblock copolymers consisting of a polyimide block and a thermally labile polymer block. A novel method, the thermal decomposition of the labile block under reduced pressure, has been developed in this work for the prevention of pore collapse inside a polyimide film.

EXPERIMENTAL

Materials

Itaconic anhydride, cyclopentadiene, ammonium vanadate(V), poly(propylene glycol) monobutyl ether (number-average molecular weight = 4000), borane–trimethylamine complex, 4-nitrophenyl chloroformate, and p-phenylenediamine were purchased from Aldrich Chemical Co. (St. Louis, MO) and used without purification. Palladium(II) hydroxide on carbon was purchased from Lancaster Chemical Co. (Ward Hill, MA)

Characterization

^{1}H-NMR spectra were taken on a Varian Gemini 300-MHz spectrometer (Palo Alto, CA) in chloroform-*d* or methyl sulfoxide-*d*₆ with tetramethylsilane as an internal standard. IR spectra were recorded on a Genesis Fourier transform infrared (FTIR) spectrophotometer (Mattson Instrument Co., Fremont, CA). The molecular weights of the polymers were determined in *N,N*-dimethylformamide at 30°C at a flow rate of 1 mL/min with a Waters gel permeation chromatograph (Milford, MA) equipped with a Styragel column. The molecular weights were estimated with respect to polystyrene standards. Thermal analysis was carried out on a Shimadzu DSC-60 and a TGA-60 (Tokyo, Japan) at a heating rate of 10°C/min in air. Spin coating was performed with a Hana 150-A spin coater (Seoul, Korea). The film thickness was measured with a P-10 surface profiler (Tencor Instruments, San Jose, CA). Photomicrographs of the films were taken with a JEOL JSM-6700F scanning electron microscope (Tokyo, Japan) at 15 kV. For the optical dielectric constants, the out-of-plane and in-plane refractive indices of polyimide thin films were measured with a Metricon 2010 prism coupler (Pennington, NJ) equipped with a He–Ne laser light source (wavelength = 632.8 nm).

Synthesis of poly(propylene glycol) (PPG)

A mixture of 4-nitrophenyl chloroformate (0.50 g, 2.5 mmol), poly(propylene glycol) monobutyl ether (4.00 g, 1.0 mmol), and pyridine (0.20 mL, 2.5 mmol) in 30 mL of tetrahydrofuran (THF) was refluxed for 13 h. After filtration to remove a generated pyridinium salt and evaporation in vacuo, a nitro-containing polymer

was obtained as a pale yellow liquid (3.60 g). To a solution of the polymer in methanol (30 mL) were added 0.146 g of borane–trimethylamine complex and 0.070 g of palladium(II) hydroxide on carbon, and the resultant mixture was refluxed for 48 h. After filtration to remove the palladium catalyst, the solvent was stripped off. The product was dissolved in chloroform and washed with water. The removal of the solvent in vacuo gave PPG as a pale yellow liquid (3.16 g).

^{1}H-NMR (CDCl₃, δ): 6.94 (d, aromatic), 6.65 (d, aromatic), 3.68–3.37 [m, OC*H*(CH₃)C*H*₂], 1.09 [s, OCH(C*H*₃)CH₂]. IR (KBr, cm^{-1}): 3339 and 3279 (NH₂ stretching), 2971 and 2870 (C—H), 1750 (C=O), 1512 (aromatic C=C).

Synthesis of the triblock copolymers

Rel-[1*S*,5*R*,6*R*]-3-oxabicyclo[3,2,1]octane-2,4-dione-6-spiro-3'-(tetrahydrofuran-2',5'-dione) (DAn) was prepared from itaconic anhydride and cyclopentadiene according to a previously reported procedure, and its ^{1}H-NMR and FTIR data well agreed with those reported.[8] Three triblock copolymers (**P27**, **P16**, and **P8**) were synthesized in a similar manner, and the preparation of **P27** can be described as follows. A mixture of DAn (0.896 g, 4.00 mmol) and *p*-phenylenediamine (0.411 g, 3.95 mmol) in *N,N*-dimethylacetamide (DMAc; 10 mL) was heated at 60°C for 6 h. After it cooled to room temperature, PPG (0.350 g, 0.088 mmol) was added, and the resultant solution was stirred for 18 h. Acetic anhydride (4 mL) and pyridine (3 mL) were added to the solution, and the mixture was refluxed for 15 h. Washing with water (100 mL) and methanol (100 mL), followed by drying in vacuo, gave a light-brown solid (1.208 g).
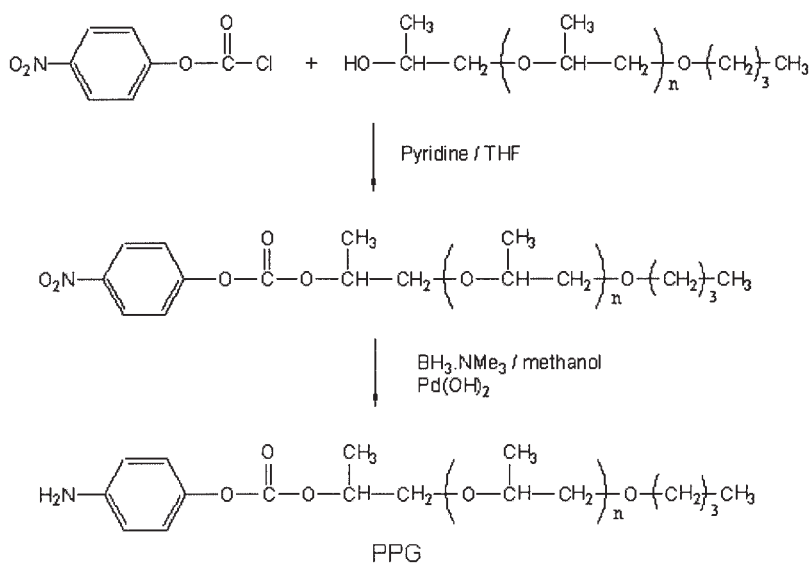
Scheme 1 Synthesis of PPG.

P27, P16, P8
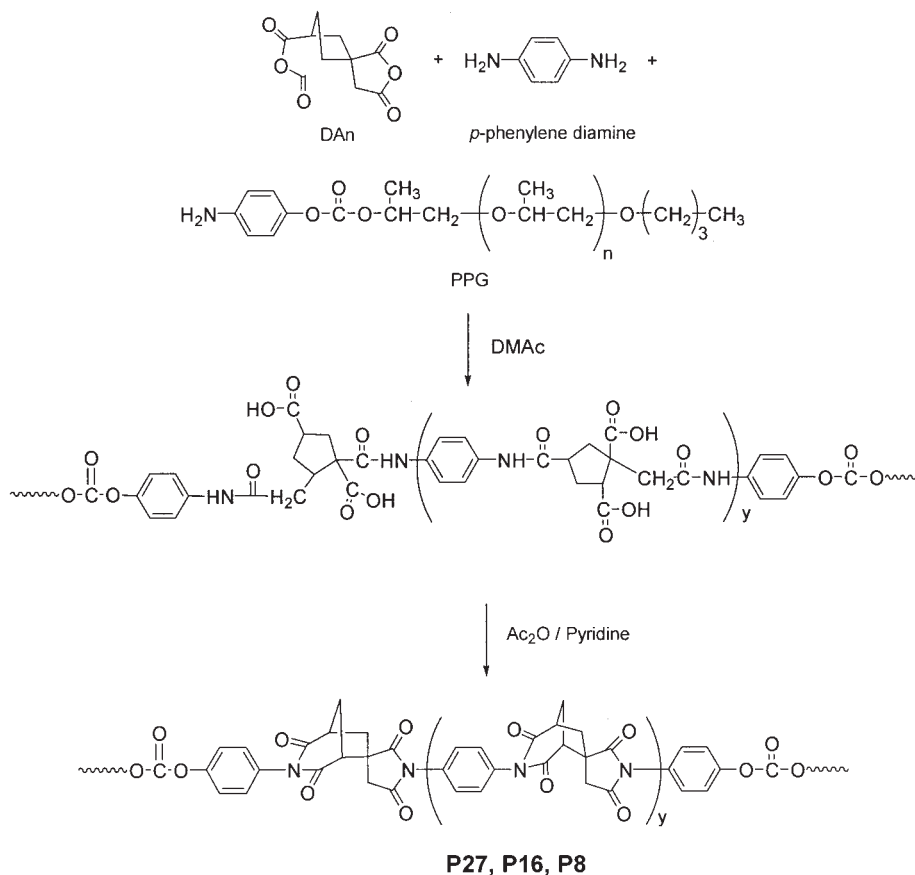
Scheme 2 Synthesis of the triblock copolymers.

IR (KBr, cm^{-1}): 2969 and 2933 (C—H), 1781 (asymmetric C=O stretching), 1718 and 1692 (symmetric C=O stretching), 1513 (aromatic C=C), 1358 (C—N).

Preparation of the porous polyimide films

A copolymer solution was prepared by the dissolution of a copolymer (0.10 g) in 2 mL of methyl sulfoxide followed by filtration with a membrane filter with a 0.2-μm pore size. The solution was applied to silicon wafers, and the resultant films were annealed at 170°C for 3 h. The film thickness was in the range of 7–15 μm. The films were subjected to heating at 240°C for 90 min in a vacuum oven to induce the thermal degradation of the PPG block. The pressure inside the oven was varied from 1 to 760 mmHg.

RESULTS AND DISCUSSION

Synthesis of the triblock copolymers

Porous polyimide films can be prepared from triblock copolymers consisting of a thermally stable polyimide block and a thermally labile polymer block, the latter being the dispersed phase.[2] The phase-separated domain of the labile block is thermally decomposed,

leaving pores of a size and shape corresponding to the initial morphology. In this work, PPG was synthesized as a labile polymer by a two-step procedure, as shown in Scheme 1. Nitrophenyl groups were introduced by the reaction of 4-nitrophenyl chloroformate with hydroxyl end groups of poly(propylene glycol) monobutyl ether.[19] The nitro groups were then subjected to

TABLE I
Molecular Weights, PPG Contents, and Dielectric Constants for the Triblock Copolymers (P27, P16, and P8) and the Homopolymer (P0)

| | | | PPG content (wt %) | | | |
| | | | | Incorporated | | Dielectric |
Code	$M_w{}^a$	$M_n{}^a$	Charge	TGA	NMR	constant^b
P27	48,800	44,700	27	19	17	2.42
P16	53,700	52,200	16	13	13	2.52
P8	71,200	68,400	8	8	8	2.60
P0	62,400	60,200	0	0	0	2.73

^{a} The weight-average molecular weight (M_w) and number-average molecular weight (M_n) were measured by gel permeation chromatography.
^{b} The values for **P27, P16,** and **P8** were obtained from their porous films, and the value for **P0** was obtained from its nonporous film.
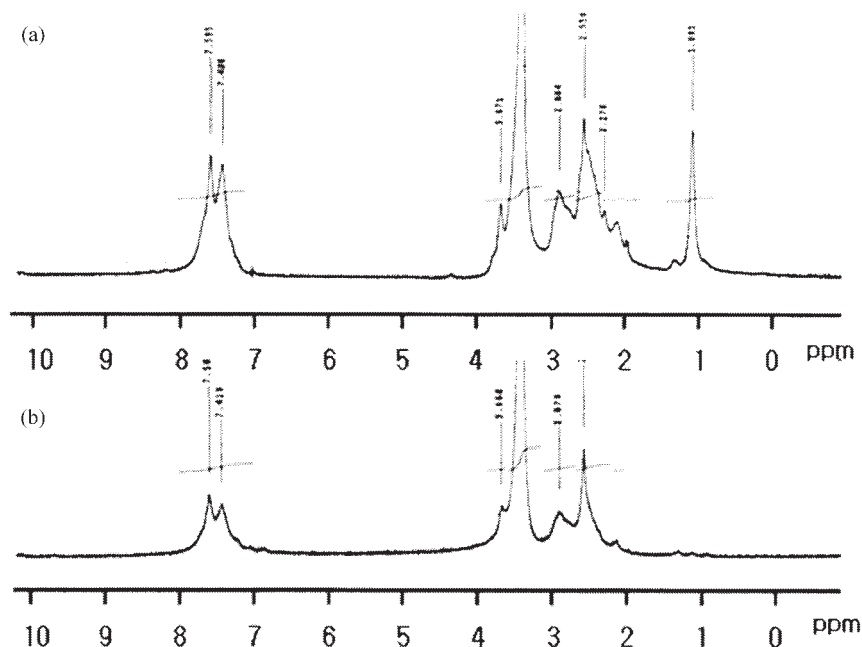
Figure 1 ^{1}H-NMR spectra of **P16** (a) before and (b) after heating at 240°C for 90 min under a pressure of 710 mmHg.

reduction with a palladium catalyst to obtain PPG. In FTIR spectroscopy, an absorption band at 1528 cm^{-1} due to stretching of the nitro group disappeared, and new bands at 3339 and 3279 cm^{-1} due to stretching of the amino group appeared after the reduction. The formation of PPG was also supported by ^{1}H-NMR spectroscopy (with CDCl$_3$ as the solvent): double doublet peaks around 7.8 ppm due to the nitrophenyl group shifted to around 6.8 ppm after the reduction, indicating the conversion of the nitro group to the amino group.

The triblock copolymers (**P27**, **P16**, and **P8**) were synthesized from DAn, *p*-phenylenediamine, and PPG (Scheme 2 and Table I). PPG was added to a reaction mixture of DAn and *p*-phenylenediamine to obtain poly(amic acid) having the PPG blocks as end groups. Imidization of the poly(amic acid) was performed in the presence of acetic anhydride. In ^{1}H-NMR spectroscopy (with methyl sulfoxide-d_6 as the solvent), carboxylic and amide proton peaks at 12.4 and 9.9 ppm, respectively, disappeared after the imidization reaction, and a methyl proton peak of the PPG block at 1.1 ppm was observed, indicating the formation of the copolymers [Fig. 1(a)]. This was supported by the IR spectral data described in the Experimental section. For comparison, a homopolymer (**P0**) was prepared without the addition of PPG. The molecular weights of the polymers are summarized in Table I.

On the basis of a comparison of the two areas (7.0–8.0 ppm for aromatic protons and 1.1 ppm for methyl protons in the PPG block) in the ^{1}H-NMR spectrum for each copolymer, the PPG content in the copolymers was calculated and is summarized in Table I. The copolymer composition was also studied by thermo-
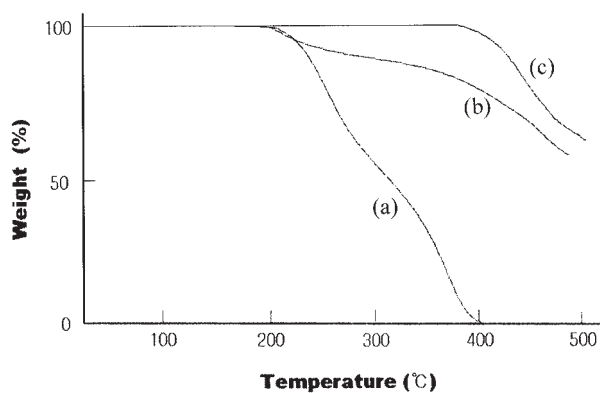

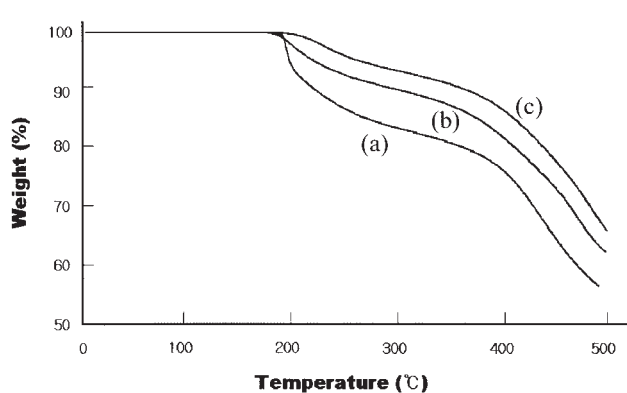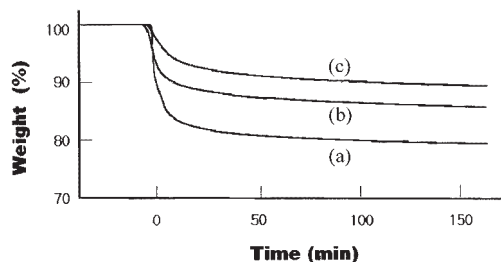**Figure 2** TGA thermograms of (a) PPG, (b) **P16**, and (c) **P0**.

Figure 3 TGA thermograms of (a) **P27**, (b) **P16**, and (c) **P8**.

Figure 4 TGA isotherms of (a) **P27**, (b) **P16**, and (c) **P8** obtained by the heating of the copolymers at 240°C.

gravimetric analysis (TGA) through the measurement of the weight loss of the PPG block upon the heating of the copolymers. The TGA results were in good agreement with the values confirmed by ^{1}H-NMR. The amounts of PPG observed, however, were lower than the amounts originally charged into the copolymer synthesis in the cases of **P27** and **P16**. This discrepancy might be due to the loss of low-molecular-weight fractions, high in PPG content, during the polymer isolation process.[21]

Thermal properties of the polymers

TGA thermograms of PPG, **P16**, and **P0** are shown in Figure 2. Thermal decomposition began for PPG at 210°C and for **P0** at 407°C. The triblock copolymer **P16** showed two-step decomposition [Fig. 2(b)]. It was

thought that the first and second steps, beginning at 207 and 395°C, were due to the degradation of the PPG and polyimide blocks, respectively.

Figure 3 shows TGA thermograms of the three copolymers (**P27**, **P16**, and **P8**) containing different amounts of the PPG block. As the PPG weight percentage in the copolymers increased, the weight loss due to the thermal degradation of the PPG block increased. The isothermal decomposition of the three copolymers was performed at 240°C, and their TGA isotherms are shown in Figure 4. It was confirmed by ^{1}H-NMR spectroscopy that the peak at 1.1 ppm due to the methyl protons in the PPG block completely disappeared after heating at 240°C for 90 min [Fig. 1(b)].

To prevent pore collapse during the thermal decomposition of the labile block, the glass-transition temperature (T_g) of the polyimide matrix needs to be higher than the thermal decomposition temperature of the PPG block.[2] Differential scanning calorimetry analysis was carried out to investigate T_g of polyimide **P0**, but T_g was not observed.[22]

Preparation of the porous polyimide films

The films of the triblock copolymers were prepared by the spin coating of the copolymer solutions followed by annealing at 170°C. The thermolysis of the PPG block was performed by the heating of the samples at 240°C in a vacuum oven to obtain porous polyimide
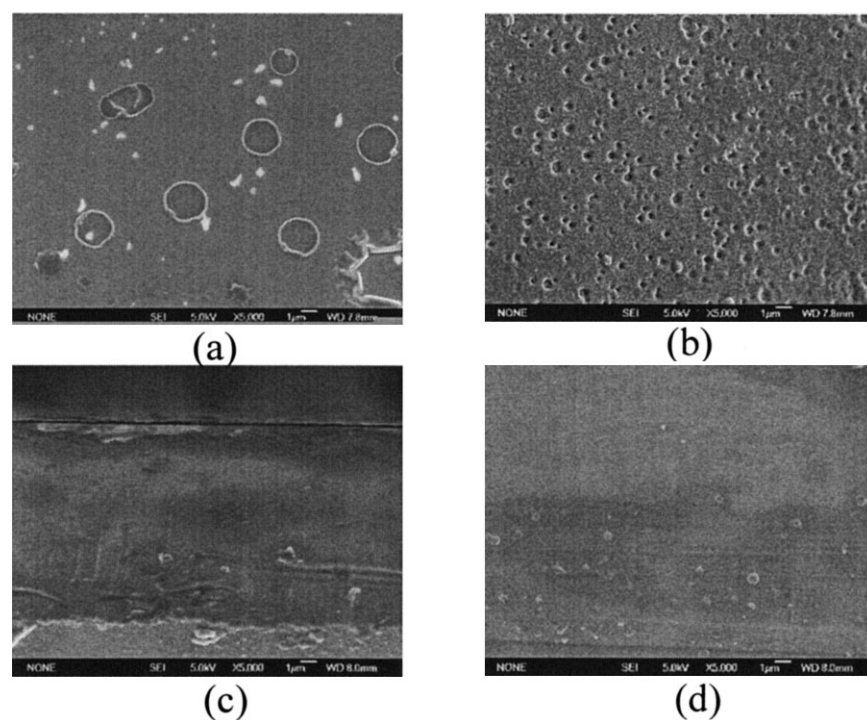
Figure 5 SEM micrographs of cross sections of films prepared by the thermolysis of **P16** under pressures of (a) 1, (b) 710, (c) 735, and (d) 760 mmHg.
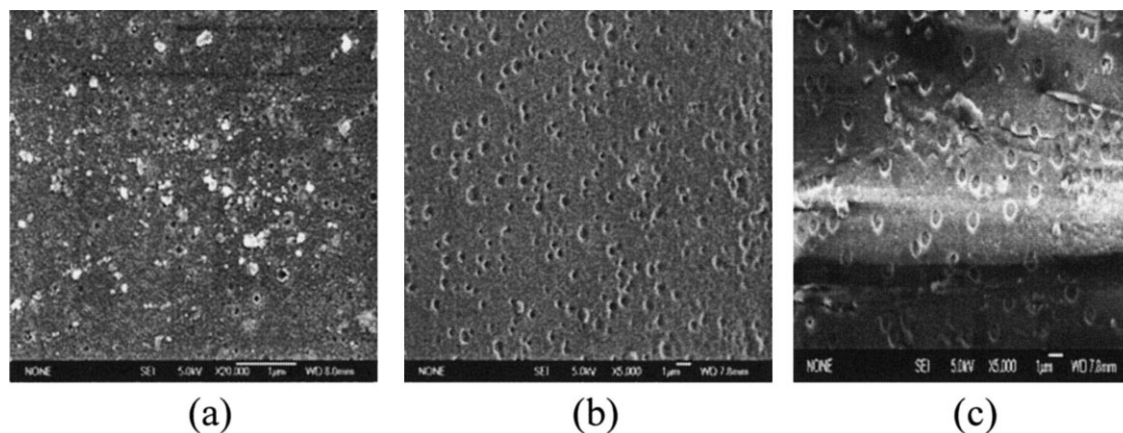
Figure 6 SEM micrographs of cross sections of porous films prepared from copolymers (a) **P8**, (b) **P16**, and **P27** under 710 mmHg.

films. Figure 5 shows scanning electron microscopy (SEM) micrographs of cross sections of the films prepared by the thermolysis of **P16** under various pressure conditions. The thermal treatment under 760 or 735 mmHg did not leave pores inside the film [Fig. 5(c,d)], and pores were only observed on the film surfaces; this indicated that internal pores once formed upon thermolysis but collapsed soon. One main reason for the pore collapse in the polyimide is known to be the plasticization of the polyimide matrix by degradation products.[2] Under a lower pressure of 710 mmHg, however, closed pores having diameters of 200–500 nm were observed inside the film [Fig. 5(b)]. The reduced pressure condition might have assisted the degradation products in rapidly diffusing from the polyimide matrix and/or the pore structure in being held, resulting in the prevention of pore collapse. Very big pores with diameters larger than 2 μm formed under a high vacuum of 1 mmHg [Fig. 5(a)]. It was thought that the pores formed upon thermolysis and expanded because of the high vacuum.

As shown in Figure 6, polyimide films with closed pores were successfully obtained by the heating of the films of the three copolymers (**P8**, **P16**, and **P27**) at 240°C and 710 mmHg. As the weight percentage of the PPG block increased, the pore size increased: **P8** gave pores with diameters below 100 nm, and **P27** gave pores of about 1 μm. This was attributable to the increase in the domain size of the phase-separated PPG block in the polyimide film with increasing PPG content.

The dielectric constants for a nonporous **P0** film and porous films prepared from **P27**, **P16**, and **P8** were measured with an optical method (474.08 THz) and calculated with Maxwell's identity ($\varepsilon = n_{TM}^2$). The **P0** film had a relatively low dielectric constant of 2.73 (Table I). The incorporation of pores into the polyimide resulted in reduced dielectric constants, and the film prepared from **P27** showed the lowest value of 2.42. The nanoporous polyimide film prepared from **P8** showed a dielectric constant of 2.60.

CONCLUSIONS

Porous thin films of a partially aliphatic polyimide were successfully prepared. The pores collapsed during the thermal treatment of the block copolymers under (near) atmospheric pressure, but they remained under a reduced pressure of 710 mmHg. Nanoporous films were prepared from **P8**, and larger pores were obtained from **P27** and **P16**. The pore size was controllable through changes in the content of the labile polymer, PPG. It is thought that the pore size can be further controlled through changes in the molecular weight of the labile polymer. The novel method developed in this work, that is, the thermal decomposition of the labile polymer block under reduced pressure, would be very useful in the preparation of nanoporous polyimides as low-dielectric-constant materials.

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