

Porous Polyimide Films Prepared by Thermolysis of Porogens with Hyperbranched Structure

Dong Wook Kim,¹ Yongku Kang,¹ Moon Young Jin,¹ Sangil Seok,¹ Jong Chan Won,¹ Changjin Lee,¹ Jungboon Yi,² Jeongsoo Kim,² Jongku Kang,³ Jae Sup Shin³

¹Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Daejeon 305-600, Korea

²Department of Polymer Science and Engineering, Chungnam National University, Daejeon 305-764, Korea

³Department of Chemistry, Chungbuk National University, Cheongju 361-763, Korea

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ABSTRACT: Two hyperbranched molecules, benzenetricarboxylic acid dendritic benzyl ether ester (BTRC–BE) and benzenetricarboxylic acid polyethylene glycol ester (BTRC–PEG), were prepared and tested as pore-generating agents (porogens) for the preparation of porous polyimide. The hyperbranched molecules were thermally stable during the imidization process and completely decomposed well below the degradation temperature of polyimides, indicating that they possessed desirable thermal decomposition characteristics as porogens for the porous polyimide. From the SEM analysis dispersed domains were observed in the poly(amic acid) films containing BTRC–BE, whereas no phase separation was observed in the poly(amic acid) films containing BTRC–PEG. This may be attributable to the different polar-

ities of the porogens because the hydrophobic BTRC–BE was phase-separated in the hydrophilic poly(amic acid) matrix but BTRC–PEG was well mixed with poly(amic acid). The morphology developed in the poly(amic acid) film was retained after imidization and decomposition of the porogens; thus only BTRC–BE produced the porous polyimide. As the content of BTRC–BE decreased from 20 to 5 wt %, the pore size decreased from 390 ± 100 to 90 ± 50 nm and the pore density also decreased. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1711–1718, 2004

Key words: porous polyimides; porogens; hyperbranched; thermal properties; phase separation

INTRODUCTION

Polyimides have been the focus of extensive academic research and industrial applications because of its excellent thermal stability and good mechanical properties.¹ Recently porous polyimide has also gained increasing interest for many applications such as low dielectric insulators,^{2–8} gas-separation membranes,⁹ and light heat insulators.¹⁰ Several techniques have been introduced to prepare porous polyimide such as use of blowing agents,^{11,12} the phase-inversion method,^{9,13} and pyrolysis of thermally labile phase-separated compounds.^{2–8,14–18} The last method, originally developed by the IBM group, is a very promising route to a nanoporous polyimide and uses a phase-separated block copolymer consisting of a thermally stable polyimide block and thermally labile block, where the latter constitutes a dispersed phase. Toward this end, poly(propylene oxide),^{4,5} poly(methylmethacrylate),⁶ poly(α -methylstyrene),⁷ and poly(lactones)⁸ have been used as labile coblocks with polyimide. Recently Takeichi et al.^{16–18} also reported prep-

aration of a porous polyimide from poly(urethane-imide) films obtained by the reaction between poly(amic acid) and prepolymers of polyurethane. The thermally labile urethane components, which were grafted into polyimide during the imidization process, were phase-separated in the imide matrix, and then pores with a size of 0.7–30 μm , depending on the component ratio, were generated in the polyimide through thermal decomposition.

Investigative interest in the field of dendritic molecules, which have highly branched structures emanating from a central core with multiple end groups, has increased explosively in recent years as new synthetic strategies are reported and novel applications are explored.^{19–21} One of the promising applications of such highly branched molecules is found for templating agents in the preparation of porous materials. The thermally labile hyperbranched molecules incorporated in the organosilicate matrix, for example, were phase-separated as the dispersed domains and they were thermolyzed to generate nanoporous composites, which show ultralow dielectric constant.^{22–25} In such a case the control of porosity would be accomplished by tailoring the chemical structure of dendritic molecules, such as the nature of the peripheral group and branching units, given that the pore size and

Correspondence to: C. Lee (cjlee@kriict.re.kr).

shape depend strongly on miscibility between the matrix and the labile component.

Although the dendritic molecules have often been used as the porogens for the organosilicate matrix, little work has been done for them to be used for the preparation of porous polyimide. In this work, two hyperbranched molecules with different polarities were prepared and used as the pore-generating agents (porogens) for the preparation of porous polyimide. The poly(amic acid) films incorporated with porogen materials were fabricated and cured thermally. Subsequently the thermally labile components were decomposed at elevated temperatures to generate a porous polyimide. Phase separation of the porogens in the poly(amic acid) and polyimide matrix, and the size and density of the pores in the porous polyimide were studied by scanning electron microscopy (SEM).

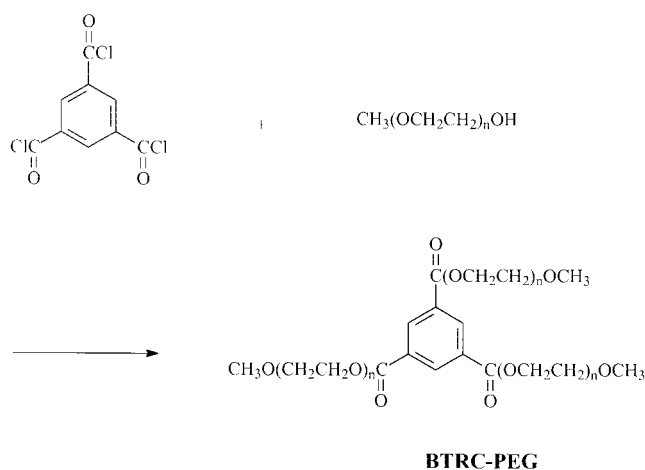
EXPERIMENTAL

Materials

Poly(ethylene glycol)methyl ether ($M_n = 750$) was obtained from Aldrich Chemical (Milwaukee, WI) and purified by flash column chromatography using a mixture of methanol and methylene chloride as an eluent before use. 1,3,5-Benzenetricarbonyl trichloride, benzyl alcohol, epichlorohydrin, tetrabutylammonium iodide, methallyl dichloride, sodium hydride, and triethylamine were purchased from Aldrich Chemical and used without further purification. 4,4-Oxydianiline (ODA, Aldrich) was purified by vacuum sublimation and pyromellitic dianhydride (PMDA, Aldrich) was recrystallized from 2-butanone. All solvents including tetrahydrofuran (THF), dimethylacetamide (DMAc), toluene, and methylene chloride were purified by standard procedures.

Synthesis of BTRC-PEG

BTRC-PEG (benzenetricarboxylic acid polyethylene glycol ester) was synthesized as shown in Scheme 1 and the detailed procedure is as follows. Poly(ethylene glycol)methyl ether (46.5 g, 62 mmol) and triethylamine (6.28 g, 62 mmol) were dissolved in methylene chloride and the solution was cooled in the ice-water bath. The methylene chloride solution of 1,3,5-benzenetricarbonyl trichloride (5 g, 18.8 mmol) was added dropwise to the solution and the mixture was stirred for 24 h. After the reaction was completed, the solution was washed with an aqueous solution of sodium bicarbonate and the organic portion was dried with $MgSO_4$. After evaporating the solvent, the residue was purified by column chromatography using a mixture of methanol and methylene chloride (methanol : methylene chloride = 1 : 15) as an eluent to give a light yellow liquid (BTRC-PEG, yield: 60%). 1H -



Scheme 1 Synthesis of porogen BTRC-PEG.

NMR ($CDCl_3$); δ (ppm) = 3.37 (s, $-OCH_3$, 9H), 3.53–3.71 (m, $-OCH_2CH_2O-$), 3.85 [t, $-C(O)OCH_2CH_2-$, 6H], 4.53 [t, $-C(O)OCH_2CH_2-$, 6H], 8.87 (s, aromatic protons, 3H).

Synthesis of BTRC-BE

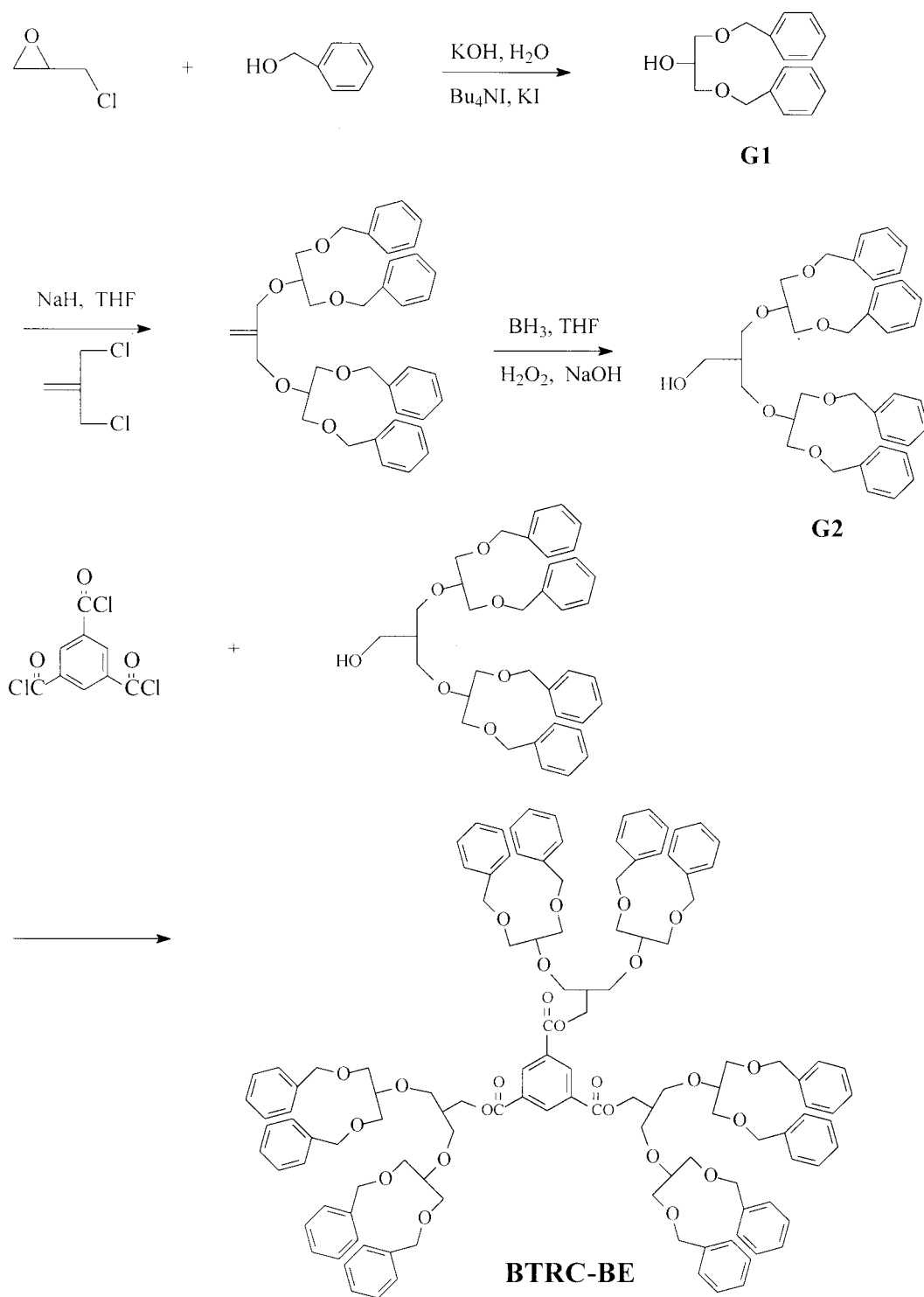
BTRC-BE (benzenetricarboxylic acid dendritic benzyl ether ester) was synthesized as shown in Schemes 2 and 3-(2-benzyloxy-1-benzyloxymethylethoxy)-2-(benzyloxy-1-benzyloxymethyl ethoxymethyl)-1-propanol (dendritic benzyl ether alcohol) was prepared following the literature procedure.²⁶

Synthesis of 3-[2-benzyloxy-1-(benzyloxymethyl)ethoxy]2-[2-benzyloxy-1-(benzyloxymethyl) ethoxy]methyl]-1-propanol (**G2**)²⁶

Epichlorohydrin was reacted with benzyl alcohol to give 1,3-bis(benzyloxy)-2-propanol (**G1**, yield: 82%). 1H -NMR ($CDCl_3$), δ (ppm) = 2.61 (s, 1H), 3.43–3.61 (m, 4H), 3.96–4.03 (m, 1H), 4.51 (s, 4H), 7.23–7.35 (m, 10H).

The reaction between 1,3-bis(benzyloxy)-2-propanol (**G1**) and methallyl dichloride in the presence of sodium hydride to give 7-methylene-1, 13-diphenyl-4,10-bis (benzyloxymethyl)-2,5,9,12-tetraoxatridecane (yield: 68%). 1H -NMR ($CDCl_3$), δ (ppm) = 3.39–3.61 (m, 8H), 3.65–3.73 (m, 2H), 4.10–4.16 (s, 4H), 4.42–4.53 (s, 8H), 5.17–5.24 (s, 2H), 7.18–7.35 (m, 20H).

7-Methylene-1, 13-diphenyl-4,10-bis (benzyloxy-methyl)-2,5,9,12-tetraoxatridecane was treated with BH_3 and then with H_2O_2 aqueous solution to yield **G2** (yield: 62%). 1H -NMR ($CDCl_3$), δ (ppm) = 2.03–2.18 (m, 1H), 3.06–3.13 (s, 1H), 3.42–3.64 (m, 16H), 4.41–4.60 (s, 8H), 7.18–7.35 (m, 20H).

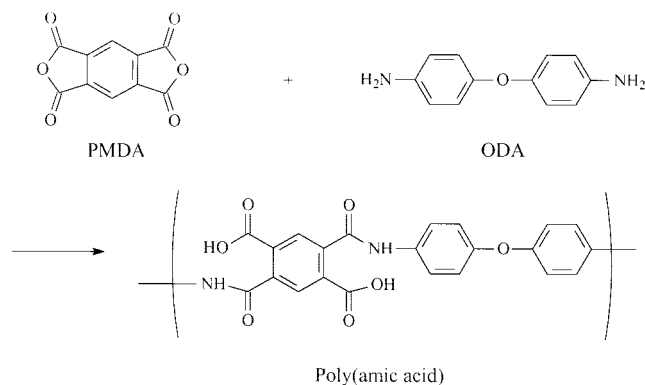


Scheme 2 Synthesis of porogen BTRC-BE.

Synthesis of BTRC-BE

G2 (9 g, 14.69 mmol) and 1,3,5-benzenetricarbonyl trichloride (1.18 g, 4.45 mmol) were added to methylene chloride (80 mL) and the mixture was stirred at 0°C. A solution of triethylamine (1.62 g, 16.02 mmol) in methylene chloride was then added dropwise. After

stirring the mixture for 12 h, it was poured into saturated aqueous NH₄Cl and the aqueous layer was extracted several times with methylene chloride. The combined organic layer then dried over anhydrous MgSO₄ and the solvent was removed under vacuum. The residue was purified by column chromatography



Scheme 3 Preparation of poly(amic acid).

using a mixture of ethylacetate and hexane as an eluent (BTRC-BE, yield: 38%). $^1\text{H-NMR}$ (CDCl_3), δ (ppm) = 2.35–2.42 (m, 3H), 3.34–3.81 (m, 43H), 4.36–4.53 (s, 30H), 7.11–7.19 (m, 60H), 8.74 (s, 3H).

Preparation of porous polyimide

4,4'-Oxydianiline (ODA, 4.00 g, 20 mmol) was dissolved in 80 mL of DMAc and the solution was cooled to 0°C in an ice-water bath. Under nitrogen flow, pyromellitic dianhydride (PMDA, 4.36 g, 20 mmol) was added to the solution and vigorously agitated by a mechanical stirrer. When the viscosity of the solution increased and stirring was no longer possible, the reaction was stopped, to yield a yellow viscous poly(amic acid) solution (Scheme 3). The inherent viscosity of the poly(amic acid) was 2.5 dL/g at the concentration of 0.5 g/dL in DMAc at 30°C when measured with a Ubbelohde viscometer.

The poly(amic acid) solution was diluted with DMAc to 5 wt % and then BTRC-PEG or BTRC-BE was added to the solution and mixed well with a homogenizer. The resulting solution was coated onto a glass substrate with a doctor blade and then dried in an oven at 100°C for 1 h to remove the excess solvent. Subsequently the films were placed in the furnace under nitrogen flow and the temperature of the furnace was increased to 200°C at the rate of $10^\circ\text{C}/\text{min}$ and maintained at 200°C for 1 h, then increased again to 300°C and maintained at 300°C for 3 h, which produced a yellow film with a thickness of about 50 μm . The films were then heated to 440°C over a 2 h period and held for 10 h to decompose the thermally labile components in a nitrogen atmosphere.

Measurements

$^1\text{H-NMR}$ spectra were recorded with a Bruker model DPX-300 spectrometer (Bruker Instruments, Darmstadt, Germany). Variable-temperature thermal gravimetric analysis (TGA) was performed on a TA Instru-

ments (New Castle, DE) model 2950 in a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. Scanning electron micrographs were observed with a Philips Instruments (Eindhoven, The Netherlands) XL30S FEG on the cross section of cryogenically fractured films in liquid nitrogen.

RESULTS AND DISCUSSION

Figure 1(a) shows the $^1\text{H-NMR}$ spectrum of BTRC-PEG. The peaks at 4.53 ppm are attributed to the ester bond formed by the reaction of 1,3,5-benzenetricarbonyl trichloride and poly(ethylene glycol)methyl ether. The observed $^1\text{H-NMR}$ spectrum was consistent with the assigned structure. In particular, the appearance of only one single aromatic proton peak at 8.87 ppm indicated all three arms were successfully substituted. Otherwise, another aromatic proton peaks should appear at 8.93 and 8.80 ppm.

BTRC-BE was prepared by the convergent route developed by Jayaraman and Fréchet,²⁶ as shown in Scheme 2. Epichlorohydrin was reacted with benzyl alcohol to yield **G1**. The reaction of **G1** with methallyl dichloride and subsequent treatment with BH_3 and H_2O_2 yielded **G2**. Finally, the **G2** was attached to the core unit, 1,3,5-benzenetricarbonyl trichloride, to produce BTRC-BE. Once again the $^1\text{H-NMR}$ spectrum [Fig. 1(b)] was consistent with the assigned structure.

The thermal characteristics of the prepared hyperbranched compounds were examined by TGA and the results are shown in Figure 2. The decomposition of BTRC-BE started at 320°C and completed at 430°C and for BTRC-PEG, decomposition occurred from 350 to 450°C . Because imidization of poly(amic acid) prepared from PMDA and ODA started at about 100°C , more than 95% of imidization was completed at 250°C , and the polyimide degraded above 500°C , and thus both compounds were suitable for the porogen.¹

The prepared hyperbranched materials were well mixed with the DMAc solution of poly(amic acid). The resulting clear and transparent solution was cast onto the glass substrate with a doctor blade and then dried at 100°C for 1 h. A free-standing film was obtained after peeling off from the substrate. Figure 3(a) shows the TGA thermogram for the poly(amic acid) films containing 20 wt % of BTRC-BE after drying. Three transitions are clearly observed in the weight changes in the range of 50 – 700°C . The first transition between 100 and 200°C is attributed to the evaporation of residual solvent and the loss of water generated from the imidization. The second weight loss that begins at around 340°C must be attributed to decomposition of the BTRC-BE in the films. The third stage over 550°C corresponds to the thermal degradation of the imide component. Figure 3(b) shows the TGA thermogram of polyimide film containing the porogens BTRC-BE that was prepared after imidization of the correspond-

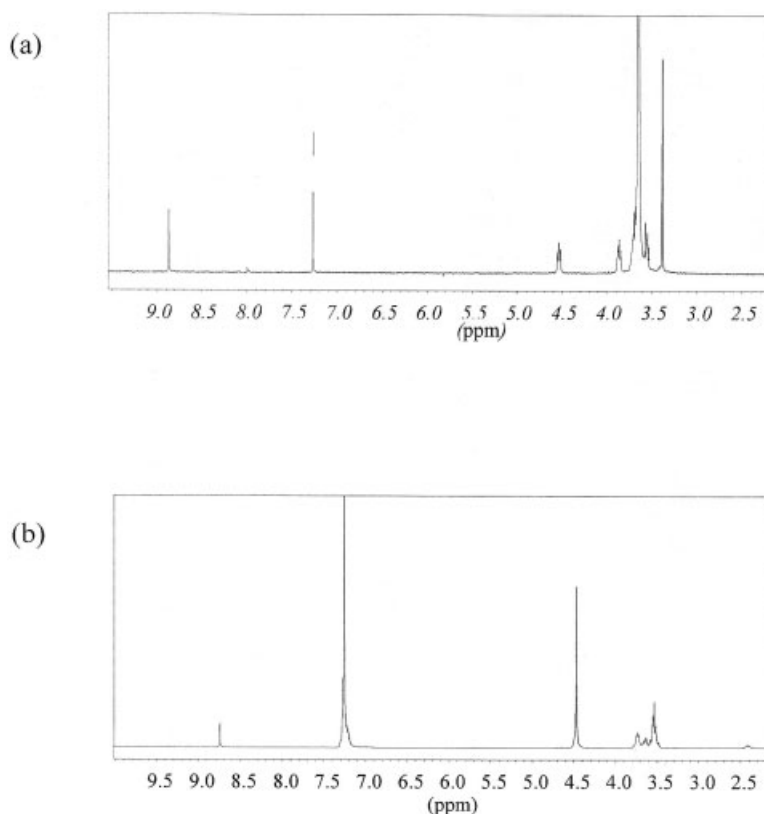


Figure 1 ¹H-NMR spectra of (a) BTRC-PEG and (b) BTRC-BE.

ing poly(amic acid) film in the furnace. The weight loss by the decomposition of BTRC-BE was well observable in Figure 3(b). The observed weight loss was about 17%, which was a little smaller than the originally added amounts of porogen, and thus small amounts of porogen may be decomposed during the imidization process. After heating the film at 440°C, complete decomposition of porogen was indicated be-

cause no weight loss up to 550°C was observed in Figure 3(c) for the polyimide film after heat treatment at 440°C.

Similar thermograms were also observed for the poly(amic acid) film containing BTRC-PEG, as shown in Figure 4(a). However, Figure 4(b) shows much less weight loss (~ 11%), indicating that the PEG side

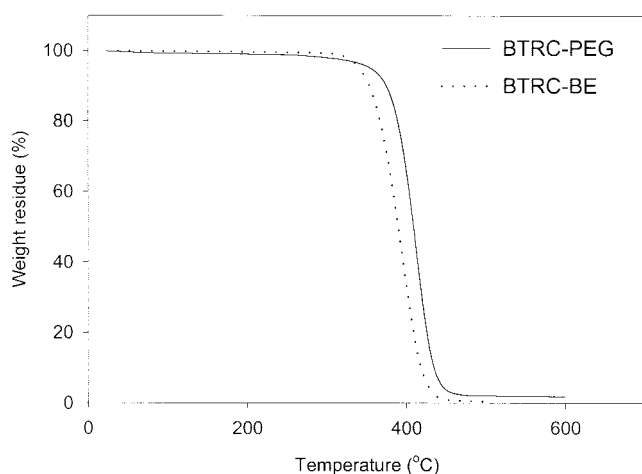


Figure 2 TGA thermogram of the pristine BTRC-BE and BTRC-PEG.

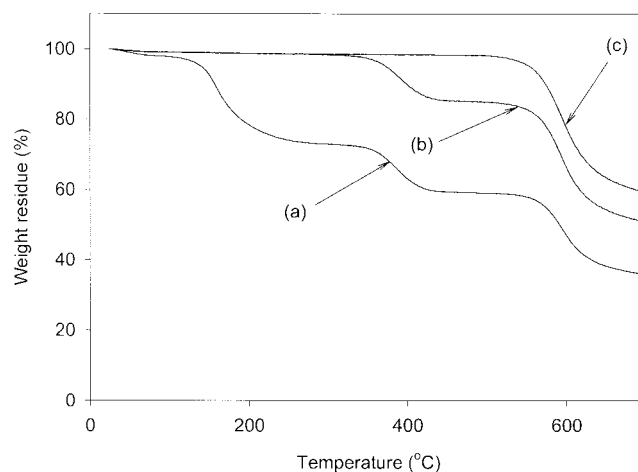


Figure 3 TGA thermograms of (a) poly(amic acid) film containing BTRC-BE after drying at 100°C for 1 h, (b) polyimide film containing BTRC-BE, and (c) polyimide film after decomposition of BTRC-BE.

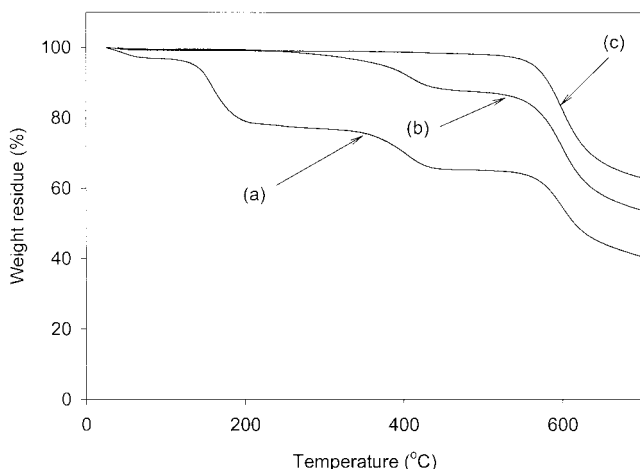


Figure 4 TGA thermograms of (a) poly(amic acid) films containing BTRC-PEG after drying at 100°C for 1 h, (b) polyimide film containing BTRC-PEG, and (c) polyimide film after decomposition of BTRC-PEG.

chain was thermally less stable than the benzyl ether side chain of BTRC-BE.

Two hyperbranched molecules used in this study had similar molecular weights (2000 for BTRC-BE and 2400 for BTRC-PEG), although they consisted of different branches and end groups, resulting in different polarities: BTRC-BE is hydrophobic, whereas BTRC-PEG is hydrophilic. Thus these compounds had different miscibilities with the poly(amic acid) and showed a different phase-separation behavior. After the poly(amic acid) films incorporated with the hyperbranched molecules was dried at 100°C for 1 h, the initially transparent films containing BTRC-BE became opaque, whereas the films with BTRC-PEG were still transparent. The cross-sectional SEM image of the dried poly(amic acid) films containing BTRC-BE (20 wt %) [Fig. 5(a)] clearly showed spherical domains dispersed in the matrix. Phase separation seemed to occur during drying of the initially homogeneous solution of the poly(amic acid) and BTRC-BE, and the porogen materials formed a dispersed phase, resulting in the opaque film. On the contrary, no phase separation was observed in the poly(amic acid) films containing BTRC-PEG. Because the poly(amic acid) was quite polar and hydrophilic in nature, BTRC-PEG was miscible at the molecular level, but the hydrophobic BTRC-BE was not miscible and separated out.

Such phase-separation morphology was retained during the curing process, as shown in Figure 5(b). Even after decomposition of the porogens, the pores were commensurate with the initial morphology, although the initially spherical domains were contracted and deformed to oval-shape pores. It is noted that the polyimide films keep shrinking during the thermal decomposition of the porogens and the films have a tendency to shrink preferentially in the thickness di-

rection because of the anisotropy of the cast films.^{14,27} This caused the pore to be like an oval rather than a sphere. The pores were well dispersed in the entire polyimide matrix and the size of pores was in the range of 390 ± 100 nm (length of the long axis) at a loading content of 20 wt % of the porogens.

In the case of BTRC-PEG, no phase separation occurred after imidization of the poly(amic acid) films and no pore structure was observed even after thermal decomposition of BTRC-PEG up to 450°C, as shown in Figure 6. This suggested that phase separation would be observed only if the porogens were separated out and formed a dispersed domain in the poly(amic acid) matrix before imidization. The molecular volume, which would be generated by decomposition of BTRC-PEG, was assumed to collapse during the decomposition process.

Figure 7 shows the SEM images for the polyimide films containing 5 wt % BTRC-BE after thermolysis of the porogen. As the content of BTRC-BE decreased

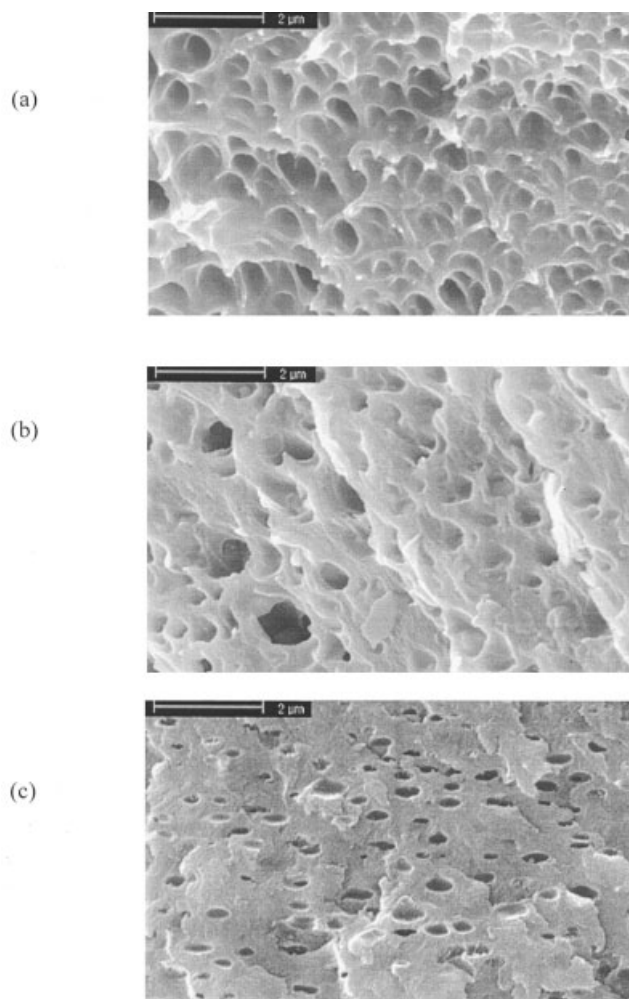


Figure 5 SEM images of cross section of (a) polyamic acid film containing 20 wt % BTRC-BE, (b) polyimide films containing 20 wt % BTRC-BE, and (c) polyimide films after pyrolysis of BTRC-BE.

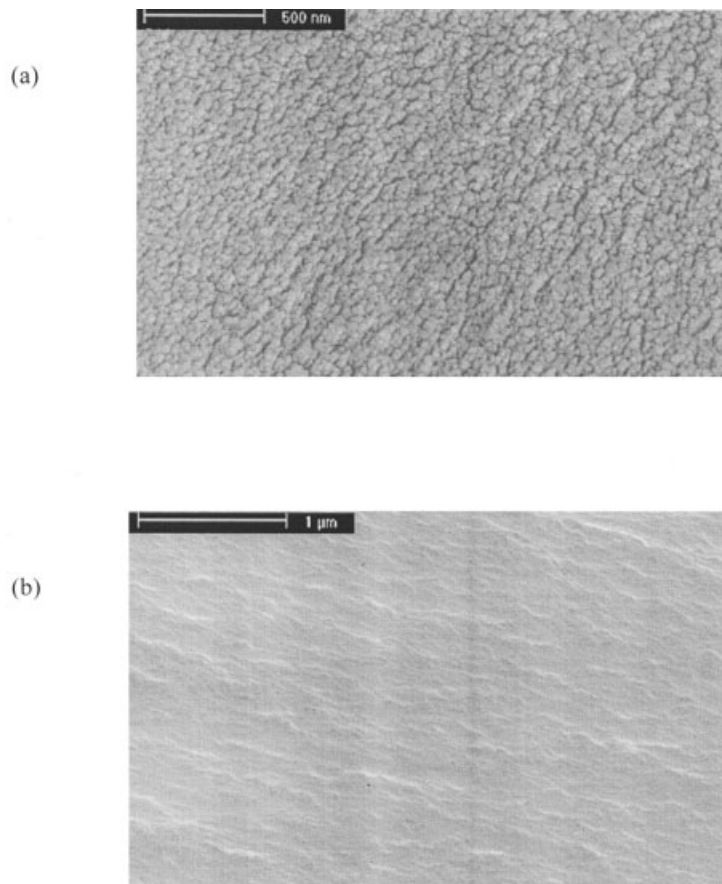


Figure 6 SEM images of cross section of (a) polyimide films containing BTRC-PEG and (b) polyimide films after thermolysis of BTRC-PEG.

from 20 to 5 wt %, the pore size decreased to 90 ± 50 nm and the pore density also decreased. This suggests that the porosity would be controlled by the content of the porogens.

CONCLUSIONS

Two hyperbranched molecules with different polarities were prepared and used as the templating agents

for the preparation of porous polyimide. The polarity of the porogens strongly affected miscibility between the porogens and poly(amic acid), which governed subsequent phase-separation behavior and pore morphology in the polyimide. Thus, hydrophobic BTRC-BE was phase-separated in the poly(amic acid) and succeeded in generating porous polyimide, whereas the hydrophilic BTRC-PEG failed. Our result also showed that the size and density of the pores could be controlled by the content of porogens.

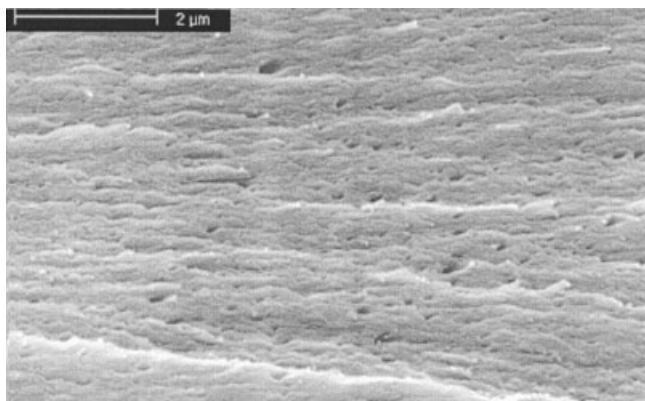


Figure 7 SEM image of cross section of polyimide film incorporated with 5 wt % BTRC-BE after pyrolysis.

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