Investigation of the Thermal Properties of Novel Adamantane-Modified Polybenzoxazine

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ABSTRACT: Two novel structures of adamantane-modified benzoxazines were synthesized from 4-(1-adamantyl)-phenol through the incorporation of adamantane as a pendant group into the polybenzoxazine backbone. Both ^{1}H-NMR and Fourier transform infrared spectra were used to characterize these structures. The rigid structure of the adamantane tended to hinder the chain mobility (boat anchor effect) and substantially enhanced the thermal properties, including the glass-transition temperature and decomposition temperature, especially for poly(6-adamantyl-3-methyl-3,4-dihydro-2H-1,3-benzoxazine). In the poly(6-adamantyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine) system, however, the opposite result for the glass-transition temperature was observed and it was interpreted as lower crosslinking density. The phenyl group was bulkier than the methyl group, and the movement of the molecular chain was hindered between bridging points during the curing process; this resulted in a lower crosslinking density and a lower glass-transition temperature than those of poly(6-adamantyl-3-methyl-3,4-dihydro-2H-1,3-benzoxazine). © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 932–940, 2004

Key words: crosslinking; blends; differential scanning calorimetry (DSC)

INTRODUCTION

Benzoxazines are cyclic heterocycles generated by the Mannich-like condensation reaction, and their chemistry and oligomeric products have been reported recently.[1–3] Benzoxazine polymerizes via a thermally induced ring-opening reaction to form a phenolic-like structure by a Mannich base bridge (—CH_2—NR—CH_2—)[4,5] and overcomes the shortcomings of traditional phenolic resins.[6] Polybenzoxazines (PBZZs), a class of thermosetting resins, offer a number of outstanding properties, including low melt viscosity, no release of volatiles during curing, no need for catalysts, low water absorption, a relatively low dielectric constant, a high glass-transition temperature (T_g), high thermal stability [decomposition temperature (T_d)], good mechanical properties, and a wide molecular design flexibility.[3,4,6]

In general, a polymer containing a linear *n*-alkyl substitute tends to have a reduced T_g value, and a longer substitute is expected to result in a lower T_g. On the other hand, a cyclic alkyl substitute tends to raise T_g.[7,8] In addition, positioning the mass center of the substitute closer to the polymer backbone will increase the bulkiness of the substitute, which thus becomes more effective for increasing T_g. Moreover, the introduction of a sterically hindered bridged or fused-ring structure to the polymer chain results in T_g values higher than predicted. Adamantane is a symmetric tricyclic hydrocarbon with three fused chair-form cyclohexane rings[9] in a diamond lattice structure, which is thermodynamically very stable. It possesses a high melting point (268°C) and high thermal stability because of its rigid and spherical structure.[10] It contains four bridgehead positions that can be easily substituted with Friedel–Craft chemistry. The adamantane moiety has been introduced into the main chains or side chains of various polymers.[9–16] These adamantane derivative polymers show unique properties, such as high thermal stability, high T_g, high thermal oxidative stability, and great chain stiffness. It is intuitive that large pendant groups tend to have such an effect because of reduced chain mobility (boat anchor effect), and the magnitude of the increase is surprisingly high for adamantane.

This study concentrates primarily on the synthesis of adamantane-modified PBZZs. By incorporating adamantane as a pendant group into the PBZZ structure, we expect to form a more stable and performance-enhanced polymer.

EXPERIMENTAL

Materials

Both 1-bromoadamantane and methylamine were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Phenol was purchased from Showa Chemical Co. (UEC, Japan). Formaldehyde, aniline, and iron(III) chloride were purchased from Aldrich Chemical.

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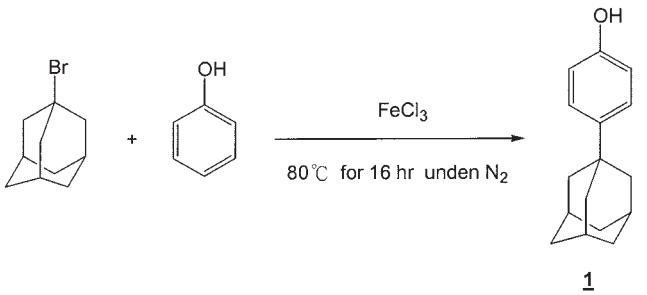


Scheme 1 Synthesis of **1**.

Synthesis of 4-(1-adamantyl)phenol (1)[10]

According to Scheme 1, a 150-mL, round-bottom flask was charged with 1-bromoadamantane (6.00 g, 27.89 mmol), phenol (39.37 g, 0.418 mol), and $FeCl_3$ (0.05 g, 3.39 mmol). The flask was fitted with a reflux condenser and an outlet leading to a beaker with an NaOH solution to trap the HBr that evolved during reaction. The reaction was carried out via stirring at 80°C for 16 h in nitrogen. The excess phenol was removed by the product being washed with hot water three times. The product was dried *in vacuo*, and the crude product was crystallized from methanol to afford 1.78 g (28%) of white crystals.

Synthesis of 6-adamantyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (2 benzoxazine)

2 benzoxazine was prepared according to Scheme 2(a).[15] An aqueous 37% formaldehyde solution (0.71 g, 8.76 mmol) and 5 mL of dioxane were mixed in a three-necked flask with nitrogen in an ice bath for 10 min. Then, the aniline (0.4079 g, 4.38 mmol), dissolved in 5 mL of dioxane, was added slowly with a dropping funnel. The mixture was stirred magnetically for 10 min before the addition of **1** (1 g, 4.38 mmol) in 10 mL of dioxane. The reaction temperature was raised to 100°C and allowed to reflux for 24 h. The solvent was then removed by the reduction of pressure, and a white powder was obtained. This crude product was dissolved in ethyl ether and washed with 1*N* NaOH and water in sequence three times, and the product solution was dried with magnesium sodium and distilled through a reduction in the pressure. Finally, a light white powder of **2** benzoxazine in an 87.5% yield was obtained.

Synthesis of 6-adamantyl-3-methyl-3,4-dihydro-2H-1,3-benzoxazine (3 benzoxazine)

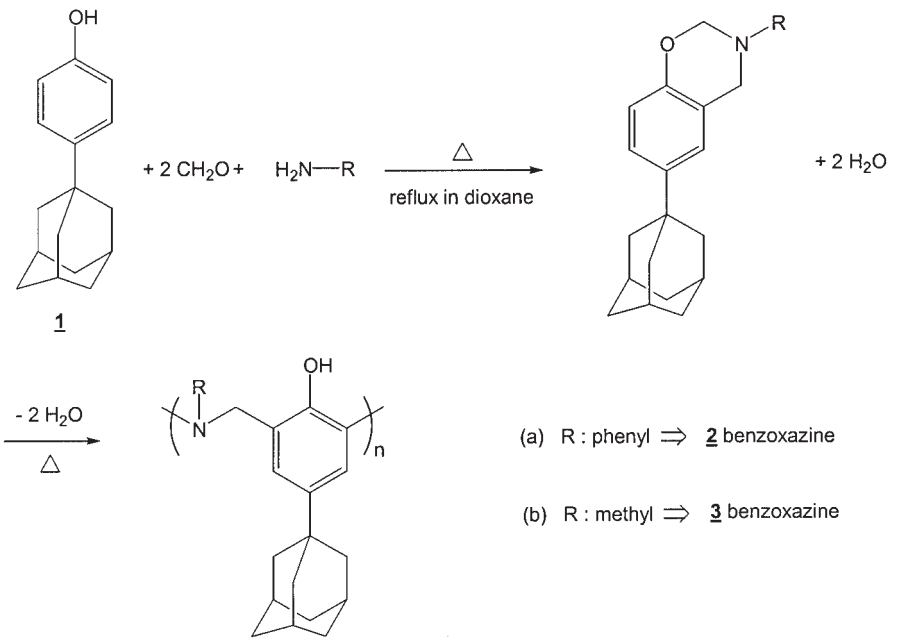
3 benzoxazine was synthesized with the same method used for **2** benzoxazine [Scheme 2(b)] with an aqueous 37% formaldehyde solution (0.533 g, 6.57 mol), 40% methylamine (0.255 g, 3.285 mmol), and **1** (0.75 g, 3.285 mmol). A white powder in a 64.5% yield was obtained with this system.

Synthesis of poly(2 benzoxazine) and poly(3 benzoxazine)

2 benzoxazine and **3** benzoxazine were both cured at 180°C for 4 h *in vacuo* to ensure the curing of the benzoxazine, and poly(**2** benzoxazine) and poly(**3** benzoxazine) were obtained as shown in Scheme 2.

NMR

^{1}H-NMR spectra were recorded on a Varian Unity Inova 500 FT NMR spectrometer (USA) operating at 500 MHz;



Scheme 2 Synthesis of **2** benzoxazine and **3** benzoxazine and their polymerization.

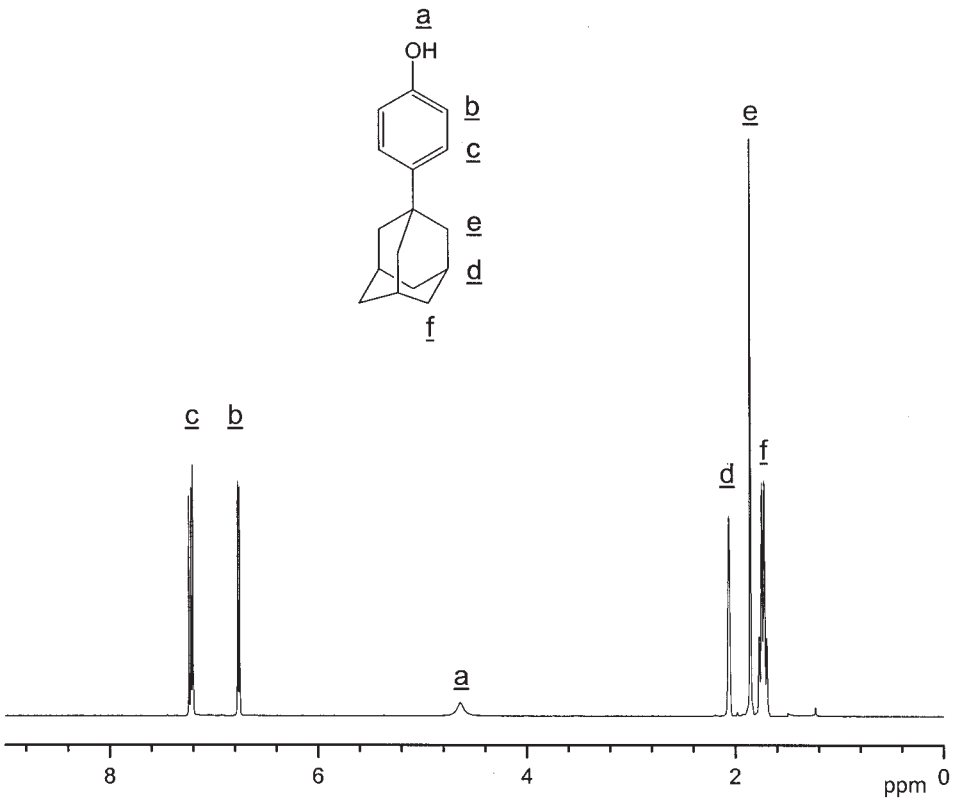


Figure 1 ^{1}H-NMR spectrum of **1**.

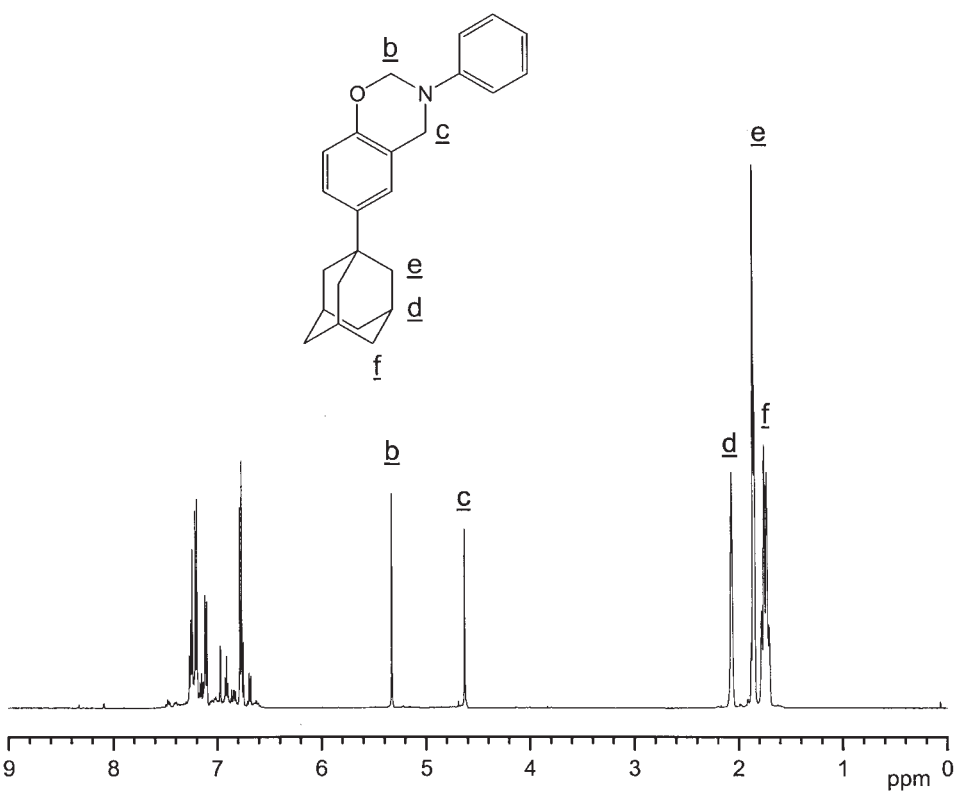


Figure 2 ^{1}H-NMR spectrum of **2** benzoxazine.

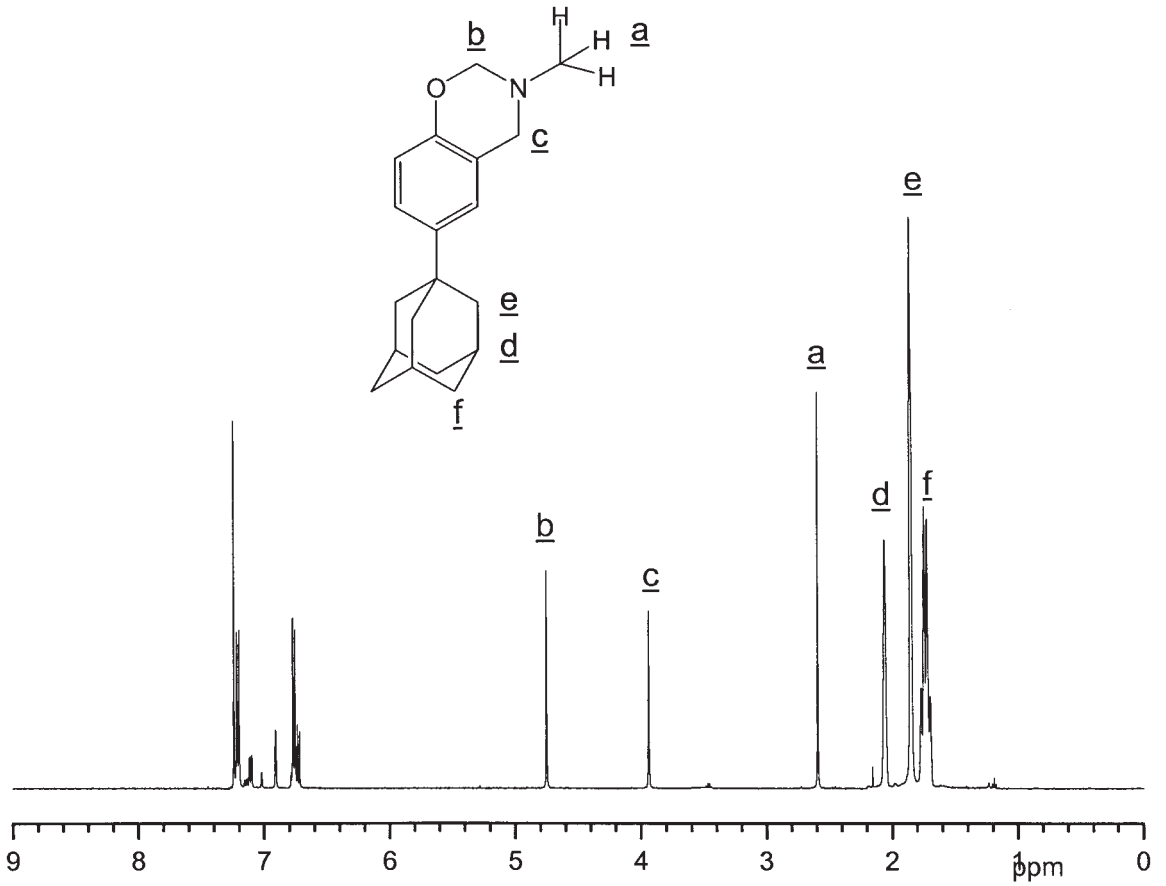


Figure 3 ^{1}H-NMR spectrum of **3** benzoxazine.

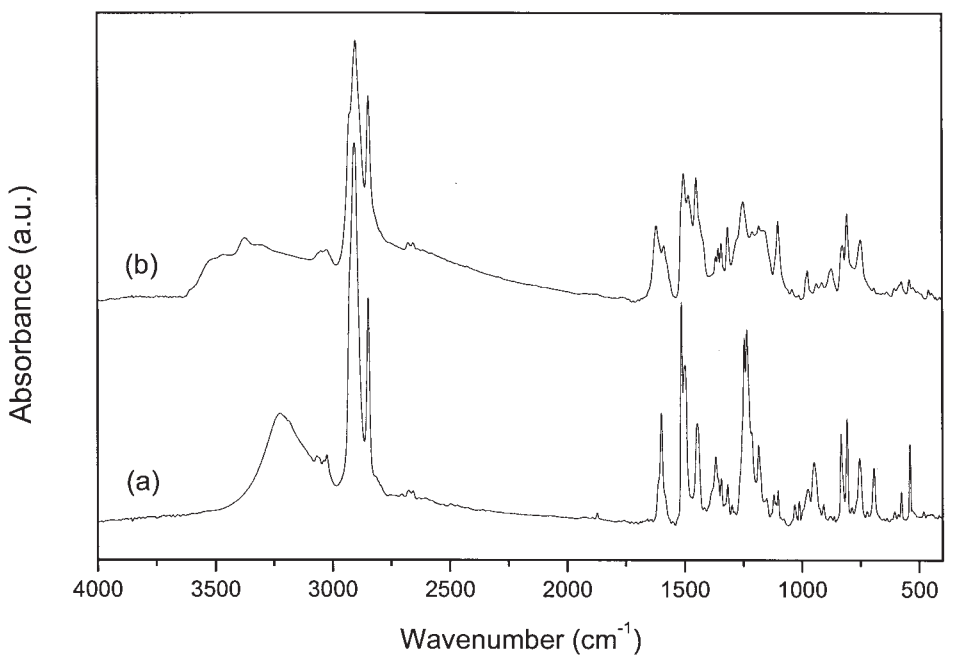


Figure 4 FTIR spectra of (a) **2** benzoxazine and (b) poly(**2** benzoxazine).

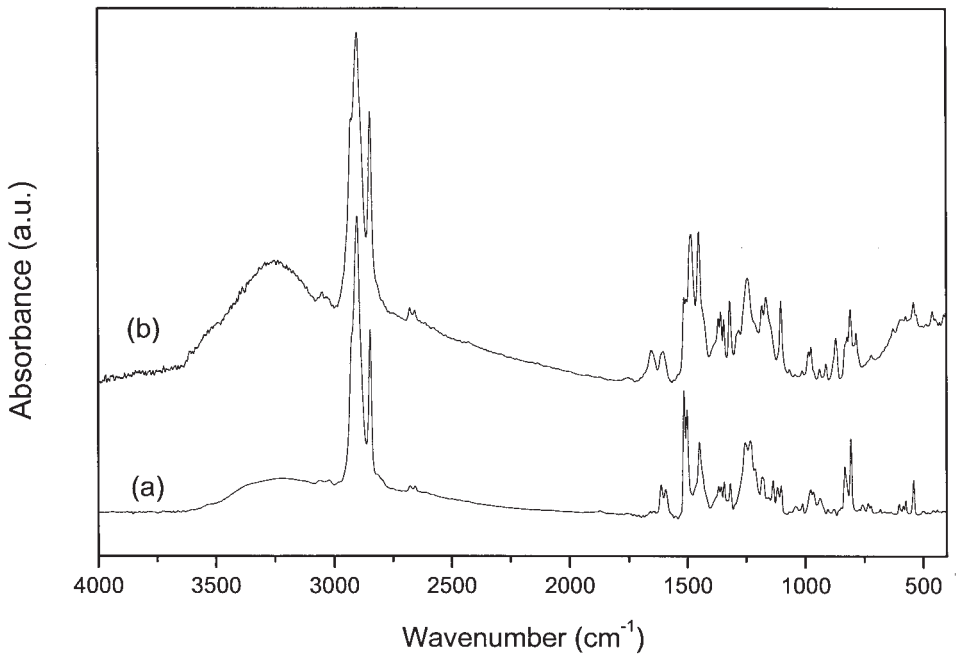


Figure 5 FTIR spectra of (a) **3** benzoxazine and (b) poly(**3** benzoxazine).

the chemical shifts are reported in parts per million (ppm). Deuterium chloroform was used as the solvent.

Fourier transform infrared (FTIR) spectroscopy

FTIR measurements were recorded on a Nicolet Avatar 320 FTIR spectrophotometer (USA), and 32 scans were collected with a spectral resolution of 1 cm^{-1}. Infrared spectra of the benzoxazine were obtained with the conventional NaCl method. The film used in this study was thin enough to obey the Beer–Lambert law. The sample chamber was purged with nitrogen during the measurement to maintain sample film drying.

Differential scanning calorimetry (DSC)

The calorimetric measurements were taken with a TA Instruments DSC-2010 differential scanning calorimeter

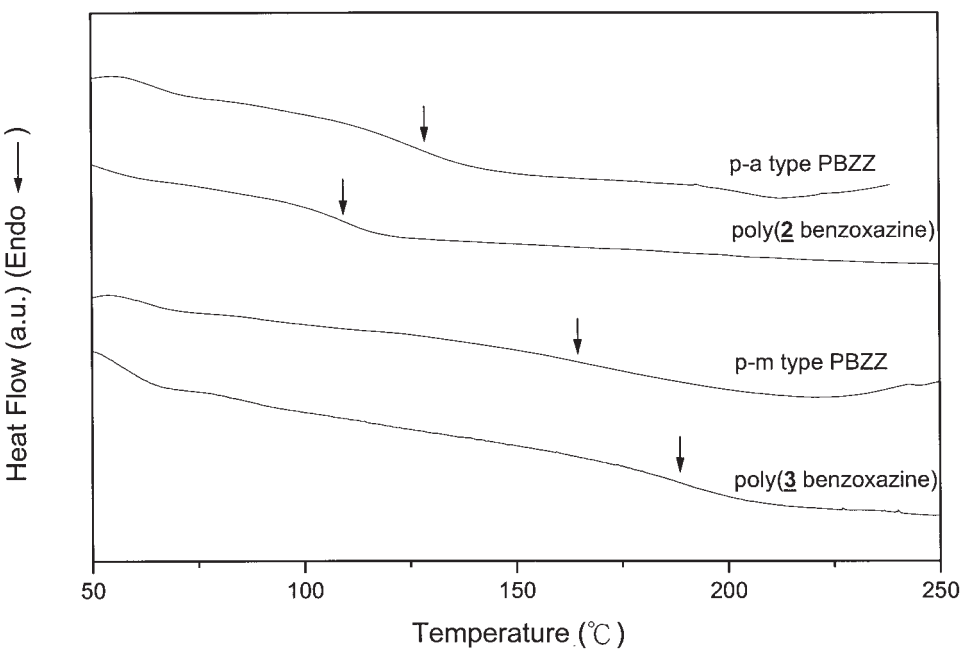
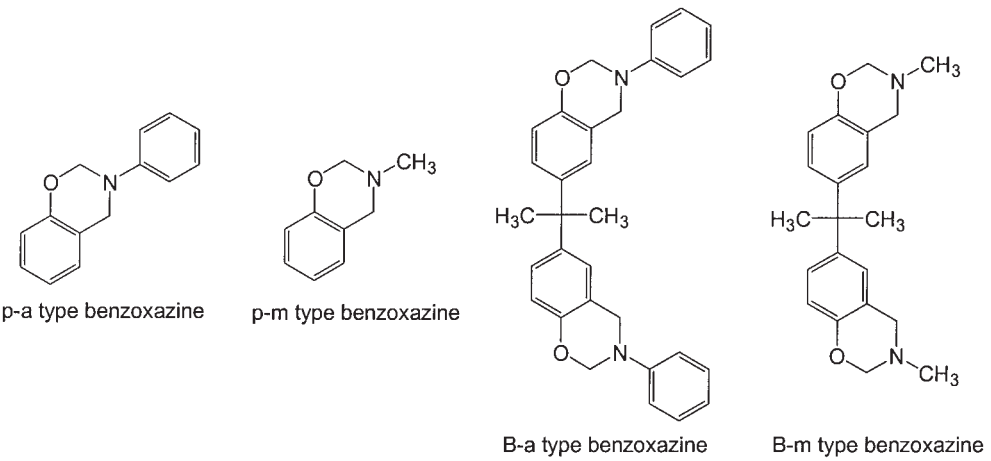


Figure 6 DSC scans of p-a PBZZ, poly(**2** benzoxazine), p-m PBZZ, and poly(**3** benzoxazine).



Scheme 3 Structures of p-a, p-m, B-a, and B-m PBZZs.

(USA) used under a nitrogen flow of 25 mL/min. The sample was preheated at a scanning rate of 20°C/min from 30 to 260°C and was maintained at 260°C for 2 min. The measurements were made with 5–10 mg samples in a DSC sample cell by quick cooling to 30°C from the melt of the first scan. The second scanning rate was 20°C/min from 30 to 300°C, and T_g was taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquids and glass lines.

Thermogravimetric analysis (TGA)

The thermal stability of the cured samples was investigated with a TA Instruments Q 50 (USA). Each cured sample (10–20 mg) was placed in a Pt cell and heated at a heating rate of 10°C/min from 30 to 700°C at a nitrogen flow of 60 mL/min.

RESULTS AND DISCUSSION

NMR analyses

Figure 1 shows the ^{1}H-NMR spectrum ($CDCl_3$, 500 MHz, δ) of **1**: 1.72 (q, 6H, adamantane), 1.85 (d, 6H, adamantane), 2.06 (s, 3H, adamantane), 4.64 (s, 1H, hydroxyl), 6.77 (d, 2H, Ar), and 7.22 ppm (t, 2H, Ar). After the cyclization of the oxazine, the characteristic benzoxazine peaks for Ar—CH_2—N and N—CH_2—O can be observed by ^{1}H NMR.[5,6] Figure 2 shows the

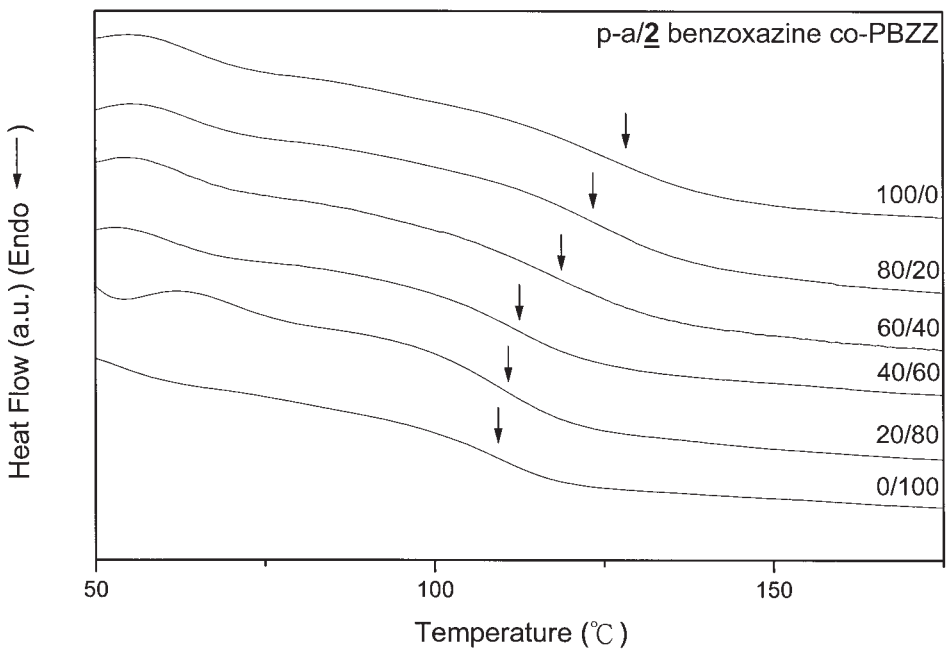


Figure 7 DSC scans of p-a/**2** benzoxazine-*co*-PBZZ copolymers with different compositions.

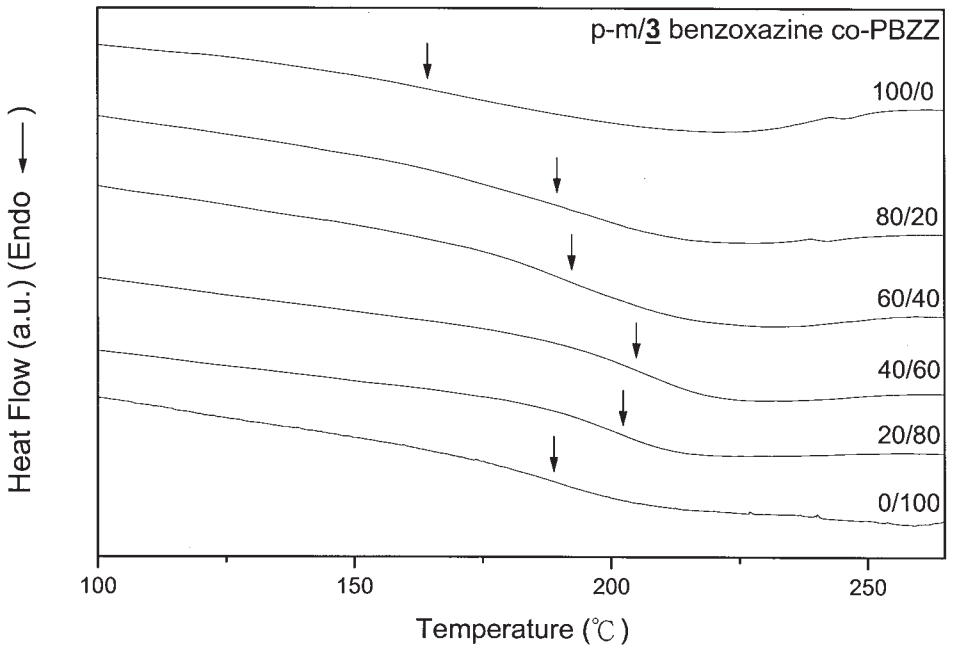


Figure 8 DSC scans of p-m/**3** benzoxazine-*co*-PBZZ copolymers with different compositions.

^{1}H-NMR spectrum ($CDCl_3$, 500 MHz, δ) of **2** benzoxazine: 1.72 (q, 6H, adamantane), 1.85 (d, 6H, adamantane), 2.06 (s, 3H, adamantane), 4.62 (s, 2H, Ar—CH_2—N), 5.33 (s, 2H, N—CH_2—O), and 6.67–7.23 ppm (8H, Ar). Figure 3 shows the ^{1}H-NMR spectrum ($CDCl_3$, 500 MHz, δ) of **3** benzoxazine: 1.72 (q, 6H, adamantane), 1.85 (d, 6H, adamantane), 2.06 (s, 3H, adamantane), 2.59 (s, 3H, methyl) 3.94 (s, 2H, Ar—CH_2—N), 4.75 (s, 2H, N—CH_2—O), and 6.71–7.24 ppm (3H, Ar). With these ^{1}H-NMR results, we confirmed that **1**, **2** benzoxazine, and **3** benzoxazine were successfully synthesized.

FTIR spectroscopy analyses

Figure 4(a,b) shows the FTIR spectra of **2** benzoxazine and poly(**2** benzoxazine); the bands at 753 and 693 cm^{-1}, corresponding to the monosubstituted benzene, are present even after curing. However, the characteristic absorption band of the oxazine ring at 948 cm^{-1} has disappeared, and the absorptions at 1512 cm^{-1} from the trisubstituted benzene ring and at 1246 cm^{-1} from the CH_2 wagging are both reduced. A new absorption band appears at 1502 cm^{-1} from the tetrasubstituted benzene ring mode. Besides, the absorptions at 1031 and 1235 cm^{-1}, corresponding to the symmetric and asymmetric C—O—C bonds of the benzoxazine, disappear after the curing process. Furthermore, a broad hydroxyl band is formed between 3096 and 3640 cm^{-1} because of the ring-opening process.

Figure 5(a,b) shows FTIR spectra of **3** benzoxazine and poly(**3** benzoxazine). Bands at neither 753 nor 693 cm^{-1} (referred to monosubstituted benzene) appear in comparison with **2** benzoxazine. In addition, similar absorption bands at 965, 1513, 1254, 1484, 1040, and 1231 cm^{-1} appear, corresponding to the characteristic absorption bands of **2** benzoxazine. The FTIR spectra in Figures 4(a) and 5(a) agree well with the ^{1}H-NMR results, again confirming the structures of **2** and **3** benzoxazines. Furthermore, the FTIR spectra in Figures 4(b) and 5(b) interpret the variations of **2** and **3** benzoxazines before and after curing.

T_g analyses

Adamantane has been incorporated into many polymers over the past several years because of the unusual physical and thermal properties of the multicyclic cage structure. Its rigid and spherical structure results in a very high melting point and excellent thermal stability for the parent molecule. In this study, the adamantane unit was incorporated into PBZZ as a pendant group. Figure 6 shows the DSC thermograms of p-a PBZZ, poly(**2** benzoxazine), p-m PBZZ (p-a: 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine; p-m: 3-methyl-3,4-dihydro-2*H*-1,3-benzoxazine), and poly(**3** benzoxazine). Poly(**3** benzoxazine) (189°C) possessed a higher T_g than poly(**2** benzoxazine) (109°C) because the phenyl group was bulkier than the methyl group and hindered the molecular chain movement chiefly between bridging points of the cured resin. Therefore, poly(**2** benzoxazine) had a lower crosslinking density and a lower T_g. Similar phenomenon have also been reported for B-a and B-m PBZZs.[17] Surprisingly, the T_g of p-m PBZZ increased from164 to 189°C for poly(**3** benzoxazine), whereas the T_g of p-a PBZZ decreased from 128 to 109°C for poly(**2** benzoxazine). The reason is discussed in more detail in the next section. Scheme 3 shows various benzoxazine systems, including

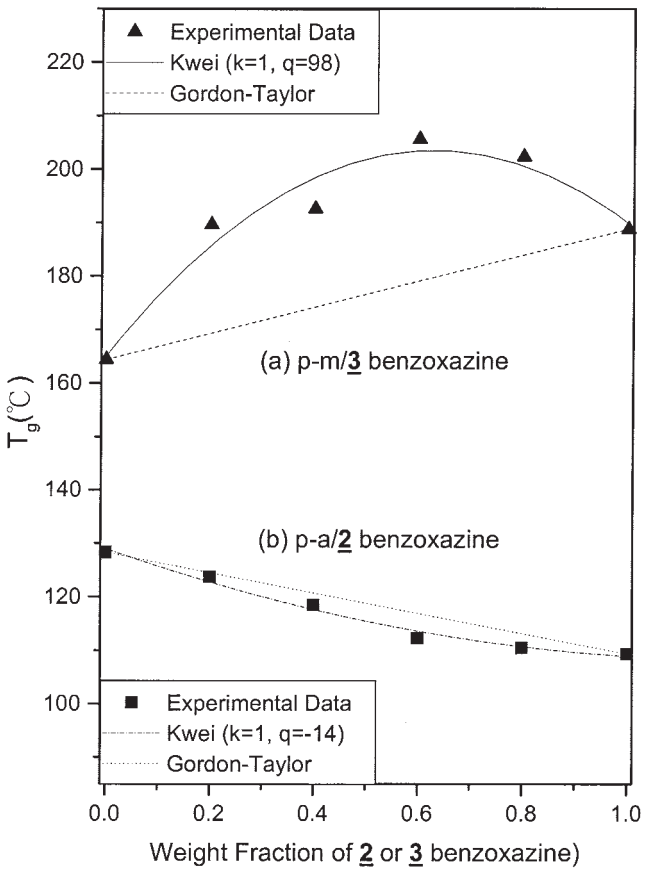


Figure 9 T_g–composition curves based on (a) p-m/**3** benzoxazine and (b) p-a/**2** benzoxazine PBZZ copolymers.

p-a, p-m, B-a, and B-m types. (B-a: 6-[1-methyl-1-(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazin-6-yl)ethyl]-3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine; B-m: 3-methyl-6-[1-methyl-1-(3-methyl-3,4-dihydro-2*H*-1,3-benzoxazin-6-yl)ethyl]-3,4-dihydro-2*H*-1,3-benzoxazine.)

To better understand the observed and unexpected T_g behavior between poly(**2** benzoxazine) and poly(**3** benzoxazine), we prepared blends with several different compositions by solution blending. The monomer mixture was stirred and dissolved in acetone, and then the solution was allowed to evaporate slowly at 50°C for 1 day. Afterwards, it was cured at 180°C for 4 h *in vacuo* to ensure the total curing of the benzoxazine. Figures 7 and 8 show the DSC thermograms of p-a/**2** benzoxazine-*co*-PBZZ and p-m/**3** benzoxazine-*co*-PBZZ; only a single T_g was present for all the compositions. The single T_g strongly implied that p-a/**2** benzoxazine-*co*-PBZZ and p-m/**3** benzoxazine-*co*-PBZZ were homogeneous.

In the p-m/**3** benzoxazine-*co*-PBZZ system, greater mobility of the methyl group of p-m and **3** benzoxazine was expected during the ring-opening process and resulted in a higher crosslinking density. Therefore, the incorporation of a greater concentration of **3** benzoxazine resulted in a product with a higher crosslinking density and a higher T_g than those of the original p-m PBZZ, as shown in Figure 8. Figure 9(a) plots T_g versus the **3** benzoxazine content, showing a positive deviation that is fitted well by the Kwei equation.[18] It describes the effect of the hydrogen-bonding interaction on T_g between polymers or a copolymer:

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{(W_1 + kW_2)} + qW_1W_2 \qquad (1)$$

where W_1 and W_2 are the weight fractions of the components and T_{g1} and T_{g2} represent the component

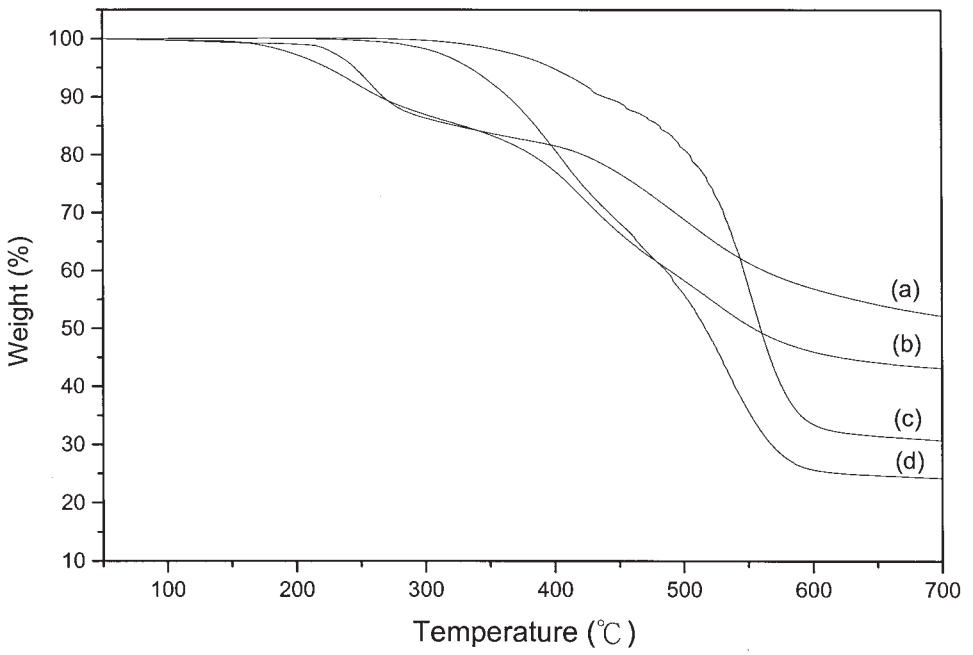


Figure 10 TGA thermograms of (a) p-m PBZZ, (b) p-a PBZZ, (c) poly(**3** benzoxazine), and (d) poly(**2** benzoxazine) in N_2.

TABLE I
Weight Loss and Char Yield of Poly(2 benzoxazine) and Poly(3 benzoxazine) in N_2

	5 wt % loss (°C)	10 wt % loss (°C)	Char yield (%) at 700°C
p-a PBZZ	224	264	43.2
p-m PBZZ	245	268	52.2
poly(**2** benzoxazine)	335	365	24.2
poly(**3** benzoxazine)	399	439	30.8

glass-transition temperatures. The large positive q value of 98 reveals that the observed positive T_g deviation was caused by the pendant group effect and the hydrogen bonding (OH···OH) between p-m PBZZ and **3** benzoxazine-*co*-PBZZ. More free hydroxyl groups of p-m PBZZ were available to bond with hydroxyl groups of poly(**3** benzoxazine), and this resulted in a positive deviation of T_g. Furthermore, it also explained why the ladder form, poly(**3** benzoxazine), had a T_g (189°C) even higher than that of B-a and B-m PBZZs with crosslinking structures.[17] (q: A parameter corresponding to the strength of hydrogen bonding in the blend. When the intermolecular interaction is stronger than intramolecular interaction in a binary blend, the value of q will be positive; otherwise, q will be negative. When the q value is larger, it represents that the interaction is stronger than the self-interaction of the blend. In case of no any interaction existed between components, the q value will be equal to zero. $k = \Delta\alpha_1/\Delta\alpha_2$ and $\Delta\alpha_i$ the difference between the volume expansion coefficient in the liquid and glassy states of the i component.)

In the p-a/**2** benzoxazine system, the bulky phenyl group present in the p-a type benzoxazine and **2** benzoxazine during the ring-opening process resulted in lower mobility, lower crosslinking density, and lower thermal properties in comparison with the p-m/**3** benzoxazine system. Increasing the **2** benzoxazine content resulted in T_g decreasing, with a negative q value of -14, as shown in Figure 9(b).

Essentially, it was a competition between T_g increasing because of the bulky pendant group and T_g decreasing because of the lower crosslinking density. In the p-a/**2** benzoxazine system, the lower crosslinking density appeared to play a more dominant role than the bulky pendant group effect and resulted in a lower T_g.

TGA

Figure 10 shows TGA thermograms of p-m PBZZ, p-a PBZZ, poly(**3** benzoxazine), and poly(**2** benzoxazine). The p-a and p-m PBZZs had substantially lower initial T_d's than poly(**2** benzoxazine) and poly(**3** benzoxazine) because of the presence of the adamantane group in their polymer chains. In particular, poly(**3** benzoxazine) showed an extremely high 5% weight-loss temperature at 399°C, as shown in Figure 10 and Table I. On the other hand, the char yields of these non-admantane types, p-a PBZZ and p-m PBZZ, were significantly higher than those of poly(**2** benzoxazine) and poly(**3** benzoxazine). The higher crosslinking density resulted in a higher char yield, and those adamantane-containing polymers, in general, had lower crosslinking density.

CONCLUSIONS

Two novel adamantane-modified benzoxazines were synthesized from **1** and were polymerized via a thermally induced ring-opening process. The steric hindrance was evident from the incorporation of the adamantane group into the PBZZ backbone during curing and resulted in a lower crosslinking density, especially in the poly(**2** benzoxazine) system. Therefore, poly(**3** benzoxazine) had a higher crosslinking density, a higher T_g, and a higher T_d than poly(**2** benzoxazine). Furthermore, the p-a/**2** benzoxazine system had a negative T_g deviation, whereas the p-a/**3** benzoxazine blends had a positive T_g deviation.

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