Facile, One-Pot Synthesis of Aromatic Diamine-Based Benzoxazines and Their Advantages Over Diamines as Epoxy Hardeners

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Received 17 December 2009; accepted 26 February 2010 DOI: 10.1002/pola.24013 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Three aromatic diamine-based benzoxazines were successfully prepared by a facile, clean, one-pot procedure from 1,4-phenylenediamine (1), 4,4'-diaminodiphenyl ether (2), and 4,4'-diaminodiphenyl methane (3), respectively. Their structures were confirmed by NMR spectra and single crystal diffractogram. The effect of the reactivity of diamines on the purity of the resultant benzoxazines was discussed. The resultant benzoxazines were applied as hardeners for cresol novolac epoxy (CNE). The processing window, the latent curing characteristic, and the miscibility of benzoxazine/CNE systems were discussed. Compared with diamines (1 and 3), (1 and 3)-based benzoxazines show latent

curing characteristic as epoxy hardeners, and wide processing windows can be obtained. Compared with diamine (2) which is immiscible with CNE in the molten state, (2)-based benzoxazine shows good miscibility with CNE. Dynamic mechanical analysis shows the $T_{\rm g}$ s of the benzoxazine/CNE thermosets are as high as 242–243 °C. Thermogravimetric analysis shows the outstanding thermal stability of the resultant thermosets. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2430–2437, 2010

KEYWORDS: crosslinking; ring-opening polymerization; thermosets

INTRODUCTION Benzoxazines are resins that can be polymerized to thermosets via thermally activated cationic ringopening reactions. Thermosets with low water absorption, superior electrical properties,¹ and low surface energy² can be obtained after curing. These properties have led to renewed interest in this field in recent years.^{3–9} According to related research, most difunctional benzoxazines are synthesized from aromatic biphenols, monoamines, and formaldehyde. The large varieties of aromatic biphenols and monoamines allow for considerable molecule-design flexibility of benzoxazines. Some special functional groups can be introduced via biphenols or monoamines to provide certain desired properties. For example, Agig and Takeichi prepared phenyl propargyl ether-based¹⁰ and allylamine-based benzoxazines¹¹ to increase T_g and thermal stability. Ishida and coworkers synthesized acetylene,^{12,13} maleimide,¹⁴ and phenylphosphine oxide¹⁵-containing benzoxazines to increase T_{g} , char yield, and flame retardancy. Kimura et al. prepared a terpenediphenol-based benzoxazine to reduce water absorption and dielectric constant.¹⁶ Su and Chang incorporated trifluoromethyl groups into benzoxazines to reduce the dielectric constant.¹⁷ Recently, linear polymers containing benzoxazine structures have been reported by Takeichi et al.,¹⁸ Yagci and coworkers,^{19,20} Ishida and coworkers,^{21–23} and Endo et al.^{24,25}

However, because of the triazine networks that result from the condensation of aromatic diamines and formaldehyde,²⁶

gelation occurs during the preparation of most aromatic diamine-based benzoxazines. As a result, benzoxazines based on difunctional^{18,27} and multifunctional aromatic amines or their derivatives²⁸ have seldom been reported. Recently, researchers at Matsushita Electric Works reported on the manufacturing of benzoxazines from aromatic diamines and paraformaldehyde using solvents such as toluene in which the aromatic diamine and paraformaldehyde have limited solubility.²⁹ The poor solubility of aromatic diamines and paraformaldehyde in the solvent reduced the formation of the triazine network and the condensations among methylolmethylol, methylol-amino, or methylol-ortho hydrogen, while the formation of benzoxazine was not retarded due to the high concentration of phenol in the solvent. Very recently, Ishida and coworkers prepared the 4,4'-diaminodiphenyl sulfone-based benzxaozine in xylene using the traditional onestep procedure.³⁰ However, to our knowledge, only limited aromatic diamine-based benzoxazines can be prepared by the traditional one-step procedure.

To prevent the gelation that results from the reaction of aromatic diamine and formaldehyde, the direct contact between formaldehyde and aromatic diamines, especially diamine with high reactivity, should be avoided. Recently, we proposed a three-pot procedure to prepare aromatic diaminebased benzoxazines.^{31,32} Almost at the same time, Andreu and Ronda prepared deuterated benzoxazines to prove the mechanism.³³ In the first pot of the procedure, aromatic

Additional Supporting Information may be found in the online version of this article. Correspondence to: C. H. Lin (E-mail: linch@nchu.edu.tw) Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 2430–2437 (2010) © 2010 Wiley Periodicals, Inc.

diamines reacted with 2-hydroxybenzaldehyde, yielding intermediate (I) with an o-hydroxy phenylimine linkage. In the second pot, the imine linkage was reduced, yielding an intermediate (II) with a secondary amine structure. In the third step, formaldehyde was added to react with the secondary amine at room temperature, resulting in a presumable intermediate with a hydroxymethylamine linkage. Thereafter, the reaction temperature was raised to induce the ring closure condensation between the hydroxymethylamine and o-hydroxy groups, forming benzoxazines. However, multi-pot and the expensive reducing agent, sodium borohydride, make the procedure unattractive for industrial application. As a result, simplifying the three-pot produce and using inexpensive reducing agent may make the procedure attractive. In this study, three aromatic diamine-based benzoxazines (4-6), were prepared by an economic, one-pot procedure using 1,4-phenylenediamine (1), 4,4'-diaminodiphenyl ether (2), and 4,4'-diaminodiphenyl methane (3), respectively, as starting materials. The structures of the benzoxazines (4-6) were confirmed by NMR spectra and single crystal diffractogram. Benzoxazines (4-6) served as epoxy hardeners. We also studied the structure-property relationship of the (4-6)/CNE thermosets.

EXPERIMENTAL

Materials

Cresol novolac epoxy (CNE) with EEW 200 g/eq was kindly supplied by Chang Chun Plastics, Taiwan under the trade name of CNE-200ELD. 2-Hydroxybenzaldehyde (Showa), 1,4-phenylenediamine (1, Acros), 4,4'-diamino diphenyl ether (2, ChrisKev), 4,4'-diaminodiphenyl methane (3, ChrisKev), and 4,4'-diaminodipheyl sulfone (ChrisKev) were used as received. *N*,*N*-dimethylacetamide (DMAc) was purchased from TEDIA, purified by distillation under reduced pressure over calcium hydride (Acros), and stored over molecular sieves. Methanol (99.5%) was purchased from various commercial sources and used without further purification.

Characterization

Thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer TGA 7 at a heating rate of 20 °C/min in a nitrogen atmosphere from 100 to 800 °C. Dynamic mechanical analysis (DMA) was performed with a Perkin-Elmer Pyris Diamond DMA with a sample size of 5.0 cm \times 1.0 cm \times 0.2 cm. The storage modulus E' and tan δ were determined as the sample was subjected to the temperature scan mode at a programmed heating rate of 5 °C/min at a frequency of 1 Hz. The test was performed by the bending mode with amplitude of 5 μ m. Thermal mechanical analysis (TMA) was performed with a Seiko TMA/SS6100 at a heating rate of 5 °C/min. The coefficient of thermal expansion (CTE) was measured in the range of 50 to 150 °C. NMR measurements were performed using a Varian Inova 600 NMR in DMSO- d_{6} and the chemical shift was calibrated by setting the chemical shift of DMSO- d_6 as 2.49 ppm. Elemental analysis was performed with a Heraeous CHN-O Rapid Elemental Analyzer using acetanilide as a standard. IR Spectra were obtained from at least 32 scans in the standard wavenumber range of 400–4000 cm⁻¹ by a Perkin-Elmer RX1 infrared spectrophotometer. High resolution mass spectra were obtained by a Finnigan/Thermo Quest MAT 95XL mass spectrometer. Single crystal diffractogram was obtained by a Bruker AXS SMART-1000 X-Ray diffractometer.

Preparation and Characterization of (4)

2-Hydroxybenzaldehyde 4.96 g (40.7 mmole), (1) 2 g (18.5 mmole), DMAc 30 mL, and the catalyst Pd/C 0.06 g were charged into a high pressure reactor (Parr Instrumental Co., United States) and reacted at ambient temperature under a hydrogen atmosphere. The reaction was completed when the indicator of the manometer stopped moving. Then, formaldehyde (37%) 3.3 g (40.7 mmole) was added into the reactor. The mixture solution was heated to 70 °C and maintained at that temperature for 12 h and then, the mixture was filtered to remove Pd/C and the filtrate was poured into methanol/water solution and stirred, yielding a yellow powder. The precipitate was filtered and dried in the vacuum oven. Yellow powder 4.97 g (78% yield) with a melting point of 180 °C (by DSC) and a delta enthalpy of 118 J/g was obtained.

HR-MS(FAB+) *m/z*: Calcd. for $C_{22}H_{20}N_2O_2$ 344.1525; Anal., 344.1526 for $C_{22}H_{21}N_2O_2$. Elem. Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72%; H, 5.85%; N, 8.13%. Found: C, 76.86%; H, 5.94%; N, 8.17%. ¹H NMR (DMSO-D₆), $\delta = 4.54(4H, H^3)$, 5.33(4H, H¹⁰), 6.67(2H, H⁸), 6.83(2H, H⁶), 6.99(4H, H¹), 7.05(4H, H⁵ and H⁷). ¹³C NMR (DMSO-D₆), $\delta = 49.27(C^3)$, 79.47(C¹⁰), 116.08(C⁸), 120.29(C⁶), 118.84(C¹), 127.08(C⁵), 127.54(C⁷), 127.54(C⁴), 141.97(C²), 153.88(C⁹). Single crystal data: $C_{22}H_{20}N_2O_2$, 0.49 × 0.18 × 0.16 mm³, monoclinic with *a* = 9.2181(8) Å, *b* = 8.8299(8) Å, *c* = 11.3588(10) Å, $\alpha = 90^{\circ}$, $\beta = 113.8880(10)^{\circ}$, $\gamma = 90^{\circ}$ with Dc = 1.353 mg/m³ for Z = 2, V = 845.35(13) Å³, T = 297 K, $\lambda = 0.71073$ Å, F(000) = 364, final R indices: *R*1 = 0.0447, WR2 = 0.1400.



Preparation and Characterization of (5)

Compound 5 was synthesized in a similar procedure with 4 using 2 as starting material. White powder (76% yield) with a melting point of 128 °C (by DSC) and a delta enthalpy of 77 J/g was obtained.

HR-MS(FAB+) m/z: Calcd. for $C_{28}H_{24}N_2O_3$ 436.1787; Anal., 436.1781 for $C_{28}H_{25}N_2O_3$. Elem. Anal. Calcd for $C_{28}H_{24}N_2O_3$: C, 77.04%; H, 5.45%; N, 6.42%. Found: C, 76.94%; H, 5.62%; N, 6.44%. ¹H NMR (DMSO-D₆), δ = 4.59(4H, H⁵), 5.38(4H, H¹²), 6.73(2H, H¹⁰), 6.84(4H, H³), 6.86(2H, H⁸), 7.08(2H, H⁹), 7.09(4H, H²), 7.10(2H, H⁷). ¹³C NMR (DMSO-D₆), δ = 49.37(C⁵), 79.18(C¹²), 116.18(C¹⁰), 119-119.14(C² and C³), 120.41(C⁸), 121.15(C⁶), 127.12(C⁹), 127.61(C⁷), 143.58(C⁴), 151.11(C¹), 153.9(C¹¹).







Preparation and Characterization of (6)

Compound (6) was prepared in a similar synthesis route with (4) using (3) as starting material. Light yellow powder (72% yield) with a melting point of 123 $^{\circ}$ C (by DSC) and a delta enthalpy of 72 J/g was obtained.

MS(FAB+) m/z: Calcd. for $C_{29}H_{26}N_2O_2$ 434.1994; Anal., 436.1987 for $C_{29}H_{27}N_2O_2$. Elem. Anal. Calcd for $C_{29}H_{26}N_2O_2$: C, 80.16%; H, 6.03%; N, 6.45%. Found: C, 80.12%; H, 6.12%; N, 6.41%. ¹H NMR (DMSO-D₆), δ = 3.70(2H, H¹), 4.58(4H, H⁶), 5.37(4H, H¹³), 6.69(4H, H⁴), 6.84(2H, H⁹), 7.01(2H, H¹⁰), 7.02(2H, H¹¹), 7.04(2H, H⁸), 7.07(4H, H³). ¹³C NMR (DMSO-D₆), δ = 39.92(C¹), 49.01(C⁶), 78.87(C¹³), 116.14(C⁴), 117.57(C¹⁰), 120.33(C⁹), 121.25(C⁷), 127.10(C³), 127.56(C⁸), 129.15(C¹¹), 133.80(C²), 145.84(C⁵), 153.89(C¹²).



Preparation of Polybenzoxazines

Mixtures of (1-3)/CNE and (4-6)/CNE with equal equivalency were melted, stirred, and transferred to an aluminum mold, and then cured at 180, 200, 220, and 240 °C for 2 h each in an air-circulating oven. Thereafter, samples were allowed to cool slowly to room temperature to prevent cracking.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers

Benzoxazine (4-6) were synthesized by a one-pot produce (Scheme 1), in which aromatic diamines (1-3), 2-hydroxybenzaldehyde, and Pd/C were charge into Parr reactors

simultaneously. After the hydrogen was introduced, the imine linkage resulting from the condensation of aromatic diamines and 2-hydroxybenzaldehyde was reduced by hydrogen in the presence of Pd/C, forming an intermediate with a secondary amine linkage. Then, formaldehyde was added and the temperature was raised to induce ring closure condensation, yielding benzoxazines (4-6). Generally, there are many reducing agents, such as NaBH₄, LiAlH₄, hydrogen/Pd-C, hydrazine hydrate/Pd-C. Among them, hydrogen is a relatively clean and inexpensive. To reduce the preparation cost, hydrogen/Pd-C was applied to replace sodium borohydride, which has been used in the three-pot procedure.^{24,25} In general, the carbonyl groups of 2-hydroxybenzaldehyde are also reduced by hydrogen/Pd-C. However, the reduction rate is much slower than the formation rate of imine due to the high reactivity of (1-3) in which the amino groups are activated by the conjugation of a *para*-position amino group, ether, and methylene, respectively. This speculation can be supported by the unsuccessful preparation (poor purity) of benzoxazine based on a less-reactive diamine, such as 4,4'-diaminodipheyl sulfone. In such a case, the formation rate of imine is reduced due to the low reactivity of 4,4'-diaminodipheyl sulfone. As a result, the carbonyl groups of 2-hydroxybenzaldehyde are more likely to be reduced by hydrogen/Pd-C. Therefore, to ensure high purity of resulting benzoxazine, the one-pot approach in this study is limited to diamines with high reactivity.

Figure 1 shows the ¹H and ¹³C NMR spectra of (4). The characteristic peaks at 4.54 and 5.33 ppm, which correspond to the O–CH₂–N and ph–CH₂–N of oxazine, respectively, verify the formation of benzoxazines. The peaks of Ar-H and Ar-C marked on Figure 1 also support the structure and purity of (4). Figure 2 shows the single crystal diffractogram of (4), further confirming the structure of (4). Benzoxaiznes (5-6) were also characterized by ¹H and ¹³C NMR spectra (Supporting Information Figures S1–S2), and the assignment of each peaks supports the structure and purity. One thing that has to be emphasized in this approach is that except for pouring the reaction mixture to methanol/water solution, no extra purification procedures like extraction, recrystallization, or column chromatography are required to obtain benzoxazine with good purity. Figure 3 shows the DSC thermograms



of as-prepared (4) and single crystal (4). The melting point of as-prepared (4) is similar to that of single crystal (4), further demonstrating the purity of this approach.

DSC Thermograms of Benzoxazines

Figure 4 shows the DSC thermograms of (4), (4)/CNE, and (1)/CNE mixtures. The melting point of benzoxazine (4) is 180 °C, whereas the exothermal peak temperature is 260 °C,



FIGURE 2 Single crystal diffractogram of (4). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



showing a wide processing window. For the (4)/CNE curing system, the melting endothermic peak temperature is

166 °C, and the exothermic peak occurred at 258 °C, also

FIGURE 3 DSC thermograms of as-prepared (4) and single crystal (4). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



FIGURE 4 DSC thermograms of (4), (4)/CNE, and (1)/CNE mixtures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

showing a wide processing window. In contrast, the exothermic reaction of 1/CNE occurs at a relatively low temperature, suggesting the poor processability and short pot-life of the system. From Figure 4, we can confirm the latent curing characteristic of (4) as an epoxy curing agent. This observation can be supported by the gel time test (Table 1). At 190 °C, the gel time of (4)/CNE is 3.19 min, whereas the gel time of (1)/CNE is only 0.12 min, also demonstrating the latent curing characteristic of (4). The rapid curing of the (1)/CNE system makes it difficult to prepare a void-free sample for property measurement. In contrast, a void-free thermoset can easily be prepared for the (4)/CNE system due to the wide processing window. As listed in Table 1, (5)/CNE and (6)/CNE also show reasonable gel time for processing. The longer gel time makes the (4-6)/CNE system attractive for IC encapsulation in which low viscosity during mold transfer is important.

Thermal Properties of Polybenzoxazines

Dynamic mechanical analyzer was applied to measure the dynamic mechanical properties of the resultant thermosets

(Fig. 5). The T_gs of P(4-6) are 220, 194, and 200 °C, respectively, which are much higher than that of the bisphenol A and aniline-based polybenzoxazine ((P(B-a)), about 160 °C) reported by Ishida and Allen.¹ As in Scheme 2, instead of bonding to a phenyl pendant, the nitrogen linkage of P(4-6)is bonded to the other repeating unit, leading to a small segmental mobility and explaining the higher $T_{\rm g}$ of P(4-6). Instead of enhancing the T_g value of polybenzoxazines by incorporating curable propargyl ether,¹⁰ allyl,¹¹ and malei-mide functional groups,^{14,34,35} which may decrease the toughness of polybenzoxazines due to the higher crosslinking density, this study demonstrates the power of the moleculeapproach to T_g enhancement. The order of T_g is P(4) > P(6) > P(5), which is related to the rigidity and crosslinking density of the polybenzoxaszines. P(5) with flexible ether linkage between two phenylene structures shows lower T_{σ} than P(6) with methylene linkage between two phenylene structures. P(4) with the smallest molecular weight between crosslinking points shows the highest $T_{\rm g}$. For the (4)/CNE thermoset, only one tan δ peak was observed, indicating that a homogeneous copolymer was obtained. As in Figure 5, the T_{g} of the (4)/CNE thermoset is as high as 243 °C, which is 23 °C higher than that of neat P(4). This indicates that the crosslinking density of P(4) was enhanced by the incorporation of CNE. It is thought that the phenolic groups, resulting from ring-opening polymerization of benzoxazine, reacted with the oxirane of CNE and thus tighten the network structure.³⁶ This speculation can be confirmed by the DMA curves of P(4) and the (4)/CNE thermoset. The height of tan δ for the (4)/CNE thermoset is much lower than that of P(4), confirming the higher crosslinking density of the (4)/CNE thermoset. In addition to latent curing characteristic, one particular benefit of using benzoxazine as a curing agent is its miscibility with epoxy resin. Generally, 4,4'-diaminophenyl ether (2) is immiscible with CNE, and an obvious two-phase morphology was observed for the (2)/CNE system in the molten state. However, the (2)-based benzoxazine, (5), is miscible with CNE in the molten state. As shown in Figure 5, only one tan δ peak was observed for the (5)/CNE

Thermosets Based on	Gel Time at 190 °C (min)	<i>E</i> ′ at 50 °C (GPa)	T _g Form DMA (°C)	T _g Form TMA (°C)	CTE (ppm/°C)	7 _d ª (°C)	Char Yield ^b (%)
(4)	2.71	2.61	220	193	54	372	53
(4)/CNE	3.19	3.30	243	220	51	378	38
(1)/CNE ^c	0.12	-	-	-	-	-	-
(5)	4.94	1.61	194	185	57	376	52
(5)/CNE	6.87	2.53	242	215	51	385	37
(2)/CNE ^d	-	-	-	-	-	-	-
(6)	3.27	2.28	200	183	57	413	46
(6)/CNE	3.68	3.19	243	225	54	406	40
(3)/CNE	0.26	2.10	272	-	-	385	16

TABLE 1 Thermal Properties of P(4-6) and (3-6)/CNE Thermosets

^a 5% Decomposition temperature (^oC) in a nitrogen atmosphere.

^b Residual weight percentage at 800 °C in a nitrogen atmosphere. $^{\rm c}$ Gel time of (1)/CNE is too short to prepare a void-free and homogeneous sample.

^d (2) and CNE are immiscible in the molten state.



FIGURE 5 DMA curves of P(4-6) and (4-6)/CNE thermosets.

thermoset, indicating that a homogeneous copolymer, not two immiscible IPN networks, was obtained. The T_g value of (5)/CNE thermoset is as high as 242 °C, which is 48 °C higher than that of P(5). In addition, T_g as high as 243 °C was also observed for the (6)/CNE thermoset, which is 43 °C higher than that of P(6). The high T_g characteristic can also be confirmed by TMA measurements. Figure 6 shows a typical TMA curve of the (6)/CNE thermoset. A onset transition at 225 °C was observed, which is 42 °C higher than that of P(6). A CTE of 54 ppm/°C was obtained, which is slightly smaller than that of P(6). Similar results were observed in other systems, and the results are listed in Table 1.

Figure 7 shows the TGA thermograms of P(4-6) and the (4-6)/CNE thermosets. The 5% degradation temperatures of P(4-6) are 372, 376, and 413 °C, respectively, which are much higher than that of P(B-a). According to previous studies, the 5% degradation temperature of conventional polybenzoxazines rarely exceeds 350 $^\circ$ C, and the release of aniline fragments is responsible for the low thermal stability of polybenzoxazines. $^{37-40}$ Therefore, the introduction of a crosslinkable site into aniline, such as ethylnyl,^{40,41} propargyl ether,¹⁰ and nitrile group¹³ has been proven to be an effective way to enhance thermal stability of polybenzoxazines. However, an enhanced crosslinking density also indicates a sacrificial toughness. As in Scheme 2, the nitrogen linkage in P(4-6) is bonded to the other repeating units, making the release of an aniline fragment difficult and causing P(4-6) to be thermally more stable than P(B-a). The order of T_d is



SCHEME 2 Proposed ideal structure of P(4-6).



FIGURE 6 TMA curves of (6)/CNE thermoset.

P(6) > P(5) > P(4). The trend is consistent with the inverse order of the electron density of nitrogen in P(4-6). As a result, it is speculated that the stability is related to the



FIGURE 7 TGA curves of (a) P(4–6) and (b) (4–6)/CNE thermosets.

electron density of the electron density of nitrogen. For the (4-6)/CNE thermosets, the 5% degradation temperatures are 378, 385, and 406 °C, respectively. The order is the same as that in P(4-6). Detailed investigation of the decomposition mechanism by TGA-Mass is under investigation to confirm the observation. As listed in Table 1, the 5% decomposition temperature and char yield at 800 °C of the (6)/CNE thermoset are 406 °C and 40%, respectively, which are higher than those of the (3)/CNE thermoset (385 °C and 16%). These results demonstrate the (4-6)/CNE thermosets have better thermal stability than the (1-3)/CNE thermosets.

CONCLUSIONS

Three aromatic diamine-based benzoxazines (4-6) were successfully prepared by a one-pot procedure. Because of the competition between the imine formation and the carbonyl reduction, the reactivity of diamine is critical to the purity of resultant benzoxazine. Benzoxazines based on diamines with high reactivity (1-3) can be successfully prepared by this one-pot procedure. In contrast, benzoxazine prepared by diamine with low reactivity such as 4,4'-diaminodiphyl sulfone lead to poor purity.⁴² The clean and inexpensive hydrogen reduction makes this one-pot attractive for industrial applications. Compared with diamines (1-3), diamine-based benzoxazines (4-6) show some advantages as epoxy hardeners. For example, the gel time of the (1)/CNE system is too short to prepare a void-free sample for DMA measurement. In contrast, the gel time of the (4)/CNE system is long enough to process a void-free sample. In addition to allowing for better processing, the longer gel time makes the (4)/CNE system attractive for IC encapsulation, in which low viscosity during mold transfer is important. In addition to latent curing characteristic, one particular benefit of using benzoxazine as an epoxy hardener is its miscibility with epoxy resin. For example, (2) and CNE are immiscible in the molten state, whereas (5)/CNE is miscible and a single $T_{\rm g}$ in the DMA measurement was observed for the (5)/CNE thermoset. T_{g} s of the (4-6)/CNE thermosets are as high as 243-244 °C, which are 23-48 °C higher than those of P(4-6). According to the height of tan δ in the DMA measurement, the (4-6)/CNE thermosets have higher crosslinking density than P(4-6), explaining the high $T_{\rm g}$ characteristic of (4–6) as CNE hardeners. The combination of long pot-life, wide processing window, miscibility with epoxy, high $T_{\rm g}$, and high dimensional stability after curing makes the (4-6)/CNE systems potential materials for IC encapsulation.

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financial support. Partial sponsorship by the Green Chemistry Project (NCHU), funded by the Ministry of Education, is also gratefully acknowledged.

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