Physical and mechanical properties of flexible polybenzoxazine resins: effect of aliphatic diamine chain length. J Appl Polym Sci 101(5):2798

2 AUTHORS, INCLUDING:

Hatsuo Ishida
Case Western Reserve University

448 PUBLICATIONS **12,844** CITATIONS

Physical and Mechanical Properties of Flexible Polybenzoxazine Resins: Effect of Aliphatic Diamine Chain Length

Douglas J. Allen, Hatsuo Ishida

Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202

ABSTRACT: A series of linear aliphatic diamine-based benzoxazine monomers has been polymerized into transparent, crosslinked specimens that are free of voids and have good mechanical integrity. The density of these polybenzoxazines is measured as a function of the amine chain length. Dynamic mechanical analysis of these linear aliphatic polybenzoxazines shows two, chain length dependent transitions. Properties, such as room temperature modulus, glass transition temperature, crosslink density, thermal degradation temperature, and char yield, of the polybenzoxazines are investigated as a function of the chain length. All these properties exhibit strong dependence on the chain length. These aliphatic amine-based polybenzoxazines are found to be much more flexible than the bisphenol-type polybenzoxazines. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2798–2809, 2006

Key words: aliphatic amine-based benzoxazine; char yield; crosslink density; dynamic mechanical analysis; polybenzoxazine; T_g; thermal stability

INTRODUCTION

Over the past decade, the research community has focused considerable effort on developing polybenzoxazines as a class of thermosetting material to overcome many of the shortcomings associated with traditional resole and novolac-type phenolic resins.[1–10] Benzoxazine monomers are readily synthesized, either in solution or by a patented melt-state process,[11] through the Mannich condensation of a phenolic derivative, formaldehyde, and a primary amine, as generalized in Scheme 1. Benzoxazines can be thermally activated and do not require acid or base catalysts for ring-opening polymerization; see Scheme 1. The unique chemistry provides tremendous opportunities for molecular design and offers a number of inherent processing benefits, including low melt viscosity, no volatile release upon cure, rapid property development, and low overall shrinkage. The polymerization of multifunctional monomers produces thermosetting polybenzoxazines that have excellent thermal, mechanical, and dielectric properties, as well as low water absorption.[12]
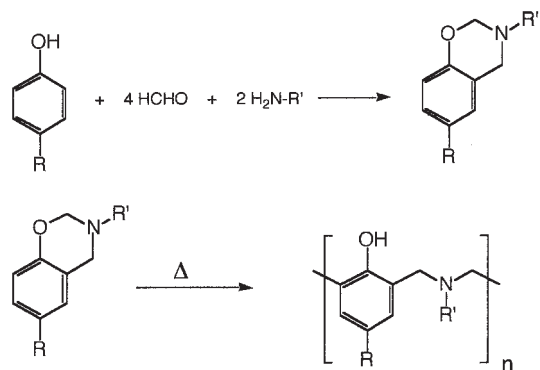
Polybenzoxazines are typically bisphenol based and, therefore, possess a rigid aromatic core in their backbone structure. Yet, despite the numerous advantages highlighted earlier, polybenzoxazines still suffer to a certain extent from the brittleness that plagues conventional thermosetting resins. As a result, much of the published benzoxazine research has targeted improvement in the toughness of these thermosetting materials. Phase-separated, physical blends of polybenzoxazine with amine-terminated (ATBN) or carboxyl-terminated (CTBN) butadiene-acrylonitrile rubber have improved fracture toughness.[13,14] As much as 12% ATBN rubber has also been covalently bonded to the benzoxazine matrix at the amine functionality during synthesis.[15] Physically interacting thermoplastic polymer modification has been achieved with poly (ε-caprolactone) (PCL), which is compatibilized by hydrogen bonding between the phenolic group of the polybenzoxazine and the carbonyl group of PCL.[16]

Copolymerization has improved mechanical performance by taking advantage of the reactivity at the phenolic hydroxyl group to chemically incorporate a flexible chain into the polybenzoxazine matrix. Epoxy[17] and polyurethane[18] each contain functionalities that have been coreacted with benzoxazine to form homogeneous, single-phase copolymer systems with improved mechanical properties. Poly (imide-siloxane) has also been blended with benzoxazines to improve toughness, either as a reactive comonomer when the poly (imide-siloxane) contains phenolic hydroxyl groups, or as a semi-interpenetrating network when it does not.[19]

Scheme 1 Synthesis (top) and thermal polymerization (bottom) of a benzoxazine monomer.

Bisphenol-A based Network
BA-a

Aliphatic Diamine-based Network
P-ad

Figure 1 Comparison of the network structures of a bisphenol-A based polybenzoxazine and a linear aliphatic diamine-based polybenzoxazine.

The majority of published benzoxazine research has focused almost exclusively on materials in which the phenolic compound, typically a bisphenol, provides the multifunctionality necessary to achieve an infinite network. This limits benzoxazines to materials with a rigid, aromatic core as the backbone of the crosslinked network. All of the previous attempts at improving the toughness of polybenzoxazines have involved the addition of a flexible component, often reactive, into the thermosetting matrix. This study, however, seeks to take advantage of the rich molecular design opportunities of benzoxazines to develop a matrix material with an inherently flexible molecular structure that is less brittle than typical benzoxazines. By switching multifunctionality of the benzoxazine to the amine portion of the structure, the limitations of the bisphenolic linkage can be eliminated, and less brittle materials can be specifically designed at the molecular level by incorporating a flexible difunctional amine as the central core. (Fig. 1)

In this study, a series of linear, aliphatic diamine-based benzoxazines, shown in Figure 2, will be synthesized and characterized to demonstrate the feasibility of increasing the inherent flexibility of the polybenzoxazine network structure itself. The effect of aliphatic chain length on the polybenzoxazine structure and properties is probed by systematic variation of the diamine compound.

EXPERIMENTAL

Materials

Phenol (99%) and 1,6-hexadiamine (99.5%) were purchased from the Acros Division of Fisher Scientific. Ethylene diamine (99%), 1,4-diaminobutane (99%), 1,8-diaminooctane (98%), and paraformaldehyde (95%) were obtained from Aldrich Chemical, while 1,12-diaminododecane (99%) was purchased from Fluka. All chemicals were used as received with no further purification.
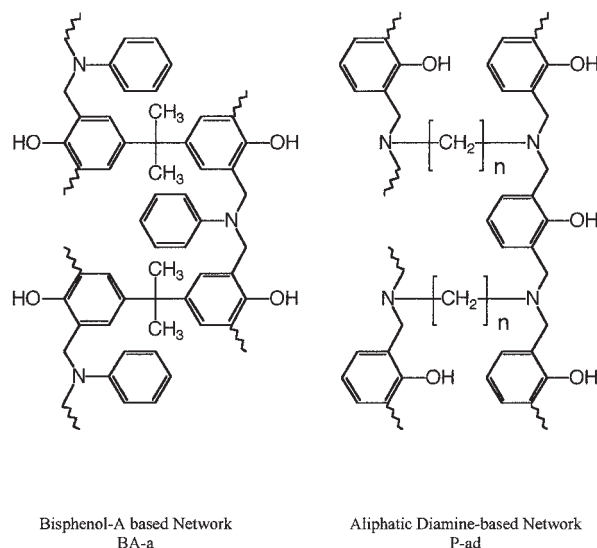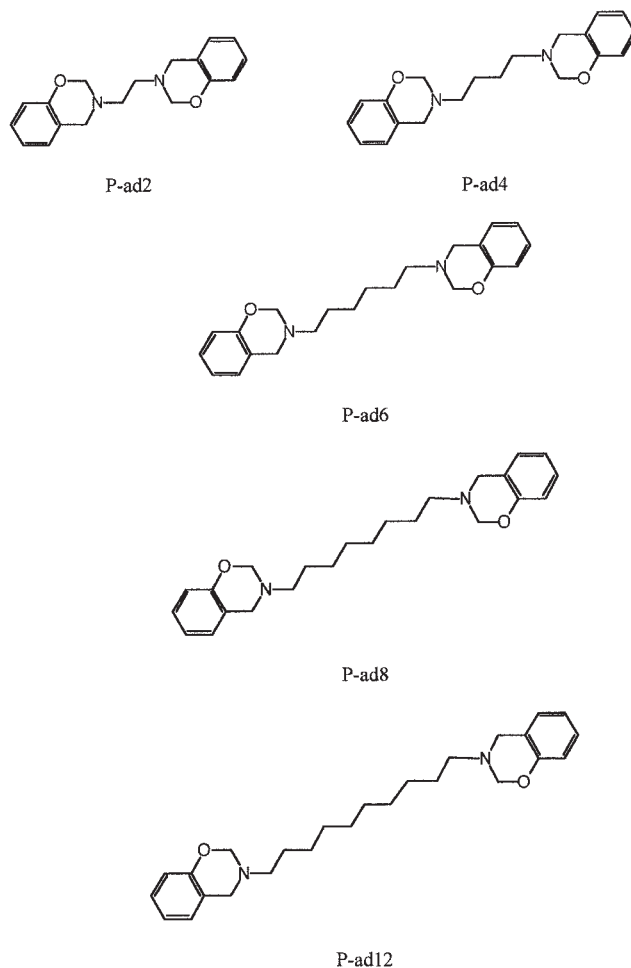

P-ad2   P-ad4

P-ad6

P-ad8

P-ad12

Figure 2 Structures and nomenclature used for the series of linear aliphatic diamine-based benzoxazine monomers.

Monomer	Diamine	Reaction time (h)	Wash alcohol	Molecular weight
P-ad2	Ethylene diamine	1.5	Methanol	296.36
P-ad4	1,4-Diaminobutane	4	Methanol	324.42
P-ad6	1,6-hexane diamine	8	1-Butanol	352.47
P-ad8	1,8-diaminooctane	10	1-Butanol	380.52
P-ad12	1,12-diaminododecane	12	1-Butanol	436.63

Synthesis of benzoxazine monomers

A modification of the solventless synthesis method, detailed elsewhere,[20] was utilized for the synthesis of each difunctional, aliphatic diamine-based benzoxazine monomer. Stoichiometric amounts (2 : 4 : 1) of phenol, paraformaldehyde, and aliphatic diamine were dry mixed in a single neck reaction flask. Approximately 5 mL of chloroform per gram of reactants were added to the flask, which was then refluxed with stirring for an optimized time period between 1.5 and 12 h, as specified for each monomer in Table I. After cooling to room temperature, the crude reaction products were washed several times with 1N NaOH solution and then rinsed with distilled water until neutral. The base washed products were dried over sodium sulfate and filtered, followed by solvent removal under vacuum. After grinding to a powder, the material was further purified by rinsing with the alcohol indicated in Table I. The purified benzoxazine monomer was then dried under vacuum at room temperature for 24 h and refrigerated until the time of use. Benzoxazine formation and purity were verified by nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and elemental analysis.

Ethylene diamine-based benzoxazine monomer

1,2-Bis(3,4-dihydro-2H-1,3-benzoxazin-3-yl) ethane was synthesized according to the procedure above, utilizing a 1.5 h reaction period and methanol as the wash alcohol. White powder.

^{1}H NMR (CDCl$_3$, 200MHz ^{1}H, 298 K, δ): 2.98 (4H, N-CH$_2$- CH$_2$), 4.04 (4H, Ar- CH$_2$-N), 4.90 (4H, O-CH$_2$-N), 6.76–7.15 (8H, Ar-H).

^{13}C NMR (CDCl$_3$, 50.3 MHz ^{13}C, 298 K, δ): 49.51 (2C, N-C-C), 50.31 (2C, Ar-C-N), 82.64 (2C, O-C-N), 116.36 (2C, Ar), 119.91 (2C, Ar), 120.51 (2C, Ar), 127.50 (2C, Ar), 127.68 (2C, Ar), 154.06 (2C, Ar).

Anal. Calcd. for C$_{18}$H$_{20}$N$_2$O$_2$: C, 72.95%; H, 6.80%; N, 9.45%. Found: C, 73.12%; H, 7.00%; N, 9.43%.

1,4-Diaminobutane-based benzoxazine monomer

1,4-Bis(3,4-dihydro-2H-1,3-benzoxazin-3-yl) butane ethane was synthesized according to the procedure above, utilizing a 4 h reaction period and methanol as the wash alcohol. White powder.

^{1}H NMR (CDCl$_3$, 200MHz, 298 K, δ): 1.61 (4H, CH$_2$-CH$_2$- CH$_2$) 2.76 (4H, N- CH$_2$- CH$_2$), 3.97 (4H, Ar-CH$_2$-N), 4.85 (4H, O-CH$_2$-N), 6.74–7.15 (8H, Ar-H).

^{13}C NMR (CDCl$_3$, 50.3 MHz ^{13}C, 298 K, δ): 25.62 (2C, C-C-C), 50.12 (2C, Ar-C-N), 51.09 (2C, N-C-C), 82.42 (2C, O-C-N), 116.30 (2C, Ar), 120.16 (2C, Ar), 120.41 (2C, Ar), 127.49 (2C, Ar), 127.60 (2C, Ar), 154.15 (2C, Ar).

Anal. Calcd. for C$_{20}$H$_{24}$N$_2$O$_2$: C, 74.04%; H, 7.46%; N, 8.64%. Found: C, 73.88%; H, 7.432%; N, 8.52%.

1,6-Hexadiamine-based benzoxazine monomer

1,6-Bis(3,4-dihydro-2H-1,3-benzoxazin-3-yl) hexane ethane was synthesized according to the procedure above, utilizing an 8 h reaction period and 1-butanol as the wash alcohol. White powder.

^{1}H NMR (CDCl$_3$, 200MHz, 298 K, δ): 1.35, 1.56 (8H, CH$_2$- CH$_2$- CH$_2$) 2.69, 2.73, 2.76 (4H, N- CH$_2$- CH$_2$), 3.97 (4H, Ar- CH$_2$-N), 4.85 (4H, O-CH$_2$-N), 6.74–7.15 (8H, Ar-H).

^{13}C NMR (CDCl$_3$, 50.3 MHz ^{13}C, 298 K, δ): 27.05 (2C, C-C-C), 28.00 (2C, C-C-C), 50.17 (2C, Ar-C-N), 51.22 (2C, N-C-C), 82.37 (2C, O-C-N), 116.27 (2C, Ar), 120.19 (2C, Ar), 120.38 (2C, Ar), 127.47 (2C, Ar), 127.56 (2C, Ar), 154.14 (2C, Ar).

Anal. Calcd. for C$_{22}$H$_{28}$N$_2$O$_2$: C, 74.97%; H, 8.01%; N, 7.95%. Found: C, 75.15%; H, 8.21%; N, 8.14%.

1,8-Diaminooctane-based benzoxazine monomer

1,8-Bis(3,4-dihydro-2H-1,3-benzoxazin-3-yl) octane was synthesized according to the procedure above, utilizing a 10 h reaction period and 1-butanol as the wash alcohol. White powder.

^{1}H NMR (CDCl$_3$, 200MHz, 298 K, δ): 1.30, 1.55 (12H, CH$_2$- CH$_2$- CH$_2$) 2.68, 2.72, 2.76 (4H, N- CH$_2$- CH$_2$), 3.98 (4H, Ar- CH$_2$-N), 4.85 (4H, O-CH$_2$-N), 6.74–7.15 (8H, Ar-H).

^{13}C NMR (CDCl$_3$, 50.3 MHz ^{13}C, 298 K, δ): 27.12 (2C, C-C-C), 28.06 (2C, C-C-C), 29.41 (2C, C-C-C), 50.20 (2C, Ar-C-N), 51.31 (2C, N-C-C), 82.38 (2C, O-C-N), 116.28 (2C, Ar), 120.24 (2C, Ar), 120.37 (2C, Ar), 127.47 (2C, Ar), 127.55 (2C, Ar), 154.17 (2C, Ar).

TABLE II
Optimized Polymerization Profile Used to Prepare Samples for Density Measurement, Dynamic Mechanical, Flexural, and Thermogravimetric Analysis

	Temperature (°C)	Time (h)
P-ad2	140/160/180/185	1
P-ad4	140/160/180/185	1
P-ad6	140/160	1
	180	4
P-ad8	140/160/180/185	1
P-ad12	140/160	1
	180	3

Anal. Calcd. for $C_{24}H_{32}N_2O_2$: C, 75.75%; H, 8.48%; N, 7.36%. Found: C, 75.59%; H, 8.60%; N, 7.44%.

1,12-Diaminododecane-based benzoxazine monomer

1,12-Bis(3,4-dihydro-2H-1,3-benzoxazin-3-yl) dodecane was synthesized according to the procedure above, utilizing a 12 h reaction period and 1-butanol as the wash alcohol. White powder.

^{1}H NMR (CDCl$_3$, 200MHz, 298 K, δ): 1.25, (16H, CH$_2$- CH$_2$- CH$_2$), 1.55 (4H, CH$_2$- CH$_2$- CH$_2$) 2.69, 2.73, 2.76 (4H, N- CH$_2$- CH$_2$), 3.98 (4H, Ar- CH$_2$-N), 4.85 (4H, O-CH$_2$-N), 6.74–7.15 (8H, Ar-H).

^{13}C NMR (CDCl$_3$, 50.3 MHz ^{13}C, 298 K, δ): 27.20 (2C, C-C-C), 28.11 (2C, C-C-C), 29.47 (2C, C-C-C), 29.52 (2C, C-C-C), 29.54 (2C, C-C-C), 50.22 (2C, Ar-C-N), 51.36 (2C, N-C-C), 82.39 (2C, O-C-N), 116.28 (2C, Ar), 120.26 (2C, Ar), 120.36 (2C, Ar), 127.48 (2C, Ar), 127.55 (2C, Ar), 154.18 (2C, Ar).

Anal. Calcd. for $C_{28}H_{40}N_2O_2$: C, 77.02%; H, 9.23%; N, 6.42%. Found: C, 77.13%; H, 9.11%; N, 6.65%.

Sample preparation

Polymerized samples of each benzoxazine were prepared for dynamic mechanical analysis, flexural analysis, thermogravimetric analysis, and polymer density measurement in the following manner. Small sheets of each material were cured without any added initiators or catalysts in a vertical mold consisting of a 3mm silicon rubber spacer clamped between two glass plates treated with a silicon-based release agent. The monomer filled mold was heated under vacuum at 100°C–120°C for 1h to remove any air entrapped during the mold filling process and eliminate any trace solvent. The benzoxazine resin was then step cured in a convection oven according to the previously optimized profile[21] outlined for each material in Table II. Upon completion of curing, the samples were allowed to freely cool to room temperature. Individual test samples were cut to appropriate dimensions with a diamond saw, and then polished on the machined surfaces until visually smooth.

NMR

The structure of the diamine-based benzoxazine monomers was verified by both proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy utilizing a Varian Gemini XL-200 spectrometer operating at a proton frequency of 200MHz and a corresponding carbon frequency of 50.3 MHz. Monomers were dissolved in deuterated chloroform with all peaks referenced relative to tetramethylsilane (TMS). Proton spectra were obtained using 64 transients and a concentration of 1 wt %, while 1024 transients and a concentration of 5 wt % were used for the ^{13}C spectra.

Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra of the benzoxazine monomers and polymers were obtained on a Biorad FTS-60A spectrometer with a potassium bromide (KBr) beamsplitter and a deuterated triglycine sulfate (DTGS) detector. The spectrometer was purged with dry nitrogen and operated in transmission mode utilizing the coaddition of 256 scans at a resolution of 2cm^{-1}. The monomer spectra were obtained from 1 to 2 mg samples cast from chloroform onto 25mm KBr plates.

Density measurement

Gas pycnometry was used to measure the density of the cured materials using a Quantachrome Ultrapycnometer 1000 with helium as the purge gas. Density at 26°C was taken as the average of 12 measurements for each sample, using several samples for each material.

Dynamic mechanical analysis

Dynamic mechanical spectra were obtained with a Rheometrics Dynamic Mechanical Spectrometer (RMS-800) equipped with a 2000/200g-cm dual-range force rebalance transducer set for the high range. Specimens with dimensions of approximately 60 × 12.5 × 3 mm were tested in a rectangular torsion fixture. A sinusoidal shear strain of 0.1% was applied at a frequency of 1 Hz during each temperature sweep experiment. Linearity of the chosen shear strain was verified by a strain sweep prior to each experiment. Measurements were collected every 2°C as the samples were heated at a rate of approximately 2°C/min from –150°C to well above the glass transition of each material.

Thermogravimetric analysis

The thermal stability of the aliphatic diamine-based benzoxazines was measured by thermogravimetric analysis (TGA) using a TA Instruments 2950 High

Resolution Thermogravimetric Analyzer equipped with an evolved gas analysis (EGA) furnace. Weight loss was monitored as 20 mg samples were heated at a rate of 10°C/min to a maximum temperature of 800°C under a 90 mL/min dry nitrogen purge.

Mechanical properties

Flexural properties of the cured polybenzoxazines were measured in accordance with ASTM D790M using an Instron Model 5567 fitted with a 30kN static load cell and a standard 3-point bending fixture. Six samples with dimensions of 60 × 10 × 3 mm were tested for each material using Series IX control and analysis software. Samples were flexed until breakage at a rate of 1.28 mm/min using a support span of 48mm. Flexural strain was calculated based upon crosshead movement.

RESULTS AND DISCUSSION

Benzoxazine polymerization occurs via a thermally activated cationic reaction of the oxazine ring, and thus no external initiators or catalysts are required to produce polybenzoxazines from the aliphatic diamine-based series of monomers. The benzoxazine samples for this investigation were cured according to temperature profiles that were individually optimized in a parallel study on their polymerization behavior to yield a maximum glass transition temperature with minimal degradation. The polymeric benzoxazine materials appeared transparent and void-free, ranging in color from dark amber for P-ad2, to a pale yellow for P-ad12.
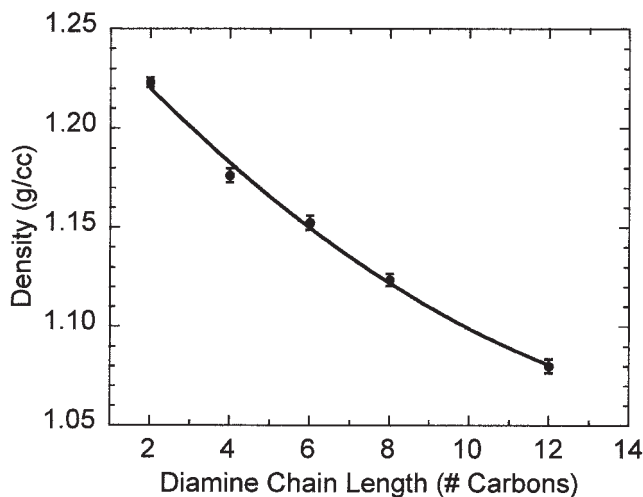
Figure 3 Room temperature density of aliphatic diamine-based polybenzoxazines.
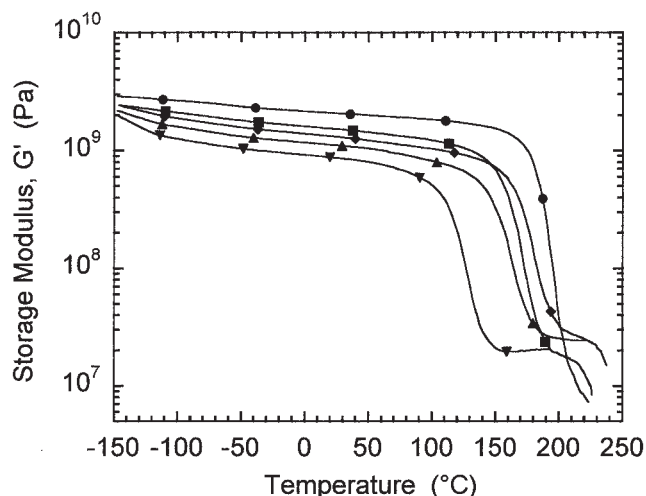
Figure 4 Storage moduli for the linear aliphatic diamine-based series of polybenzoxazines, including P-ad2 (●), P-ad4 (■), P-ad6 (♦), P-ad8 (▲), and P-ad12 (▼).

Polymer density

The room temperature densities of the aliphatic diamine-based polybenzoxazines were measured by gas pycnometry and are plotted as a function of diamine chain length in Figure 3. The polymer densities decrease monotonically over the range of aliphatic chain lengths investigated in this study, from a high of 1.22 g/cm^3 for P-ad2, to a low of 1.08 g/cm^3 for P-ad12. Typical bisphenol-based benzoxazines have densities ranging from 1.08 g/cm^3 for n-butyl amine based material,[22] to 1.26 g/cm^3 for polybenzoxazine based upon bisphenol-A with 3,5 xylidene.[5]

Dynamic mechanical analysis

The dynamic mechanical properties of the aliphatic diamine-based polybenzoxazines were measured over the temperature range from –150°C to beyond the glass transition temperature (T_g) of each material. The elastic or storage modulus, G′, for this series of polybenzoxazines is presented in Figure 4. Not surprisingly, the elastic modulus is very much dependent on the length of the diamine over the entire sub-T_g temperature range, becoming less stiff as the length of the flexible aliphatic chain increases. This is clearly demonstrated in Figure 5, which shows the systematic decrease in storage modulus at room temperature for the polybenzoxazine series as a function of aliphatic diamine chain length, from 2.1 GPa for the shortest chain compound, P-ad2, to 0.9 GPa for the longest, P-ad12. Despite the substitution of a flexible aliphatic diamine for the multifunctional core, the modulus of P-ad2 is remarkably similar to the 2.2 GPa observed for the most extensively studied polybenzoxazine, 6,6′-Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)iso-
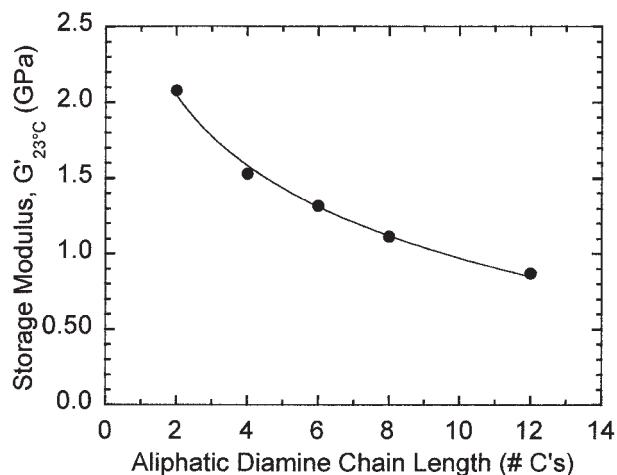
Figure 5 Room temperature storage moduli of the diamine-based series of polybenzoxazines as a function of aliphatic chain length.

Figure 7 Glass transition temperatures of the diamine-based series of polybenzoxazines as a function of aliphatic chain length.

propane (BA-a), which has a rigid aromatic bisphenol compound for its backbone. The P-ad2 polybenzoxazine has just a two-carbon chain separating each Mannich bridge, and thus may have steric contributions to rigidity in addition to the effects of crosslink density, both of which would be expected to diminish as diamine chain length increases.

The loss modulus spectrum or viscous component, G″, for each aliphatic diamine-based polybenzoxazine is shown in Figure 6. The glass transition temperature of each material can be determined from the peak maximum of the loss modulus, and is presented for this series of polymers in Figure 7. The T_gs observed for these polybenzoxazines are surprisingly high given the flexible nature of the multifunctional amine core molecule used in the preparation of each mono-
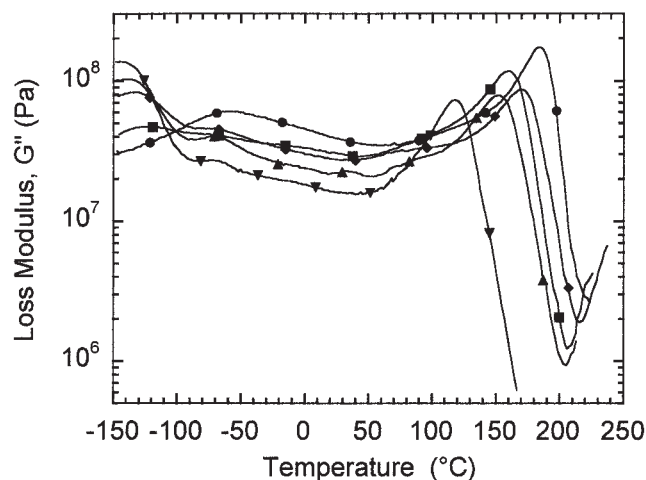
mer. The glass transition temperature of the polybenzoxazine with the shortest chain, P-ad2, is approximately 184°C, which exceeds that of many bisphenol-based benzoxazines, including the 170°C transition of BA-a, the widely researched material mentioned earlier. P-ad6, with an aliphatic diamine chain containing six carbons, has a T_g equivalent to BA-a, while P-ad4 and P-ad8 are not too much lower at 160°C and 151°C, respectively. Even with a long, 12-carbon aliphatic chain, P-ad12 undergoes its glass to rubber transition at a somewhat respectable 118°C.

The crosslink density of a thermosetting resin may be estimated from the plateau of the elastic modulus in the rubbery state using an equation from the statistical theory of rubber elasticity:[23]

$$G_e = \phi v RT = \phi(\rho/M_c)RT$$

where G_e is the equilibrium shear modulus in the rubbery region, ϕ is a front factor that is unity for ideal rubbers, R is the gas constant, and T is the absolute temperature. The crosslink density or concentration of network chains, v, is the number of moles of network chains per unit volume of the cured polymer. If the density of the polymer, ρ, is known, then the molecular weight between crosslinks, M_c, may also be calculated. However, this equation is strictly valid only for lightly crosslinked materials and, therefore, can only be used to qualitatively compare the level of crosslinking among the various diamine-based polybenzoxazines and for comparison to other thermosets, which have reported values that were calculated in a similar manner.

Analysis of crosslink densities for the aliphatic diamine-based series of polybenzoxazines is complicated by thermal degradation above the glass transition

Figure 6 Loss moduli for the linear aliphatic diamine-based series of polybenzoxazines, including P-ad2 (●), P-ad4 (■), P-ad6 (♦), P-ad8 (▲), and P-ad12 (▼).
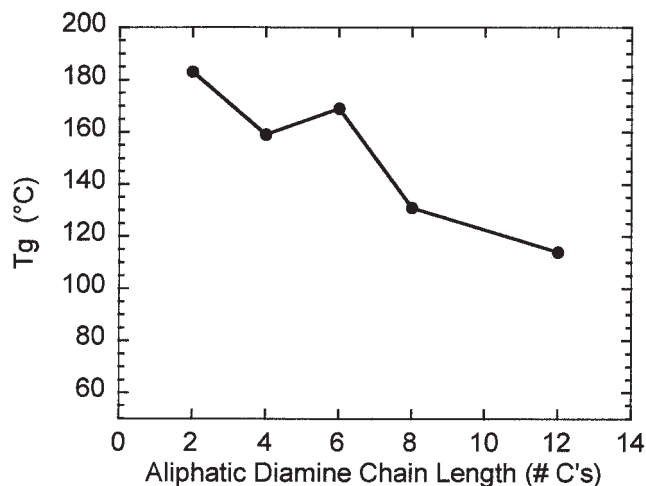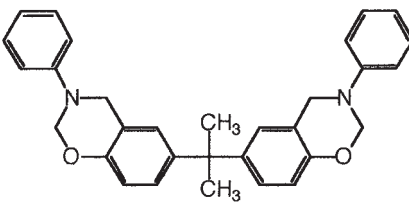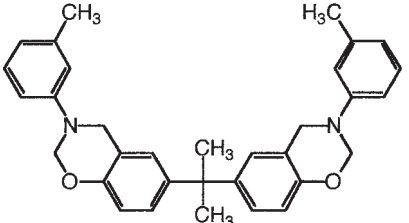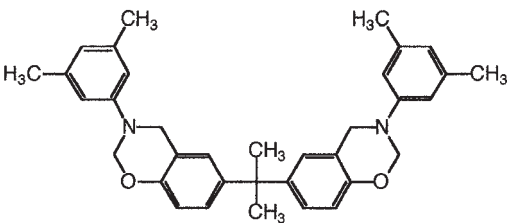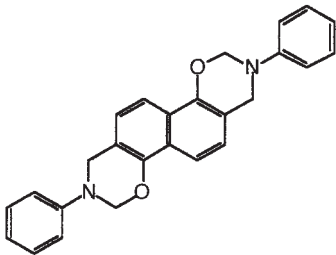
	P-ad2	P-ad4	P-ad6	P-ad8	P-ad12
Molec. Wt (g/mol)	296.36	324.42	352.47	380.52	436.63
T_g (°C)	184	160	169	151	118
Density (g/cm^3)	1.22	1.18	1.15	1.12	1.08
$G'_{23°C}$ (GPa)	2.08	1.53	1.32	1.11	0.87
$G'_{(T_g+50°C)}$ (MPa)	—	—	28.5	25.5	19.8
Crosslink density	—	—	7.13	6.48	5.40
Mc	—	—	162	173	200
Crosslinks/Molec. wt. unit	—	—	2.18	2.20	2.18

temperature for several of the materials. This degradation appears to prevent the formation of the rubbery plateau for the P-ad2 and P-ad4 polymers and, thus, the value of the shear modulus in this region is unobtainable. The P-ad6 material also shows similar degradation in this temperature range, but the value of the plateau modulus can be roughly estimated to be 28.5 MPa at 208°C. In part due to their lower glass transition temperatures combined with an onset of degradation that is relatively constant regardless of structure, the rubbery plateaus for the P-ad8 and P-ad12 polybenzoxazines are stable, with moduli that can be easily quantified as 25.5 MPa and 19.8 MPa, respectively, at a temperature of T_g + 50°C. These values for the shear modulus in the rubbery plateau were used to estimate the crosslink density and molecular weight between crosslinks for the latter three polybenzoxazines and are summarized in Table III.

As longer aliphatic diamines are incorporated into the network structure over this series of materials, the separation between each pair of Mannich bridges along the multifunctional core would also be expected to increase. Thus, it is not unexpected that the crosslink densities of the linear diamine-based series of polybenzoxazines decrease as a function of aliphatic chain length when estimated from rubber elasticity theory. However, the values of 7.1, 6.5, and 5.4 × 10^{-3} mol/cm^3 derived from the above equation for P-ad6, P-ad8, and P-ad12, respectively, are all significantly higher than the 1.1 × 10^{-3} mol/cm^3 crosslink density previously observed for bisphenol-A/aniline-based polybenzoxazine (BA-a).[5,12] The molecular weight between crosslinks for these materials also increases as a function of aliphatic chain length, from 162 g/mol for P-ad6 to 200 g/mol for P-ad12. The M_c of the amine-based polybenzoxazines can be normalized to the molecular weight of the monomer to roughly determine the number of crosslinks per molecular repeat unit. Surprisingly, for the longest three diamines, this value is constant at 2.2 crosslinks per chemical repeat unit regardless of the aliphatic diamine chain length. This value is extremely high when compared to the crosslink densities of bisphenol-

based polybenzoxazines that are listed in Table IV. Thus, it appears that this series of benzoxazine compounds maintains a high stiffness and glass transition temperature, despite the absence of a rigid aromatic

TABLE IV
Crosslink Densities of Various Bisphenol-Based Polybenzoxazines

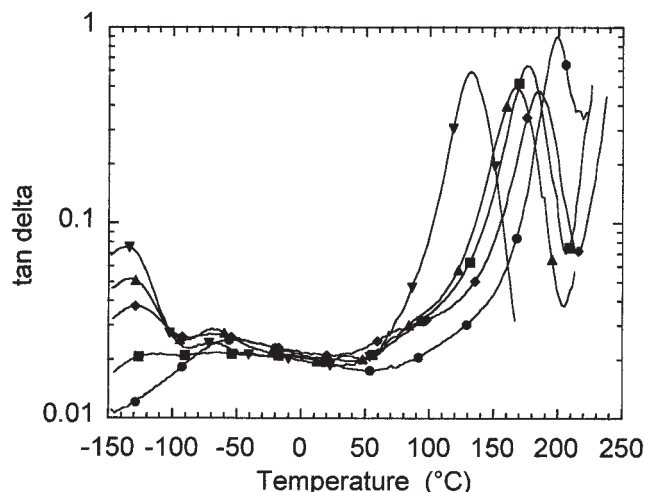| Benzoxazine	Crosslink Density (× 10^{-3} mol/cm^3)
	1.1
	2.7
	2.9
	7.4

Figure 8 Tan δ curves for the linear aliphatic diamine-based series of polybenzoxazines, including P-ad2 (●), P-ad4 (■), P-ad6 (♦), P-ad8 (▲), and P-ad12 (▼).

bisphenol core, by an increased degree of crosslinking. The value of 2.2 crosslinks per molecular weight unit implies that during polymerization, open oxazine rings must attach not only to the free *ortho*-position on the phenol as indicated in Figure 1, but also to a limited degree at an additional site. Studies of monofunctional benzoxazines have shown that, in fact, the *para*-position of the phenol is also reactive, although to a much lower degree than the primary *ortho*-position. Typically, benzoxazines have chains that are primarily linked through the bisphenol compound itself, but aside from a few exceptional materials, cannot form linkages through the amine group. In the analog diamine-based materials, however, the primary linkage is through the diamine itself, and the current data suggests that the phenol portion of the molecule may provide additional functionality and a secondary linkage that is unavailable in the normal bisphenol-type resins. The constant number of crosslinks per repeat unit would also seem to indicate that these three polybenzoxazines have a similar polymerization mechanism and network structure, varying only in aliphatic chain length, but not the position of the crosslinks.

Finally, the tan δ curves are shown for each of the aliphatic diamine-based polybenzoxazines in Figure 8. The main α-relaxation process associated with the glass to rubber transition for each of the benzoxazine polymers is located between 130°C and 200°C. Additionally, there is a β-transition that seems to be characteristic of the polybenzoxazine family that is centered near 120°C for P-ad2, 90°C for P-ad4, and at approximately 80°C for P-ad6 to P-ad12. Previous hypotheses have attributed this β-relaxation process to unreacted molecular segments or network heterogeneity.[24] However, the relatively fixed position of this broad relaxation, for a wide variety of both bisphenol and diamine-based polybenzoxazine networks, suggests that perhaps movement within the Mannich bridge itself is actually responsible for this tan δ peak. This is supported by the position of the β-relaxation for P-ad2, the material with the shortest diamine, which is shifted higher by approximately 30°C relative to the polybenzoxazines with longer aliphatic chains. A similar shift has been observed for aromatic diamine-based polybenzoxazines.[25] It is hypothesized that this very short diamine linkage impedes the short-range motion of the atoms associated with the Mannich bridge and shifts the relaxation process to higher temperatures.

A pair of γ-transitions is also apparent in the tan δ spectra of the diamine-based polybenzoxazines, the first centered between –140 and –120°C, and a second higher temperature relaxation with a peak at approximately –70 to –55°C. The lower temperature relaxation process appears to be absent from the P-ad2, but its magnitude increases significantly with diamine chain length and thus can be tentatively identified as movement of the linear aliphatic chain within the diamine segment itself. The higher temperature γ-transition appears similar to that which is present in bisphenol-based polybenzoxazines at approximately –80°C. For those materials, submotion of the pendant group on the Mannich bridge was said to be responsible for the relaxation.[24] In the aliphatic diamine-based polybenzoxazines, this peak appears to be significantly narrower and also seems to be somewhat related to the length of the aliphatic chain.

Flexural analysis

The flexural properties of the linear aliphatic diamine-based series of polybenzoxazines were tested in accordance with ASTM specifications and are summarized in Table V. The flexural modulus of elasticity is shown in Figure 9 for each polymer composition. Mirroring the trend observed by dynamic mechanical analysis, the modulus decreases as a function of the aliphatic diamine chain length, with the largest drop occurring between P-ad2 and P-ad4. The modulus of elasticity varies significantly for the aliphatic diamine-based

TABLE V
Summary of the Flexural Properties of the Linear Aliphatic Diamine-Based Series of Polybenzoxazines

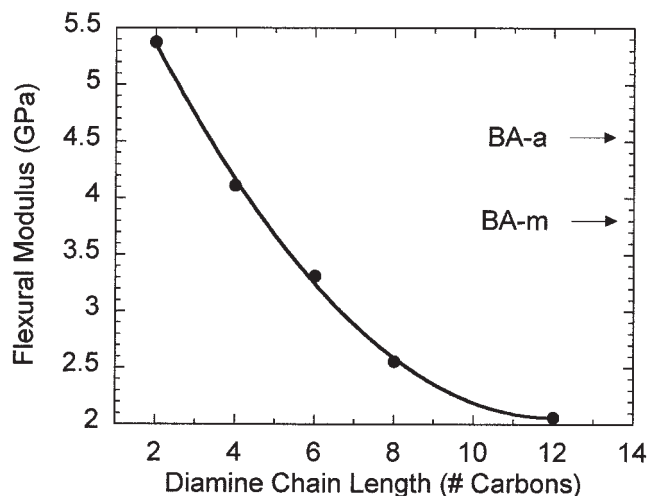| Polymer	Flexural modulus (GPa)	Stress at yield (MPa)	Strain at break (%)
P-ad2	5.4	169	3.3
P-ad4	4.1	159	4.4
P-ad6	3.3	139	5.2
P-ad8	2.6	135	9.3
P-ad12	2.1	98.4	12.4

Figure 9 Flexural moduli of the diamine-based series of polybenzoxazines as a function of aliphatic chain length as obtained in the 3-point bending experiments. Flexural moduli of two bisphenol-A based polybenzoxazines are also noted for comparison.

Figure 11 Flexural strain at yield (●) for the diamine-based series of polybenzoxazines as a function of aliphatic chain length. Also shown is the flexural strain at break (▲) for the materials in which breakage occurred subsequent to yielding. For comparison, the yield stresses of two bisphenol-A based polybenzoxazines are also indicated.

benzoxazines, ranging from a very stiff 5.4 GPa for P-ad2, to a rather flexible 2.1 GPa for P-ad12. The P-ad2 modulus exceeds even the stiffness of the bisphenol-based polybenzoxazine, BA-a, which has a flexural modulus of approximately 4.5 GPa.

The yield stress of this polybenzoxazine series is also strongly related to the length of the aliphatic chain within the diamine, as can be seen in Figure 10. The linear diamine-based polymer loses approximately 40% of its strength, from 169 MPa to 98 MPa, as the aliphatic chain is increased from 2 to 12 carbon
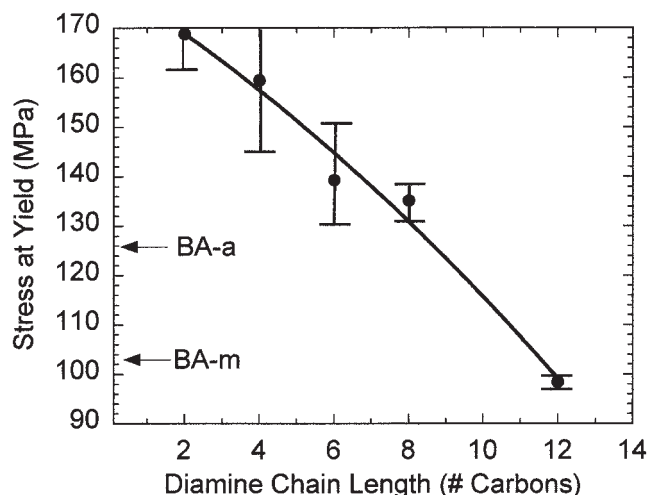

Figure 10 Flexural stress at yield for the diamine-based series of polybenzoxazines as a function of aliphatic chain length as obtained in the 3-point bending experiments. For comparison, flexural stress at yield for two bisphenol-A based polybenzoxazines are also indicated.
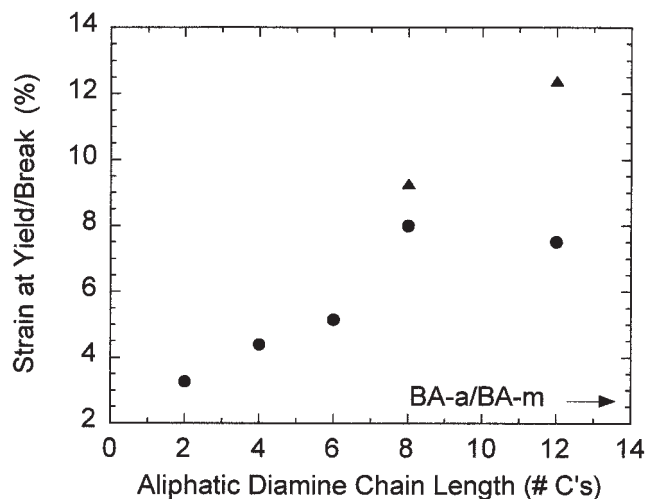
atoms. However, all of the diamine-based polybenzoxazines except for the longest chain matrix, P-ad12, have a flexural strength that is greater than the 70–120 MPa value previously reported for the benzoxazine reference material, BA-a. Earlier research has hypothesized that the mechanical properties of BA-a, like many brittle, high modulus materials, may be very sensitive to internal flaws or defects and may fracture prematurely, making a true measure of the inherent resin properties very difficult.[12,13] The linear aliphatic diamine-based series of polybenzoxazines appears to be much less sensitive to these internal irregularities, and thus their measured properties may give a more accurate indication of the properties inherent to benzoxazine matrices.

The flexural yield strain for the diamine-based polybenzoxazines, presented in Figure 11, provides a clear validation of this effort to design a tougher, more inherently flexible polybenzoxazine network at the molecular level by switching the multifunctional core molecule from an aromatic bisphenol compound to an aliphatic diamine. Without any sacrifice of strength, the entire series of diamine polybenzoxazines has a yield strain that is superior to that of the BA-a reference material, ranging from 3.3% for P-ad2 to a maximum yield strain of 8.0% for P-ad8. BA-a has shown yield strains between 2 and 2.9% in other work. It should be noted that P-ad2 through P-ad6 all experienced brittle fracture at their maximum yield stress, while P-ad8 and P-ad12 both underwent yielding and thus a maximum yield stress some time prior to fracture. Most impressive was the P-ad12 material, which in some cases did not fracture even at strain loadings
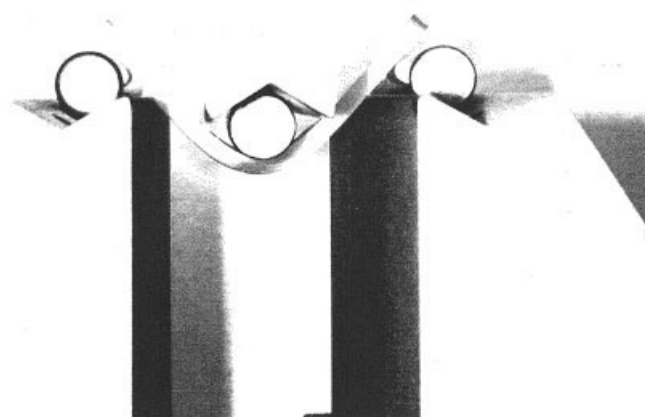
Figure 12 Image of P-ad12 exhibiting high flexibility during its 3-point bending experiment.

Figure 13 Percent weight loss for the diamine-based series of polybenzoxazines as a function of aliphatic chain length as obtained in a nitrogen environment: P-ad2 (●), P-ad4 (■), P-ad6 (◆), P-ad8 (▲), and P-ad12 (▼).

as high as 15%, which is demonstrated photographically in Figure 12. However, ASTM Method D790 is valid only for strains below 5%, and thus while qualitatively impressive, the data for P-ad8 and P-ad12 are not quantitatively accurate and can only be used to demonstrate the general trend.

Thermogravimetric analysis

Degradation plays an important role in the optimization of curing conditions for the linear aliphatic diamine-based series of polybenzoxazines as well as interfering with the estimation of crosslink density, as discussed earlier. The results of a thermogravimetric analysis of the diamine-based polybenzoxazines are summarized in Table VI, while the weight loss and derivative weight loss curves are presented in Figures 13 and 14, respectively. From the derivative weight loss curves, as well as the temperature at 1% weight loss, it is apparent that diamine chain length plays an important role in the onset temperature for thermal degradation in a nitrogen atmosphere. From this data, it appears that thermal stability increases with aliphatic diamine chain length until an 8-carbon chain is reached, beyond which the onset temperature does not change. However, the char yield systematically decreases with diamine chain length from approximately 41% for P-ad2 to only 6% for the longest chain
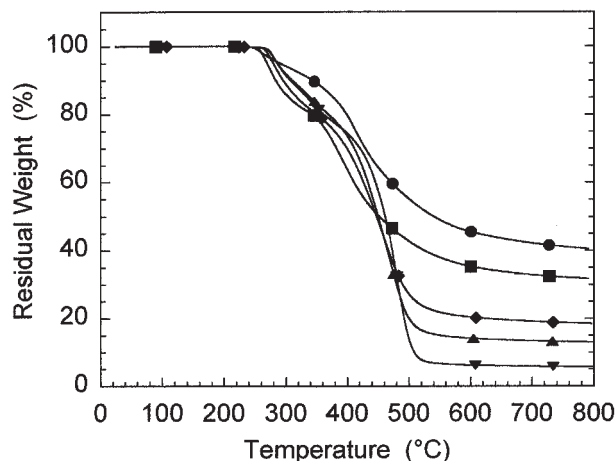
diamine, P-ad12. This behavior is certainly not unexpected considering that as the aliphatic content is being increased throughout this series of polybenzoxazines, aromatic content must inversely decrease. Interesting to note is the increased deviation from the theoretical char yield for the longer diamine chains.

From the derivative weight loss curves, it appears that each of the linear aliphatic diamine-based polybenzoxazines degrades in a two-stage weight-loss process. An infrared evaluation of the gases evolved during each weight loss event can help identify the degradation mechanisms. As can be seen in Figure 16, the infrared spectra of the gases evolved at the point of maximum weight loss during each degradation event are quite similar for each of the diamine chain lengths. The lower temperature weight loss process appears to be associated with degradation at the Mannich bridge and an associated loss of amine-related compounds. Bands relating to these amine compounds appear at 3333 and 747 cm^{-1} (-NH-), 1626 cm^{-1} (-NH$_2$), and finally the sharp peaks at 965 and 930 cm^{-1}. While no phenol-related compounds appear in the lower temperature spectrum of P-ad2, there does appear to be some weight loss related to substituted phenols in the longer diamine chains, as evidenced by the free hy-

TABLE VI
Summary of the Thermogravimetric Analysis Results for the Linear Aliphatic Diamine-Based
Series of Polybenzoxazines

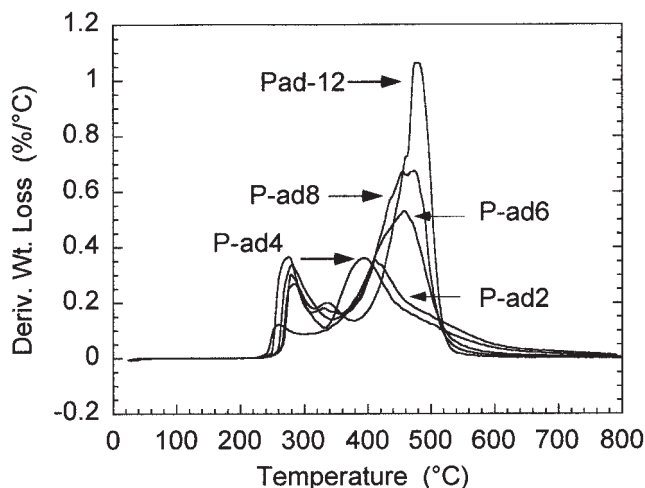| Polymer	Temp 1% (°C)	Temp 5% (°C)	Char yld. %	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)
P-ad2	254	291	40.5	258	—	412
P-ad4	257	270	31.7	275	—	394
P-ad6	266	280	18.5	280	—	458
P-ad8	271	287	13.1	283	330	454/473
P-ad12	272	286	5.7	279	340	482

Figure 14 Derivative weight loss for the diamine-based series of polybenzoxazines as a function of aliphatic chain length as obtained in a nitrogen environment.

droxyl peaks appearing near 3650 cm^{-1} in the corresponding spectra. The infrared spectra taken from the gases evolved at the maximum of the higher temperature weight loss process are also shown in Figure 16. In this case, the spectra appear to be dominated by phenol and aliphatic-related compounds. While the amine-related peak at 3333 cm^{-1} is absent from each of these spectra, the intensity of the peak at 3650 cm^{-1} indicates the presence of a significant quantity of free hydroxyl groups, presumably from substituted phenol compounds that also have absorbances appearing near 1600 and 1505 cm^{-1}. Thus, as would be expected, the linear aliphatic diamine-based polybenzoxazines appear to degrade by very similar processes that differ
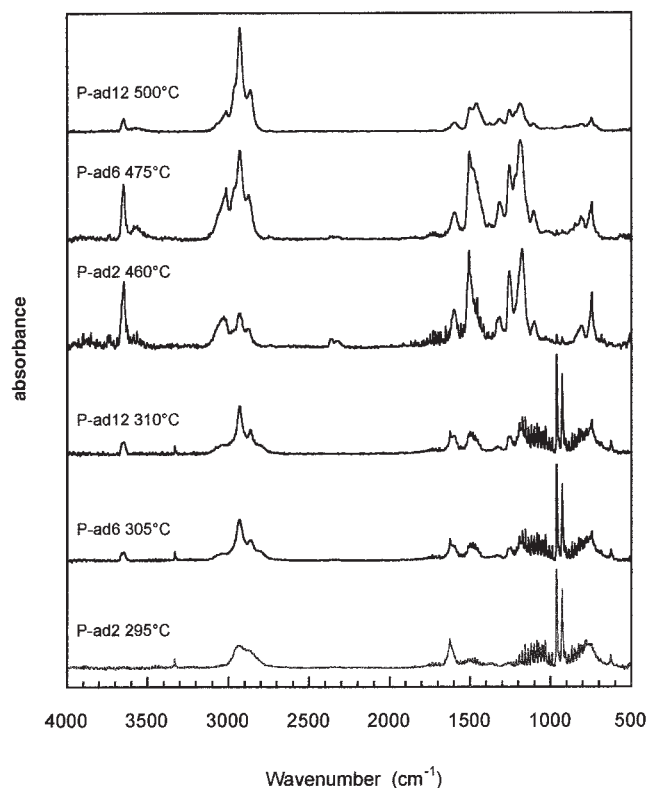

Figure 16 Infrared spectra of the gases evolved at the peak rate of degradation for the lower (bottom) and higher (upper) temperature weight loss processes of the linear aliphatic diamine-based polybenzoxazines.

primarily in the quantities of aliphatic compounds released rather than in the degradation mechanism itself.

CONCLUSIONS

A series of linear aliphatic diamine-based benzoxazine monomers has been successfully polymerized into transparent, crosslinked specimens that are free of voids and have good mechanical integrity. The density of these polybenzoxazines was shown to decrease as a function of aliphatic diamine chain length over the range from 1.22 g/cm^3 for P-ad2 to 1.08 g/cm^3 for P-ad12.

In dynamic mechanical analysis, the linear aliphatic diamine-based polybenzoxazines exhibited two fairly strong, aliphatic chain length dependent, low temperature relaxation processes. The room temperature modulus was also shown to be a strong function of diamine length, decreasing from a rather stiff 2.1 GPa for P-ad2 to 0.87 for the polymer with the longest aliphatic chain, P-ad12. The glass transition temperatures of P-ad2 and P-ad6 surpassed 170°C and were remarkable in that both were equivalent or higher than many bisphenol-based polybenzoxazines. Even with a long aliphatic chain, the glass transition tem-
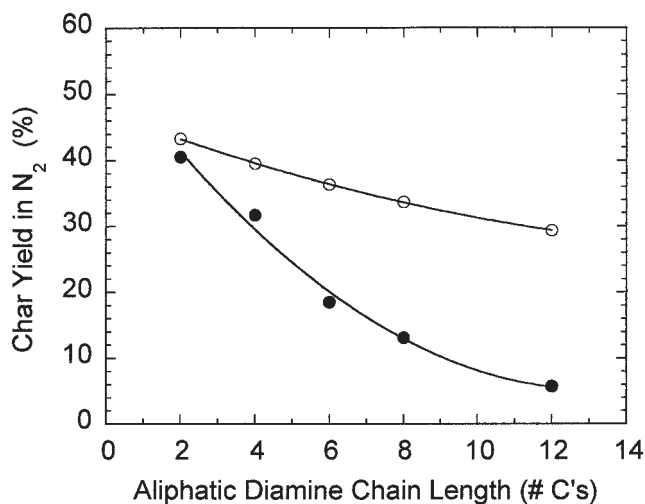

Figure 15 Percentage char yield (●) in a nitrogen environment and theoretical char yield (○) for the diamine-based series of polybenzoxazines as a function of aliphatic chain length.

perature of P-ad12 was almost 120°C. The crosslink densities of several aliphatic diamine-based polybenzoxazines were estimated from the plateau of the elastic modulus in the rubbery phase. Surprisingly, the calculated crosslink densities all exceeded 5×10^{-3} mol/cm^3, suggesting that each of these aliphatic diamine-based polybenzoxazines may have a crosslink density that is more than five times greater than that of the bisphenol-based polybenzoxazine BA-a.

Aliphatic chain length proved to be a very important factor in the thermal degradation of the diamine-based polybenzoxazines. In general, the onset temperature for degradation increases as a function of aliphatic chain length, but the actual degradation mechanism appears to be largely independent of aliphatic content. The char yield in nitrogen of P-ad2 is quite acceptable, at greater than 40%, but decreases quickly as a function of chain length.

The results of flexural analysis fully justified the development of the linear aliphatic diamine-based polybenzoxazines. Even the stiffest, most brittle material in this series of polymers, P-ad2, demonstrated a flexural modulus, strength, and strain that far surpassed that of typical bisphenol-based polybenzoxazines. The diamine-based benzoxazine with the longest aliphatic chain, P-ad12, displayed very impressive flexibility, and in some cases did not fail at strains far exceeding the limits of applicability of the 3-point bending experiments. Thus, with the linear aliphatic diamine-based polymers just presented, an inherently flexible polybenzoxazine network structure has been developed.

References

1. Lui, J. P.; Ishida, H. Polym and Polym Compos 2002, 10, 191.
2. Agag, T.; Takeichi, T. Macromolecules 2001, 34, 7257.
3. Kimura, H.; Matsumoto, A.; Sugito, H.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. J Appl Polym Sci 2001, 79, 555.
4. Brunovska, Z.; Lyon, R.; Ishida, H. Thermo Acta 2000, 357, 195.
5. Ishida, H.; Sanders, D. P. J Polym Sci Part B: Polym Phys 2000, 38, 3289.
6. Kim, H. J.; Brunovska, Z.; Ishida, H. Polym 1999, 40, 6565.
7. Kimura, H.; Matsumoto, A.; Hasegawa, K.; Fukuda, A. J Appl Polym Sci 1999, 72, 1551.
8. Kimura, H.; Murata, Y.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. J Appl Polym Sci 1999, 74, 2266.
9. Shen, S. B.; Ishida, H. J Polym Sci Part B: Polym Phys 1999, 37, 3257.
10. Ning, X.; Ishida, H. J Polym Sci Part A: Polym Chem 1994, 32, 1121.
11. Ishida, H. U.S. Patent 5,543,516 (1996).
12. Ishida, H.; Allen, D. J. J Polym Sci Part B: Polym Phys 1996, 34, 1019.
13. Jang, J.; Seo, D. J Appl Polym Sci 1998, 67, 1.
14. Jang, J.; Yang, H. Compos Sci Technol 2000, 60, 457.
15. Ishida, H.; Lee, Y. H. Polym and Polym Comp 2001, 9, 121.
16. Ishida, H.; Lee, Y. H. Polym 2001, 42, 6971.
17. Ishida, H.; Allen, D. J. Polym 1996, 37, 4487.
18. Takeichi, T.; Guo, Y.; Agag, T. J Polym Sci Part A: Polym Chem 2000, 38, 4165.
19. Takeichi, T.; Guo, Y. Polym J 2001, 33, 437.
20. Brunovkska, Z.; Lui, J. P.; Ishida, H. Macromol Chem Phys 1999, 200,1745.
21. Allen, D. J.; Ishida, H. In preparation.
22. Ishida, H.; Low, H. Y. Macromolecules 1997, 30, 1099.
23. Treloar, L. R. G. The Physics of Rubber Elasticity; Oxford Univ. Press: London, 1949; p 66.
24. Ning, X.; Ishida, H. J Polym Sci Part A: Polym Chem 1994, 32, 921.
25. Allen, D. J. Unpublished data.