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ARTICLE

Low-Viscosity Polyether-Based Main-Chain Benzoxazine Polymers: Precursors for Flexible Thermosetting Polymers

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ABSTRACT: A pioneering class of proccessable thermoplastic/thermosetting crossover polymers made of commercially available chemicals has been developed. The striking feature of this class of polymers is its inherently low viscosity at room temperature that facilitates the processability. The polymers have been synthesized from the polycondensation reaction of bisphenol A, formaldehyde, and amine-terminated poly(ether diamine). The structure of the polymers has been confirmed by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and Fourier transform infrared spectroscopy (FTIR). The polymers are cross-linked via thermal treatment to produce tough and flexible thermosetting materials without using any external initiators, accelerators, catalysts, or reactive diluents. Differential scanning calorimetry (DSC) and FTIR are used to study cross-linking behavior of these polymers. Atomic force microscopy (AFM) has been employed to study the phase behavior of the cross-linked polymers as a function of poly(ether diamine) chain length and wettability. Thermal properties of the cross-linked polymers have been studied by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

1. Introduction

The interest in benzoxazine resin is growing rapidly, and many useful materials are currently being developed in this innovative class of thermosetting resins. Benzoxazine is a biheterocyclic molecule which is synthesized by the combination of a primary amine, a phenolic derivative, and formaldehyde as first reported in 1944 by Holly and Cope.[1] In the early 1970s, benzoxazine oligomers were blended with epoxy resins as a property modifier,[2] though no properties of polybenzoxazines were reported. It was not until the early 1990s when the thermally activated, ring-opening polymerization of benzoxazine resin was first studied; at this time unique properties of polybenzoxazines were first recognized and published.[3] Since then, benzoxazine research started gaining momentum due to the outstanding properties of benzoxazine monomers and the resultant polybenzoxazines. Not only are the properties of polybenzoxazines comparable or even superior to traditional phenolic resins, but polybenzoxazines also overcome many of the problems associated with phenolic resins.[4] For example, benzoxazine polymerization exhibits negligible volumetric shrinkage,[5] does not require any harsh acid catalyst, and has no reaction byproduct. Furthermore, polybenzoxazines possess excellent mechanical properties as well as thermal stability. Benzoxazines also have immense molecular design flexibility, which allows them to be tailored to a specific application simply by substituting different functionalities into the primary amine or phenolic reactants. Accordingly, polybenzoxazines exhibit properties that are suitable for applications where traditionally epoxies, bismaleimides, cyanate esters, and polyimides are used. In addition, they can also be used for novel applications that utilize the unusual properties of benzoxazine resins and polybenzoxazines.

A new area of benzoxazine research has been developed where polymeric benzoxazines are synthesized by replacing starting monofunctional amines (or monofunctional phenols) of classical monomeric benzoxazines with difunctional phenols (or difunctional amines).[6−25] The result is a polymer with repeating benzoxazine units in the main chain. At this point, the benzoxazine behaves like an ordinary thermoplastic which has good solubility, processability, and film formation. Upon thermal treatment at an elevated temperature, this thermoplastic polymer can be cross-linked via thermally activated ring-opening polymerization of the oxazine ring in the main chain. Thus, this thermoplastic/thermosetting crossover molecule offers the advantage of thermoplastic processability with thermosetting polymer properties. Good dimensional stability, creep resistance, and excellent thermal and chemical resistance are some of the common advantages of thermosetting polymers that are observed in cross-linked main-chain-type polybenzoxazines.

Many polybenzoxazines derived from monomeric-type benzoxazines are brittle, as is expected of typical thermosetting resins. Therefore, for some applications, improved toughness might be necessary. Simply adding rubbery material will not achieve good adhesion at the phase-separated interface. Therefore, it is of interest to develop elastomeric main-chain-type polybenzoxazines as toughening agents to modify more brittle but stronger benzoxazine resins. Polybenzoxazines have been synthesized using monofunctional polyetheramines producing a classical benzoxazine monomer.[26] Other attempts to overcome benzoxazine's brittleness in the past are reported, including the incorporation of siloxane linkages or copolymerization with isocyanate.[27−31] With the incorporation of a relatively long polyether backbone in the structure of the main-chain benzoxazine, the product will be a unique elastomer. Jeffamine is the commercial name of a large family of inexpensive, primary-amine-terminated bifunctional poly(ether diamine)s. Commercial applications of Jeffamine in the past have included organic coatings and epoxy resin toughening agents.[26,32] In this study, cross-linked polybenzoxazines

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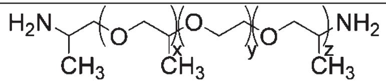
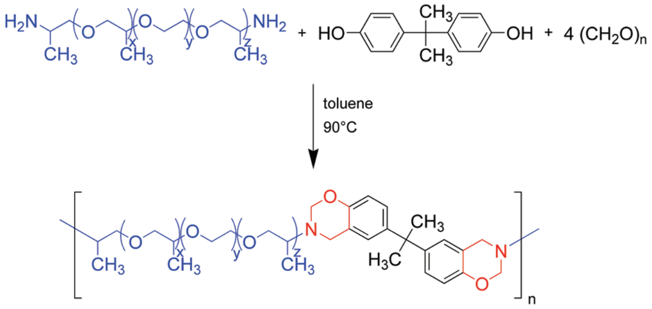
Table 1. Poly(ether diamine) Chemical Structure and Abbreviations

Trade name	Abbreviation	Chain structure		Molecular weight (g/mol)
		y	x + z	
Jeffamine ED-600	eda600	~9.0	~3.6	600
Jeffamine ED-900	eda900	~12.5	~6.0	900
Jeffamine ED-2003	eda2000	~39	~6.0	2000
Polyetherdiamine structure				

Scheme 1. Poly(ether diamine)-Based Main-Chain Polybenzoxazine Synthesis



based on a series of poly(ether diamine)s will be synthesized and characterized.

2. Experimental Section

2.1. Materials. Poly(ether diamine)s of varying molecular weights (95%) were kindly supplied by Huntsman; chemical structure and abbreviations are in Table 1. Bisphenol A (97%) (BA) and paraformaldehyde (96%) were used as purchased from Acros Organics. Toluene and hexanes (mixture of isomers) were used as purchased from Fisher Scientific.

2.2. Synthesis of Poly(ether diamine)-Based Main-Chain Benzoxazine Polymer. All polymer synthesis followed the same procedure: a mixture of 1 mol equiv of poly(ether diamine), 1 mol equiv of BA, and 4 mol equiv of paraformaldehyde in toluene (20% solid content) was combined with magnetic stirring at 90 °C for 8 h, according to Scheme 1. The reaction mixture was allowed to cool to room temperature, followed by evaporation of toluene by stream of air. The resulting viscous, transparent-yellow compound was washed in hexanes several times and placed under vacuum for at least 48 h at room temperature. The polymer designation is poly(BA-eda). In order to indicate the specific structure of the poly(ether diamine), molecular weight information is added; e.g., poly(BA-eda600) indicates the molecular weight of 600.

2.3. Cross-Linking of Poly(ether diamine)-Based Main-Chain Benzoxazine Polymer. The polymers were dissolved in toluene to achieve a 20% solution. A film was cast over a silane-treated glass plate to prevent surface adhesion. Toluene was evaporated first *in vacuo* at room temperature for 2 h and then in a convection oven at 50 °C for 72 h. Cross-linking took place in a convection oven at temperatures of 120, 150, and 180 °C for 2 h each.

2.4. Analytical Procedures. Proton nuclear magnetic resonance (^{1}H NMR) spectra were taken on a Varian Gemini 2000 NMR operating at a proton frequency of 300 MHz. All samples were dissolved in deuterated chloroform, and tetramethylsilane was used as an internal standard.

Fourier transform infrared (FTIR) spectroscopy was carried out on a Bomem Michelson MB100 FTIR spectrometer with a deuterated triglycine sulfate detector. After casting a thin film onto a KBr plate and purging with dry air, coadded spectra of 64 scans were recorded at a spectral resolution of 4 cm^{-1}.

Differential scanning calorimetry (DSC) was performed with a TA Instruments 2920 DSC at a heating rate of 10 °C/min from 25 to 300 °C and nitrogen flow rate of 62 mL/min; 2 mg samples were sealed between aluminum hermetic pans and lids for all tests.

Atomic force microscopy (AFM) was used in a tapping mode on Veeco MultiMode V microscope with a silicon-doped antimony cantilever with force constant of 20−80 N/m and working frequency of 327−383 kHz.

Dynamic mechanical analysis (DMA) was performed with a TA Instruments Q800 DMA with a heating rate of 3 °C/min from −100 to 100 °C at 1 Hz. Samples of 4 mm width were cut from films with approximate thickness of 0.2 mm.

Thermogravimetric analysis (TGA) was performed with a TA Instruments Q500 TGA with a heating rate of 10 °C/min from 25 to 800 °C and nitrogen purge at a flow rate of 40 mL/min; 2 mg samples were placed in an open platinum crucible for all tests.

3. Results and Discussion

3.1. Preparation of Main-Chain-Type Benzoxazine Polymers. Main-chain-type polybenzoxazines were synthesized from the polycondensation of a poly(ether diamine) with molecular weight of 600, 900, or 2000, bisphenol A, and paraformaldehyde, according to Scheme 1. Varying poly(ether diamine) chain length allows for design flexibility of the main-chain-type benzoxazine polymer. While the bifunctional poly(ether diamine)s are a novel ingredient in benzoxazine synthesis, BA is a typical phenolic component for benzoxazine synthesis. BA is common reagent for a wide range of commercial polymers, including polyesters, polycarbonates, and various epoxy resins. The synthesized polymer is a main-chain-type benzoxazine, which consists of repeating units of a bifunctional benzoxazine structure bonded to a relatively large polyetherdiamine structure.

All of the polymers are soluble in common solvents like toluene, chloroform, and dioxane as well as dimethylformamide, dimethylacetamide, and dimethyl sulfoxide. Toluene is a preferred solvent for the synthesis due to good polymer solubility and minimal health concerns, which is sometimes an issue with other solvents. Because of the poly(ethylene glycol) backbone of poly(ether diamine), improved solubility in water might be expected. Increased poly(ether diamine) molecular weight led to increased solubility in water: poly(BA-eda600) is insoluble in water, slight solubility in water is achieved with poly(BA-eda900), and complete solubility is observed with poly(BA-eda2000). Solubility in alcohols also increases as poly(ether amine) molecular weight increases. A viscosity study of the polymers is shown in Figure 1. All of the polymers are viscous liquids are room temperature, with viscosity increasing with polyetheramine molecular weight.

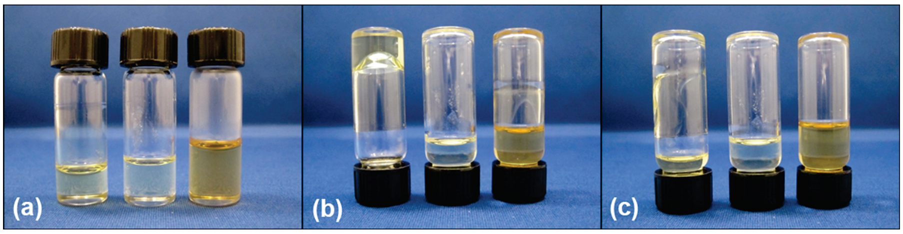


Figure 1. Polymer viscosity demonstration: (a) polymers in vials (poly(BA-eda600), poly(BA-eda900), and poly(BA-eda2000) from left to right), (b) 1 min after flipping, and (c) 30 min after flipping.

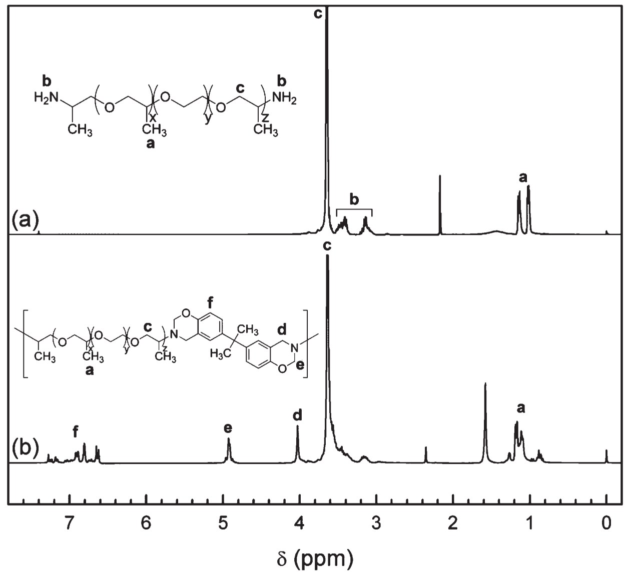


Figure 2. ^{1}H NMR spectra of (a) eda600 and (b) poly(BA-eda600).

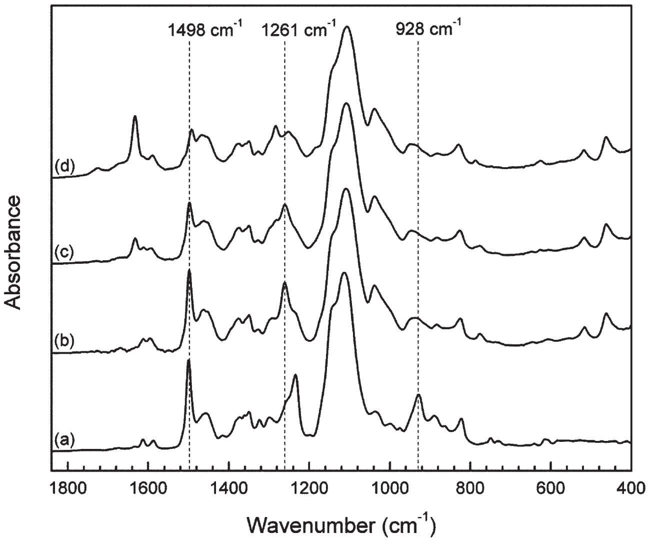


Figure 3. FTIR spectra of (a) eda600, (b) uncured poly(BA-eda600), (c) poly(BA-eda600) cured at 150 °C for 2 h, and (d) poly(BA-eda600) cured at 180 °C for 2 h.

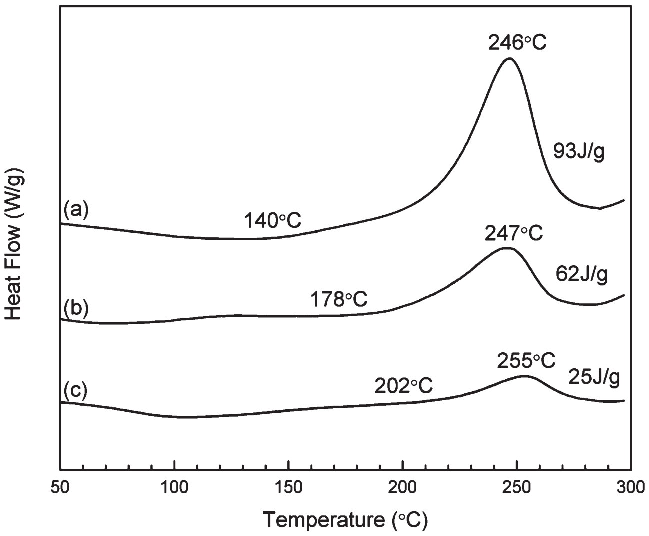


Figure 4. DSC thermograms for un-cross-linked polymers: (a) poly(BA-eda600), (b) poly(BA-eda900), and (c) poly(BA-eda2000).

The structure of the benzoxazine polymers was confirmed by ^{1}H NMR spectra. ^{1}H NMR spectra of poly(ether diamine) with molecular weight 600 and its corresponding benzoxazine polymer are shown in Figure 2. The resonances at 1.0–1.2 and 3.7 ppm are due to $-CH_3$ and $O-CH_2-$ groups of the poly(propylene oxide) structure, respectively. Benzoxazine structure is identified by the presence of the characteristic chemical shifts of the resonances of equal integrated intensity due to the methylene groups in the cyclic benzoxazine structure. The resonance at 4.0 ppm is due to the protons in $C-CH_2-Ph$, and the resonance at 4.9 ppm is due to the protons in $O-CH_2-N$. Chemical shifts due to the aromatic protons of the benzoxazine structure appear between 6.6 and 7.3 ppm. Polymers synthesized using longer poly(ether diamine) starting material show similar ^{1}H NMR spectra. However, the characteristic benzoxazine resonances are weaker in intensity due to the longer polyether backbone.

FTIR spectra of the synthesis and cross-linking of poly(BA-eda600) are shown in Figure 3. All spectra show strong bands at 2870 cm^{-1} due to the CH_2 antisymmetric stretching mode of the polyether chain present in each material. Further, the strong peak occurring at 1109 cm^{-1} for all samples is due to the antisymmetric $C-O-C$ stretching mode in the polyether chains. During polymerization up to 180 °C, reduction of the intensity is observed on the bands at 1498 and 1261 cm^{-1}, which are assigned to the trisubstituted benzene ring vibration and the antisymmetric $C-O-C$ stretching mode in the oxazine ring, respectively.

The polymer film was placed under vacuum at room temperature to remove the solvent. Samples were then transferred to a convection oven. In order to achieve further evaporation of the solvent before beginning of cross-linking, samples were held at 50 °C for 72 h. DSC thermograms depicted in Figure 4, illustrating the cross-linking behavior of the polymers. DSC results show a single exothermic peak which is due to the ring-opening polymerization of the benzoxazine, resulting in a cross-linked structure as supported by insolubility in any solvent. All exothermic peaks are fairly broad, with total enthalpies of 93, 62, and 25 J/g for poly(BA-eda600), poly(BA-eda900), and poly(BA-eda2000), respectively.

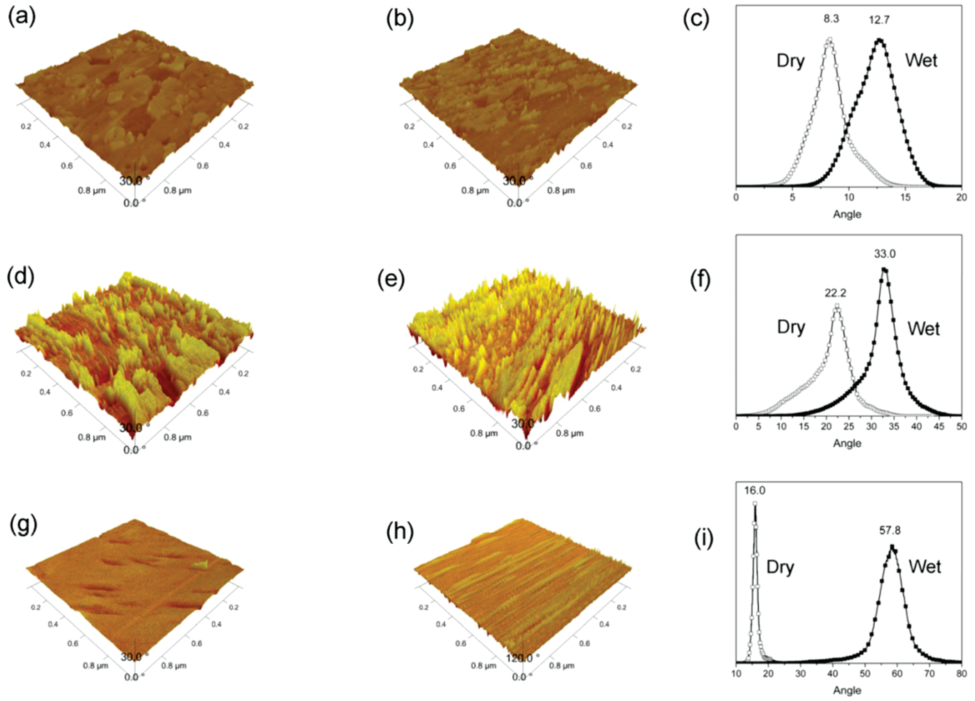


Figure 5. AFM phase images for cross-linked poly(BA-eda600) (a) dry, (b) wet, and (c) distribution of phase lag; for cross-linked poly(BA-eda900) (d) dry, (e) wet, and (f) distribution of phase lag; and for cross-linked poly(BA-eda2000) (g) dry, (h) wet, and (i) distribution of phase lag. Images scan size is 1 × 1 μm with 30° scale except for wet poly(BA-eda2000) which has scale of 120° to show the features of the phase image (h).

As poly(ether diamine) length in the polymer is increased, the exothermic heat of polymerization attributed to benzoxazine ring-opening decreases due to a dilution effect. The onset of polymerization increases as poly(ether diamine) length increases; onset temperatures of poly(BA-eda600), poly(BA-eda900), and poly(BA-eda2000) are 140, 178, and 202 °C, respectively, whereas exotherm peak positions are 246, 247, and 255 °C, respectively.

3.2. Phase Behavior of Cross-Linked Films. Morphology of cross-linked poly(BA-eda600), poly(BA-eda900), and poly(BA-eda2000) was investigated using AFM tapping mode. In tapping mode, both the height (i.e., topography) and the phase (i.e., variation in stiffness) of the sample surface are recorded. The phase image relies on recording the phase lag between the drive signal and the cantilever oscillation. Softer materials have large phase lag compared to stiffer materials. In polymer composites and blends, it is possible to study the phase separation and variation in surface heterogeneity using tapping mode. However, in order to use the data in qualitative and quantitative manner, all scanning parameters should be fixed to avoid contrast reversal in phase image. In our experiment, all scanning parameters were fixed for poly(BA-eda600) and poly(BA-ed900) while for poly(BA-eda2000) some parameters were changed to account for the softness of the matrix, which made it difficult to scan at similar parameters as the other two. Scanning was done using dry samples (room temperature) and on the same samples at the exact position after wetting with a drop of water, followed by evaporation before rescanning. This procedure ensured that the phase image is reliable and direct qualitative assessment and comparison between all images is possible. AFM phase images for cross-linked poly(BA-eda600), poly(BA-eda900), and poly(BA-eda2000) are depicted in Figure 5. Phase images for poly(BA-eda600) in the dry and wet states are depicted in Figures 5a and 5b, respectively. Visual inspection of the images shows an increase in the concentration of light region due to wetting. This change is rather subtle and not sufficient to assess the effect of wetting on the viscoelastic response of the sample. Thus, a quantitative distribution of phase lag is extracted from the phase image and is given in Figure 5c; a shift in phase lag from 8.3° to 12.7° is a clear indication of the wettability of the surface due to the presence of the hydrophilic soft segment. When longer polyether chain is used (i.e., 900 vs 600), the phase lag is shifted from 8.3° to 22.2° as depicted in Figure 5f. When cross-linked poly(BA-eda900) is wetted, a rather significant increase in concentration of light region is visible from Figures 5d to 5e compared to poly(BA-eda600). Phase lag distribution confirms this increase in the viscous region as depicted in Figure 5f where a clear shift in phase lag is observed from 22.2° to 33.0°. Phase images for dry and wet cross-linked poly(BA-eda2000) are depicted in Figures 5g and 5h along with phase lag distributions in Figure 5i. A similar trend in wettability effect on the morphology of cross-linked poly(BA-eda2000) is observed. Because changes in scanning parameters have to be done to produce reliable images, a slight difference in phase lag for dry poly(BA-eda2000) and poly(BA-eda900) is evident. Poly(BA-eda2000) was expected to have a higher phase lag in dry state than poly(BA-eda900), but this is not the case. The shift in phase lag distribution is rather large compared to poly(BA-eda600) and poly(BA-eda900). This is due to the differences in chain length of the poly(ether diamine).

3.3. Thermal Properties of Cross-Linked Main-Chain Benzoxazine Polymers. Dynamic mechanical analysis was used for the evaluation of the viscoelastic properties of the cross-linked polymers. Storage modulus (E') and loss modulus (E'') are plotted against temperature as shown in Figures 6 and 7, respectively. The increase in poly(ether diamine) molecular weight led to a decrease in glass transition temperature, supported by E' and E'' plots. The polymer has a low glass transition obtained from the maxima of loss modulus. The DMA data indicate that the polymer is in a rubbery state at room temperature due to a low glass transition temperature.

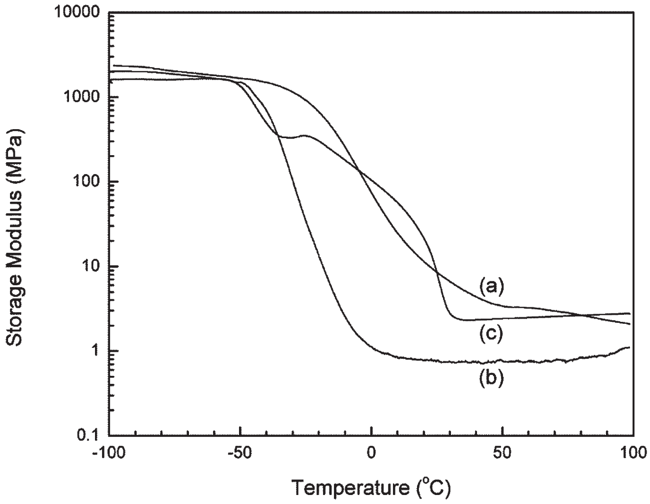


Figure 6. Storage modulus curves for (a) poly(BA-eda600), (b) poly(BA-eda900), and (c) poly(BA-eda2000).

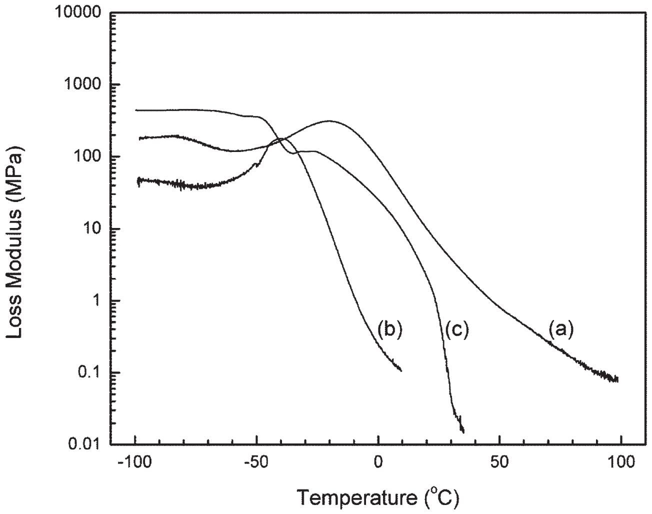


Figure 7. Loss modulus curves for cross-linked (a) poly(BA-eda600), (b) poly(BA-eda900), and (c) poly(BA-eda2000).

The rubbery plateau is relatively flat, reflecting the cross-linked structure. Glass transition temperatures as defined by the loss modulus peak for cross-linked poly(BA-eda600) and poly(BA-eda900) are −19 and −40 °C, respectively. The cross-linked poly(BA-eda2000) shows multiple glass transition temperatures: a transition at −45 °C and a very broad transition centered around 0 °C. This higher transition might consist of more than one transition, and further detailed study is needed before a clear statement can be made. Increasing the polyether length caused a decrease in glass transition temperature; however, cross-linked poly(BA-eda2000) showed a complex transition behavior, different from the other two benzoxazines. The two loss modulus peaks may be attributed to the fact that the polymer has an extra long polyether structure between benzoxazine cross-linking sites. Therefore, the dynamic mechanical spectrum might show partial feature of polyether chain without the influence of the benzoxazine cross-link points.

Thermal stability of polymers was evaluated using TGA under a nitrogen atmosphere. TGA thermograms are shown in Figure 8. The onset temperature of degradation of the polymers increased with poly(ether diamine) length. The values of 5% weight reduction temperature, T_{d5}, for poly(BA-eda600), poly(BA-eda900), and poly(BA-eda2000) are 285, 324, and 350 °C, respectively, and 10% weight reduction temperature, T_{d10}, for the respective polymers are 303, 344, and 368 °C. This increase in degradation temperature with increased polyether length is counterintuitive since increased cross-link density is expected to increase the thermal stability of usual polybenzoxazines. It is possibly related to the C−N bond concentration at the polyether chain/benzoxazine linkage that might be acting as the thermally weak link. As the polyether chain molecular weight decreases, the concentration of such links increases, which then might lead to weakening of the thermal stability. The sudden reduction of the weight around the temperature range of 350−400 °C might be attributed to the evaporation of polyether fragments. Further study is needed to verify this hypothesis; however, weakness of such bond in aliphatic amine side chain in polybenzoxazines derived from monomeric precursors has been reported.[33] A similar situation is also reported on the main-chain-type polybenzoxazine where highly fluorinated aliphatic chain is connected to the amine group through a CH_2 group. When this CH_2 group is replaced with a phenyl group, the thermal stability drastically improved.[13] Onset T_{d10} temperatures of ~300 °C are typical of elastomers such as polyurethane. However, char yield at 800 °C increased as poly(ether diamine) length decreased. Char yield for poly(BA-eda600), poly(BA-eda900), and poly(BA-eda2000) is 18.1, 15.2, and 7.0%, respectively. This trend can be attributed to a higher density of benzoxazine cross-linking in the main chain. The fact that the char yield is increased as expected for the higher cross-link density polybenzoxazine despite the weakness of the thermal stability of small molecular weight polyether chain is further support for the evaporation of the polyether segments upon the C−N bond cleavage. While this char yield is rather low in comparison to ordinary polybenzoxazines, it is nonetheless remarkably high for an elastomeric material as the majority of elastomers show near 0% char yield.

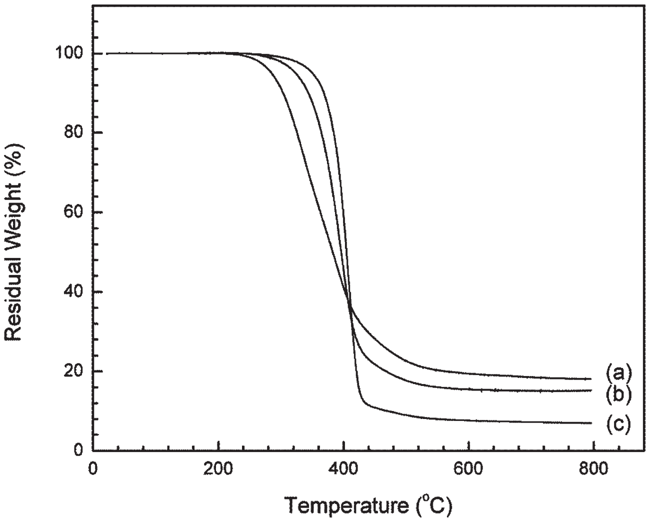


Figure 8. TGA thermograms for cross-linked poly(BA-eda600), poly(BA-eda900), and poly(BA-eda2000).

4. Conclusion

A new class of main-chain-type benzoxazine polymers of low viscosity at room temperature has been developed using a poly(ether diamine) as a starting material. This class embodies a family of easily proccessable thermoplastic/thermosetting crossover materials made from commercially available chemicals. The cross-linking of the neat polymers is straightforward via thermally activated ring-opening polymerization of the cyclic benzoxazine structure and leads to flexible thermoset polymer without any need of external additives. The unique features of this class of polymers allow potential application opportunities as toughening agent, coating materials, and membranes.

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