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Effect of Polymerizing Diacetylene Groups on the Lowering of Polymerization Temperature of Benzoxazine Groups in the Highly Thermally Stable, Main-Chain-Type Polybenzoxazines

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ABSTRACT: A series of novel benzoxazine polymers containing diacetylene groups in the main chain have been synthesized. Various propargyl and ethynyl functional benzoxazine monomers have been prepared and polymerized utilizing the oxidative coupling approach. The structure of the polymers is confirmed by ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FTIR). Differential scanning calorimetry (DSC) is used to study the thermal cross-linking of the polymers. The polymers show two exothermic peaks with the first exotherm exhibiting considerably lower cross-linking temperatures than conventional benzoxazines with onset at around 125 °C and its maximum at 185 °C. FTIR study shows that the lower temperature exothermic process relates to the partial benzoxazine polymerization. The number-average molecular weight is estimated from size exclusion chromatography (SEC) to be in the range from 15 000 to 25 000 Da. Outstandingly high thermal stability of cross-linked polymers is shown by thermogravimetric analysis (TGA).

Introduction

Polybenzoxazines are a fast developing class of thermosetting resins that possesses a number of fascinating advantages in comparison to many other types of thermosets such as phenolic, epoxy, bismaleimide, or cyanate ester resins. There is no other class of polymers that can compete with the extraordinary molecular design flexibility of benzoxazines. Near-zero shrinkage upon polymerization, low water absorption, and high char yield are some of many advantages of benzoxazine resins.[1−6] Recent directions in polybenzoxazine development mainly include reinforcing with fibers or inorganic fillers,[7−11] alloying with other polymers,[12−15] or introduction of additional functional groups into benzoxazine monomers.[16−19]

A recently active concept in benzoxazine resin research is based on the synthesis of linear polymers containing a benzoxazine moiety in the main chain, the so-called main-chain-type benzoxazine polymers. Although this concept was reported some years ago,[20,21] its validity had not been examined until very recently. This approach allows the polymer to form self-supporting films which, upon cross-linking of the internal oxazine rings, gives substantially increased ductility in comparison to the traditional monomeric approach. The pathway of earlier polymers that implemented such an approach was via condensation of diamines with bisphenols to form benzoxazine as a repeating unit in the main chain.[22−24] However, this approach suffers from branching and side reactions, and thus, the resultant molecular weight is limited. In order to overcome this drawback, a few approaches to linear benzoxazine polymers with high molecular weight were reported by utilizing various polymerization chemistry of monomers with functional groups containing benzoxazine moieties. Such examples include the synthesis of polyetherester containing oxazine rings[25] and linear polybenzoxazines with triazole rings prepared via the click chemistry approach.[26,27] The reported polymers showed reasonably high molecular weight and good mechanical properties.

A variety of chemical reactions can be used for extension of recently developed approach described above. Oxidative coupling chemistry of acetylene groups to obtain diacetylene structures takes place under oxygen atmosphere with various metallic catalysts at room temperature and possesses quantitative yield.[28−31] Certain types of diacetylenes are well-known to be topochemically polymerized in the crystalline phase via UV- or γ-irradiation or by annealing.[32−37] Resultant polymers have highly ordered and conjugated backbones which gives them interesting properties such as nonlinear optical properties and electrical conductivity.[38−42] However, solid state topochemical polymerization is limited to thin layers or single crystals[43−47] which makes this approach impractical for larger scale applications. Another class of polydiacetylenes is the amorphous polymers which are obtained via cross-polymerization in the molten state. It was demonstrated that spontaneous polymerization of diacetylene units occurred upon heating, and the process does not take place unless the material is not melted.[48,49]

Various types of semicrystalline and amorphous polymers containing diacetylene moiety in the backbone have been reported, including diacetylene polycarbonate,[50] diacetylene polyurethanes,[51,52] diacetylene polyamides,[53,54] diacetylene polyesters[55,56] and other examples.[57−60] Crystalline regions of some of the listed polymers can be topochemically cross-linked by annealing or irradiation.[51−56] In this case, diacetylene cross-polymerization does not change the degree of crystallinity of the polymer. Some of semicrystalline as well as amorphous polymers undergo only thermal cross-linking at elevated temperatures which results in complete loss of ordered structure upon polymerization.[58−60] Many of the cross-polymerized diacetylene materials were characterized by good mechanical and thermal properties and chemical resistance.

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In this study, a series of diacetylene polymers containing oxazine ring in the main chain were synthesized, and their unique thermal behavior was examined and discussed along with the model diacetylene polymer. The synthesized polymers showed unexpectedly low cross-linking temperature in comparison to conventional benzoxazines as well as extremely high thermal stability.

Experimental Section

Materials. *p*-Nitrophenol, tetrabutylammonium bromide, propargyl bromide, tin(II) chloride dehydrate, and 3-ethynylaniline were used as received from Acros Organics. Bisphenol A, benzophenone, 1,5-dihydroxynaphthalene, paraformaldehyde, *N,N,N′,N′*-tetramethylethylenediamine, and copper(I) chloride were purchased from Sigma-Aldrich. Dimethylformamide (DMF), pyridine, ethyl acetate, toluene, xylenes, dioxane, dichloromethane, methanol, hydrochloric acid, and sodium hydroxide were obtained from Fisher. All chemicals were used as received. Aminophenyl propargyl ether (APPE) was prepared following our reported method.[61] 4,4′-(Propane-2,2-diyl)-bis((prop-2-ynyloxy)benzene) was prepared according to the previously reported procedure.[62]

Characterization. ^{1}H and ^{13}C NMR spectra were acquired in deuterated chloroform on a Varian Oxford AS600 at a proton frequency of 600 MHz and its corresponding carbon frequency. Spectra were averaged from 32 transients for ^{1}H NMR and 2500 transients for ^{13}C NMR. Polymer molecular weight was determined by size exclusion chromatography (SEC) using a Waters GPC system equipped with a LDC/Milton Roy maxN series UV detector. The measurements were taken at 25 °C with DMF as a mobile phase on two Phenomenex Phenogel columns (100 and 10 nm). Molecular weight was calculated using a calibration based on polystyrene standards. Thermal behavior was analyzed with a TA Instruments 2920 differential scanning calorimeter using a heating rate of 10 °C/min in a nitrogen atmosphere. Thermogravimetric analysis was performed on a TA Instruments Q500 TGA with a heating rate of 10 °C/min in a nitrogen atmosphere at a flow rate of 40 mL/min. FTIR spectra were acquired at a resolution of 4 cm^{-1} with 32 coadditions on a Bomem Michelson MB100 equipped with a deuterated triglycine sulfide (DTGS) detector using KBr plates.

Preparation of Monomers. *6,6′-(Propane-2,2-diyl)bis(3-(4-(popargyloxy)phenyl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine) (BA-appe).* Into 20 mL vial were mixed APPE (2.94 g, 20 mmol), bisphenol A (2.28 g, 10 mmol), and paraformaldehyde (1.8 g, 60 mmol) together and reacted at 120 °C for 20 min. The crude product after cooling was dissolved in ethyl acetate, followed by washing 2 times with 1 N aqueous NaOH solution and then 2 times with water. The ethyl acetate solution was dried over sodium sulfate anhydrous, followed by evaporation of the solvent under vacuum to afford pale yellow solid (4.23 g, 74%). ^{1}H NMR (CDCl$_3$), ppm: δ = 1.57 (s, CH$_3$), 2.48 (t, ≡CH), 4.50 (s, CH$_2$, oxazine), 4.61 (d, CH$_2$), 5.25 (s, CH$_2$, oxazine), and 6.7−7.1 (14H, Ar). ^{13}C NMR (CDCl$_3$), ppm: δ = 51.29 (Ar−C−N, oxazine), 56.15 (O−C−C), 75.36 (C−C≡C), 78.77 (≡C), 80.09 (O−C−N, oxazine). FT-IR (KBr), cm^{-1}: 3286, 2120, 1327, 1231, 943.

*Bis(3-(4-(prop-2-ynyloxy)phenyl)-3,4-dihydro-2*H*-benzo[*e*]-[1,3]oxazin-6-yl)methanone (BP-appe).* BP-appe was synthesized from APPE, benzophenone, and paraformaldehyde in a manner similar to BA-appe. ^{1}H NMR (CDCl$_3$), ppm: δ = 2.49 (t, ≡CH), 4.59 (s, CH$_2$, oxazine), 4.62 (d, CH$_2$), 5.36 (s, CH$_2$, oxazine), and 6.8−7.6 (14H, Ar). ^{13}C NMR (CDCl$_3$), ppm: δ = 51.10 (Ar−C−N), 56.12 (O−C−C), 75.43 (C−C≡C), 78.65 (≡C), 81.02 (O−C−N). FT-IR (KBr), cm^{-1}: 3286, 2122, 1332, 1237, 929.

*3,3′-Bis(4-(prop-2-ynyloxy)phenyl)-3,3′,4,4′-tetrahydro-2*H*-naphtho[2,1-*e*][1,3]oxazine (15N-appe).* 15N-appe was prepared from APPE, 1,5-dihydroxynaphthalene, and paraformaldehyde similar to BA-appe. ^{1}H NMR (CDCl$_3$), ppm: δ = 2.48 (t, ≡CH), 4.60 (s, CH$_2$, oxazine), 4.64 (d, CH$_2$), 5.43 (s, CH$_2$, oxazine), and 6.8−7.7 (12H, Ar). ^{13}C NMR (CDCl$_3$), ppm: δ = 51.14 (Ar−C−N), 56.16 (O−C−C), 75.35 (C−C≡C), 78.74 (≡C), 80.93 (O−C−N). FT-IR (KBr), cm^{-1}: 3275, 2124, 1235, 961.

*3,3′-Bis(3-ethynylphenyl)-3,3′,4,4′-tetrahydro-2*H*-naphtho-[2,1-*e*][1,3]oxazine (15N-ea).* Into a 50 mL flask were mixed 3-ethynylaniline (2.34 g, 20 mmol), 1,5-dihydroxynaphthalene (1.60 g, 10 mmol), and paraformaldehyde (1.2 g, 40 mmol) in 20 mL of xylenes. The solution was stirred at 120 °C for 5 h. The crude product after cooling was recrystallized from reaction mixture, filtered, and dried under vacuum to afford beige powder (3.98 g, 90%). ^{1}H NMR (DMSO), ppm: δ = 4.14 (s, ≡CH), 4.75 (s, CH$_2$, oxazine), 5.63 (s, CH$_2$, oxazine), and 6.9−7.6 (12H, Ar). ^{13}C NMR (DMSO), ppm: δ = 48.63 (Ar−C−N), 78.99 (O−C−N), 80.48 (Ar−C≡C), 83.76 (≡C). FT-IR (KBr), cm^{-1}: 3281, 1234, 964.

Preparation of Polymers. *Poly(4,4′-(propane-2,2-diyl)bis-((prop-2-ynyloxy)benzene)) (Model Polymer).* In a 40 mL vial was dissolved 4,4′-(propane-2,2-diyl)bis((prop-2-ynyloxy)benzene) (0.91 g, 3 mmol) in 4 mL of DMF. To the solution, copper(I) chloride (30 mg, 10 mol %), 0.1 mL of *N,N,N′,N′*-tetramethylethylenediamine, and 1 mL of pyridine were added. The mixture, bubbling with oxygen, was stirred at room temperature for 6 h. 30 mL of DMF was added, and mixture was filtrated through a short silica column to remove copper. The filtrate was poured into 100 mL of water, and the resulting precipitate was filtered, washed with water, and dried under vacuum to afford white powder (0.69 g, 77%). ^{1}H NMR (CDCl$_3$), ppm: δ = 1.62 (s, CH$_3$), 4.69 (s, CH$_2$), 6.83 (d, Ar), and 7.13 (d, Ar). ^{13}C NMR (CDCl$_3$), ppm: δ = 56.16 (O−C−C≡), 70.94 (C≡C−C≡), 74.74 (C−C≡C−).

*Poly(6,6′-(propane-2,2-diyl)bis(3-(4-(popargyloxy)phenyl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine))(Poly(BA-appe)).* In 40 mL vial was dissolved BA-appe (1.71 g, 3 mmol) in 4 mL of DMF. To the solution, copper(I) chloride (30 mg, 10 mol %), 0.1 mL of *N,N, N′,N′*-tetramethylethylenediamine, and 1 mL of pyridine were added. The mixture bubbling with oxygen was stirred at room temperature for 6 h. 30 mL of DMF was added, and mixture was filtrated through a short silica column to remove copper. The filtrate was poured into 100 mL of water, and the resulting precipitate was filtered, washed with water, and dried under vacuum to afford beige powder (1.40 g, 82%). ^{1}H NMR (CDCl$_3$), ppm: δ = 1.57 (s, CH$_3$), 4.49 (s, CH$_2$, oxazine), 4.63 (d, CH$_2$), 5.23 (s, CH$_2$, oxazine), and 6.9−8.1 (14H, Ar). ^{13}C NMR (CDCl$_3$), ppm: δ = 51.20 (Ar−C−N, oxazine), 56.61 (O−C−C≡), 70.90 (C≡C−C≡), 74.81 (C−C≡C−), 80.04 (O−C−N, oxazine).

*Poly(bis(3-(4-(prop-2-ynyloxy)phenyl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methanone) (Poly(BP-appe)).* Poly(BP-appe) was synthesized from BP-appe analogous to poly(BA-appe). ^{1}H NMR (DMSO), ppm: δ = 4.65 (s, CH$_2$, oxazine), 4.83 (d, CH$_2$), 5.47 (s, CH$_2$, oxazine), and 6.5−7.8 (14H, Ar). ^{13}C NMR (DMSO), ppm: δ = 51.05 (Ar−C−N, oxazine), 56.60 (O−C−C≡), 70.91 (C≡C−C≡), 74.75 (C−C≡C−), 80.07 (O−C−N, oxazine).

*Poly(3,3′-bis(4-(prop-2-ynyloxy)phenyl)-3,3′,4,4′-tetrahydro-2*H*-naphtho[2,1-*e*][1,3]oxazine)(Poly(15N-appe)).* Poly(15N-appe) was synthesized from 15N-appe in a similar manner to poly(BA-appe). ^{1}H NMR (DMSO), ppm: δ = 4.63 (s, CH$_2$, oxazine), 4.79 (d, CH$_2$), 5.51 (s, CH$_2$, oxazine), and 6.7−7.8 (12H, Ar). ^{13}C NMR (DMSO), ppm: δ = 51.06 (Ar−C−N, oxazine), 56.66 (O−C−C≡), 70.91 (C≡C−C≡), 74.80 (C−C≡C−), 80.90 (O−C−N, oxazine).

*Poly(3,3′-bis(3-ethynylphenyl)-3,3′,4,4′-tetrahydro-2*H*-naphtho-[2,1-*e*][1,3]oxazine) (Poly(15N-ea)).* Poly(15N-ea) was synthesized from 15N-ea similar to poly(BA-appe); however, the growing polymer precipitated from the solution on the early stage of the synthesis and afforded only oligomeric structures. ^{1}H NMR (DMSO), ppm: δ = 4.78 (s, CH$_2$, oxazine), 5.65 (s, CH$_2$, oxazine), and 6.7−7.9 (12H, Ar).

Results and Discussion

Synthesis of Monomers. Propargyl functional benzoxazine monomers were prepared from bisphenol A, 1,6-dihydroxybenzophenone, or 1,5-dihydroxynaphthalene with APPE synthesized by modifying the method reported earlier[61] according to Scheme 1. The monomers were designated as BA-appe, BP-appe, and 15N-appe, respectively. The ^{1}H NMR spectrum of BA-appe is shown in Figure 1a where the presence of a propargyl proton at 2.49 ppm and typical benzoxazine resonances at 4.51 and 5.26 ppm is seen. The corresponding ^{13}C NMR in Figure 2a shows resonances at 75.36 and 78.77 ppm, indicating propargyl structure. The IR spectrum supports the structure of the monomer by the presence of bands at 3286 and 943 cm^{-1} corresponding to propargyl and benzoxazine structures, respectively.

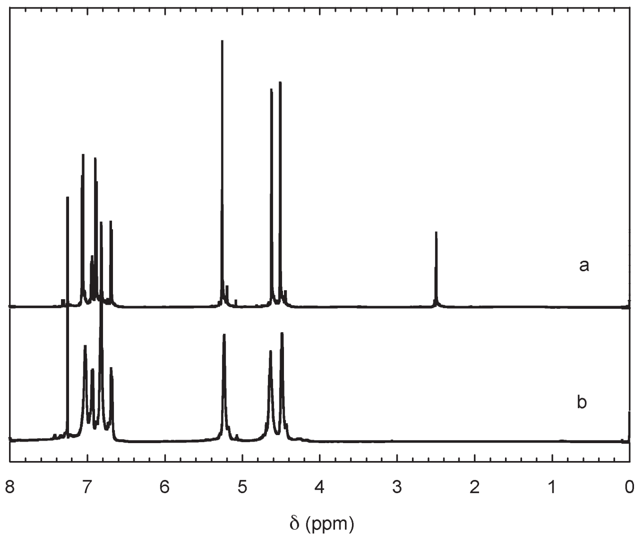


Figure 1. ^{1}H NMR spectra of BA-appe (a) and polyBA-appe (b).

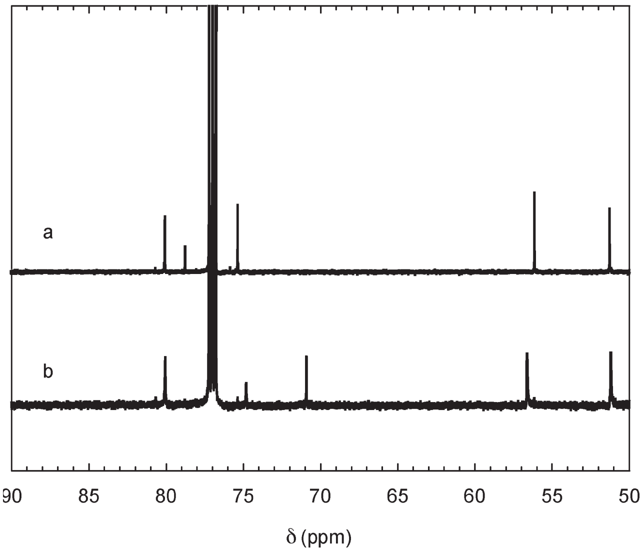
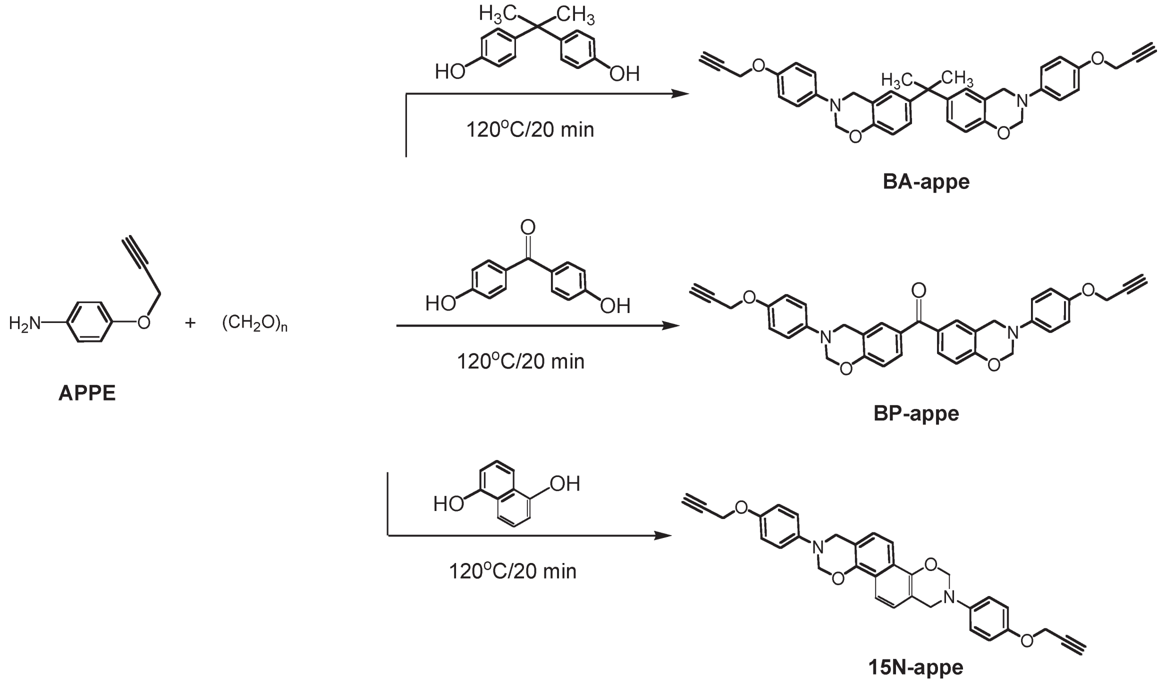
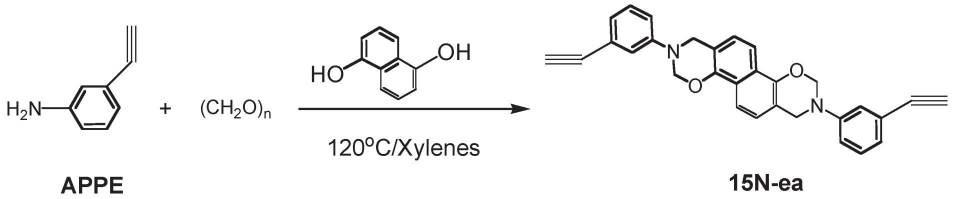


Figure 2. ^{13}C NMR spectra of BA-appe (a) and polyBA-appe (b).

Scheme 1. Synthesis of Propargyl Functionalized Benzoxazine Monomers



Scheme 2. Synthesis of Ethynyl Functionalized Benzoxazine Monomer



Also, a benzoxazine monomer based on 1,5-dihydroxynaphthalene and 3-ethynylaniline (designated as 15N-ea) was prepared. A traditional approach of preparing the benzoxazine monomer in solution at mild temperatures[1] as well as the solventless approach[63] which is much more effective in many cases did not work for these monomers. A novel variation of the solution method was applied for successful synthesis of 15N-ea with extremely high yields and minimum side reactions as shown in Scheme 2. The reactants were mixed in mixed-isomer xylenes, and the mixture was reacted at 120 °C for about 5 h. This modified approach gave the product with very high yield of 90% which was recrystallizable directly from the reaction mixture. The ^{1}H NMR spectrum shown in Figure 3 confirms formation of ozaxine ring (bands at 4.75 and 5.63 ppm) and the presence of an ethynyl group (4.14 ppm band).

Synthesis of Model Polymer. To understand the cross-linking behavior of the synthesized benzoxazine polymers, a model polymer, hereinafter called model polymer, was synthesized from 4,4′-(propane-2,2-diyl)bis((prop-2-ynyloxy)benzene) as shown in Scheme 3 according to the approach reported elsewhere.[62] The polymerization was carried out using 10 mol % CuCl and *N,N,N′,N′*-tetramethylenediamine as a catalyst and cocatalyst in DMF/pyridine mixture bubbled with oxygen. The ^{13}C NMR spectra of the model polymer along with 4,4′-(propane-2,2-diyl)bis((prop-2-ynyloxy)benzene) represented in Figure 4 shows shift of 75.36 and 78.73 ppm bands to 70.94 and 74.74 ppm, suggesting the formation of diacetylene group.

Synthesis of Benzoxazine Polymers. The polymers containing a benzoxazine group in the main chain were synthesized from the corresponding propargyl (designated as poly(BA-appe), poly(BP-appe), poly(15N-appe)) functionalized benzoxazine monomers following the same procedure as model

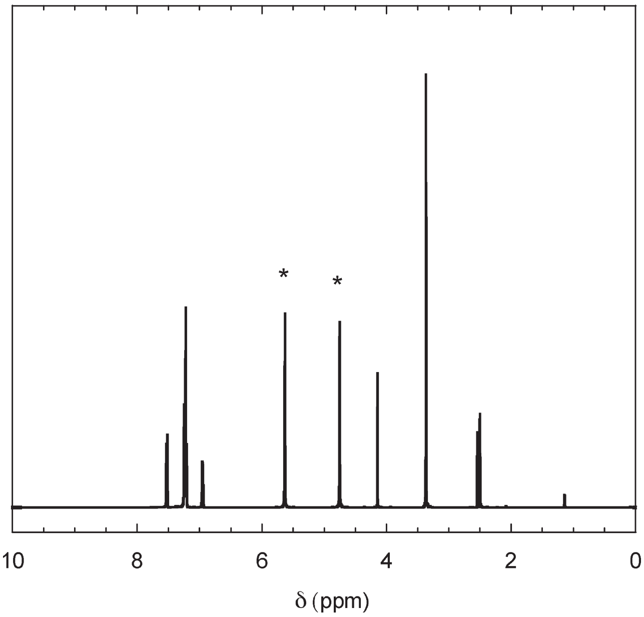
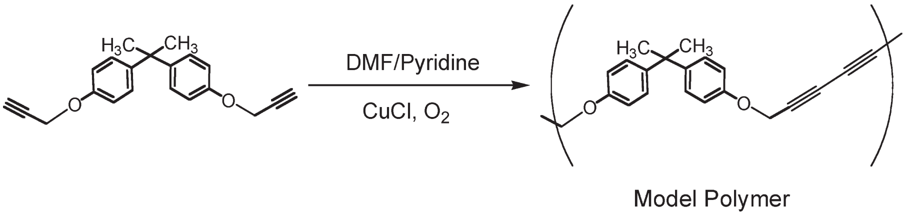
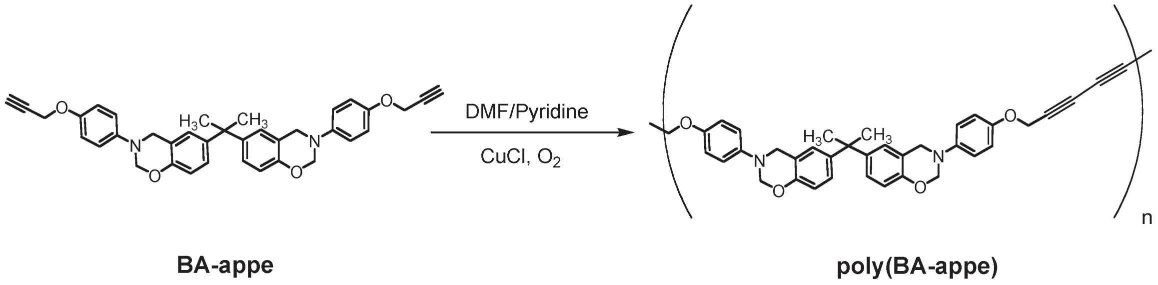


Figure 3. ^{1}H NMR spectrum of 15N-ea.

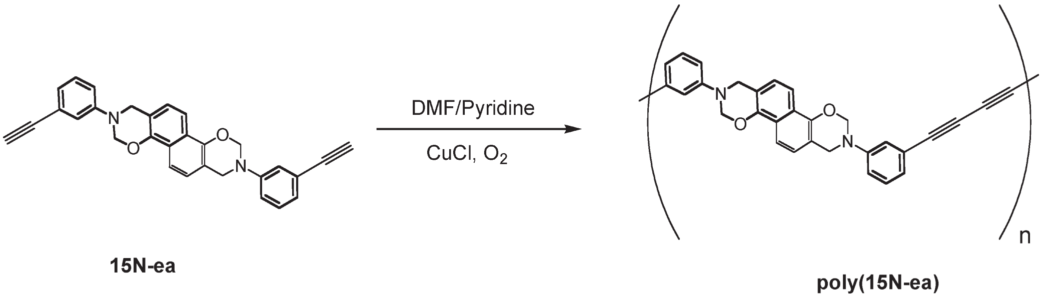
Scheme 3. Synthesis of Model Polymer



Scheme 4. Synthesis of Poly(BA-appe)



Scheme 5. Synthesis of Poly(15N-ea)



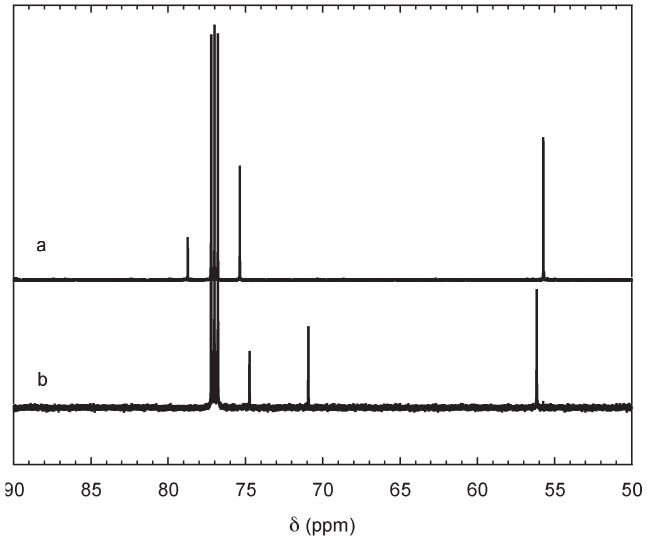


Figure 4. ^{13}C NMR spectra of 4,4′-(propane-2,2-diyl)bis((prop-2-ynyloxy)benzene) (a) and model polymer (b).

Table 1. SEC Data of the Synthesized Benzoxazine Polymers

	M_n	M_w	M_n/M_w	DP
poly(BA-appe)	21 000	40 000	1.91	37
poly(BA-appe)	25 000	48 000	1.96	45
poly(15N-appe)	14 000	21 000	1.53	28
poly(15N-ea)				

polymer shown in Scheme 4. The ^{1}H NMR spectrum (Figure 1b) shows typical oxazine ring resonances at 4.49 and 5.23 ppm without any sign of ring-opening, indicating the benzoxazine moiety survives oxidative coupling reaction conditions. Formation of diacetylene is confirmed by the shifts of propargyl bands in the ^{13}C NMR spectrum shown in Figure 2b, which is analogous to that of the model polymer. The main-chain-type polybenzoxazine based on ethynyl functionalized monomer (15N-ea) was prepared in the same way as the propargyl series (Scheme 5); however, because of the high rigidity of the formed structure, the resultant polymer precipitated in the early stage of the reaction affording only oligomeric structures.

The results of molecular weight determination of prepared polymers studied by SEC with DMF as the mobile phase are summarized in Table 1. The number-average molecular weights (M_n) were in the range from 14 000 to 25 000, which is several times larger than molecular weight of benzoxazine polymers obtained via Mannich condensation.[22,23]

Cross-Linking Behavior of Polymers. The cross-linking of propargyl-based diacetylene, model polymer, was examined by DSC as shown in Figure 5. It exhibits two exothermic peaks: the first exhibits a maximum at 185 °C and the second peak with a maximum at about 260 °C. The low-temperature exotherm at 185 °C corresponds to the cross-polymerization of diacetylene which often takes place in this temperature range for aliphatic diacetylenes[62,64] and benzoxazine, and the second peak at 260 °C can be referred to the polymerization of propargyl end groups.

Cross-linking behavior of benzoxazine polymer containing diacetylene was studied using poly(BA-appe) as an example. Figure 6 shows the DSC thermogram of the polymer as well as the initial monomer. BA-appe shows two overlapping exotherms corresponding to polymerization of benzoxazine and propargyl groups with the maximum at 241 °C. There is no diacetylene groups in this monomeric benzoxazine molecule. However, the cross-linking behavior of poly(BA-appe) is dramatically different. The DSC thermogram exhibits the first broad polymerization peak with onset at 125 °C and maximum at 185 °C. The peak at 185 °C corresponds to the reaction of the diacetylene and benzoxazine groups, whereas the peak at 241 °C relates to the reaction of the propargyl end groups. The polymerization of ozaxine ring was confirmed by FTIR. Unfortunately, the diacetylene group reaction could not be studied by infrared spectroscopy due to the weak absorption of the diacetylene group caused by the molecular symmetry. The IR spectra are presented in Figure 7. The characteristic peak of benzene ring[65] with attached oxazine ring at 943 cm^{-1} decreased its intensity by about half already after treatment at 125 °C for 1 h and almost completely disappeared after 1 h at 190 °C. The prevention of further oxazine ring-opening at low temperature could be explained by vitrification taking place during cross-linking. The band at 1496 cm^{-1}, which is characteristic for benzoxazine polymerization due to appearance of tetra-substituted benzene ring structure,[65] is observed as a shoulder in the 1500 cm^{-1} region. The second much smaller exothermic peak with the maximum at 260 °C refers to the reaction of propargyl end groups similar to that for the model polymer. The nature of such a dramatic shift of

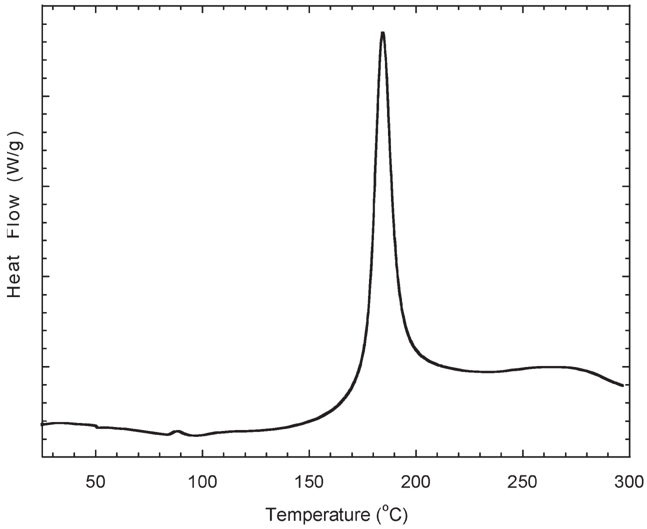


Figure 5. DSC thermogram of model polymer.

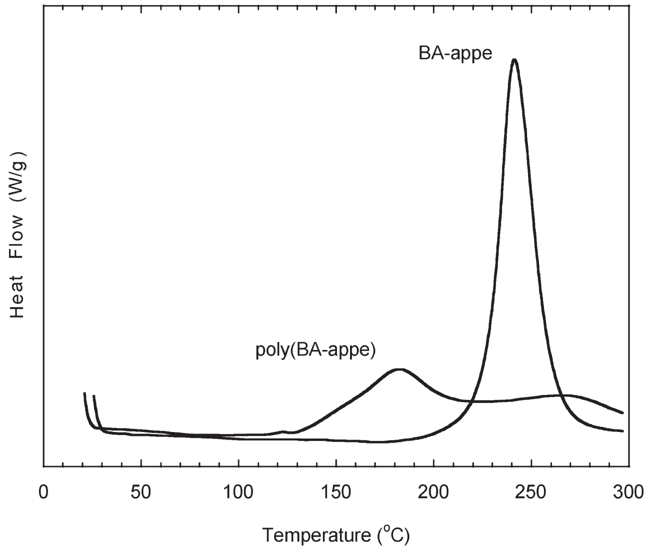


Figure 6. DSC thermograms of BA-appe and its polymer.

polymerization exotherm peak toward low temperature is not clear. Our model studies discussed in the work published elsewhere[66] proved that this phenomenon is not due to thermally activated initiation of oxazine ring-opening by the heat released during diacetylene polymerization. We can only speculate that this is taking place because of the local alignment of benzoxazine group in the melt, which is difficult to be studied by X-ray analysis. All synthesized polymers based on propargyl benzoxazine monomers (poly(BP-appe) and poly(15N-appe)) showed similar DSC features, exhibiting dramatic polymerization temperature decrease as shown in Figure 8. Expectedly, the high-temperature exotherm is larger in the case of poly(15N-appe) due to much larger amount of end groups since the molecular weight of this polymer is significantly lower as explained earlier. However, the cross-linking behavior of poly15N-ea is quite different from propargyl-based diacetylene polymer. The thermogram presented in Figure 9 shows much higher cross-linking temperature which is expected for much more rigid aromatic diacetylenes due to their decreased capability to arrange in favorable alignment for polymerization. Thus, the diacetylene containing main-chain benzoxazine polymers formed from propargyl monomers are attractive since they can be polymerized to reasonably high molecular weights and exhibit unexpectedly low temperatures of cross-linking.

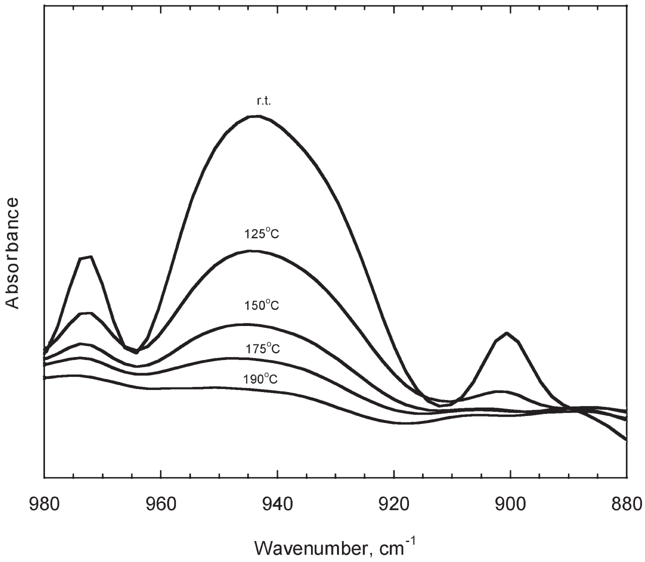


Figure 7. IR spectra of the benzene ring mode of benzoxazine in poly (BA-appe).

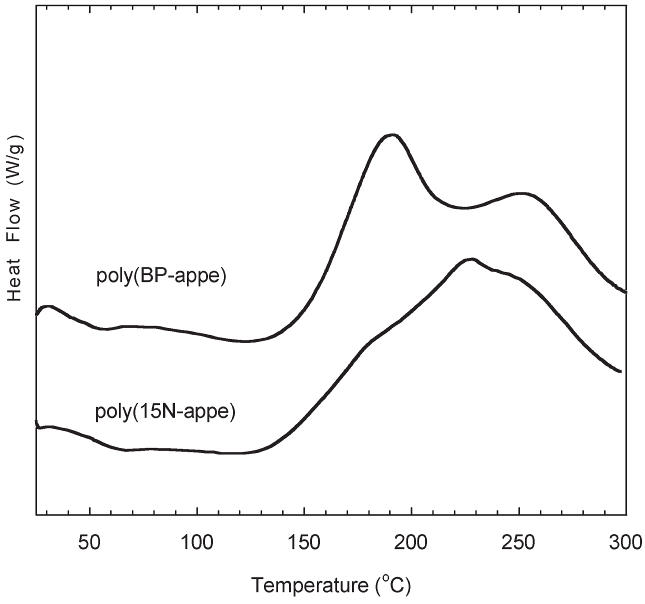


Figure 8. DSC thermograms of poly(BP-appe) and poly(15N-appe).

3.5. Thermal Stability. The thermal stability of the polymers was evaluated by TGA under a nitrogen atmosphere, and the thermograms are shown in Figure 10. The results are summarized in Table 2. Two of the polymers, namely poly (BP-appe) and poly(15N-ea), exhibited the 5% weight loss temperatures (designated as T_{d5}) above 400 °C which surpasses highly thermally stable maleimide and nitrile functionalized benzoxazine resin.[18] The char yield is high (59%) even for bisphenol A-based polymer and becomes even higher for benzophenone and 1,5-dihydroxynaphthalene-

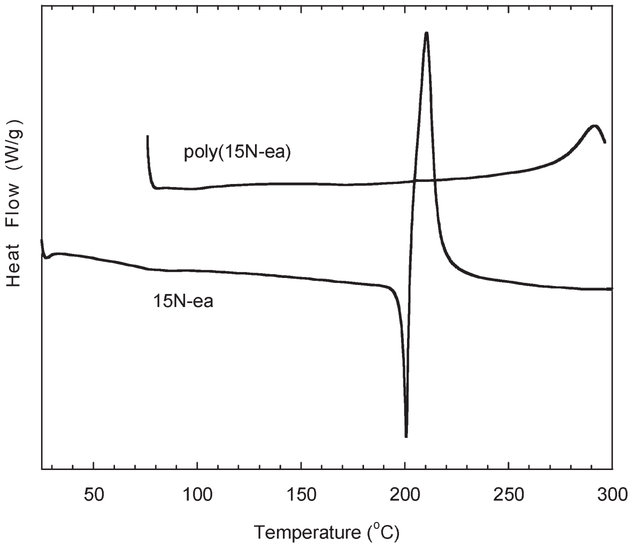


Figure 9. DSC thermograms of 15N-ea and its polymer.

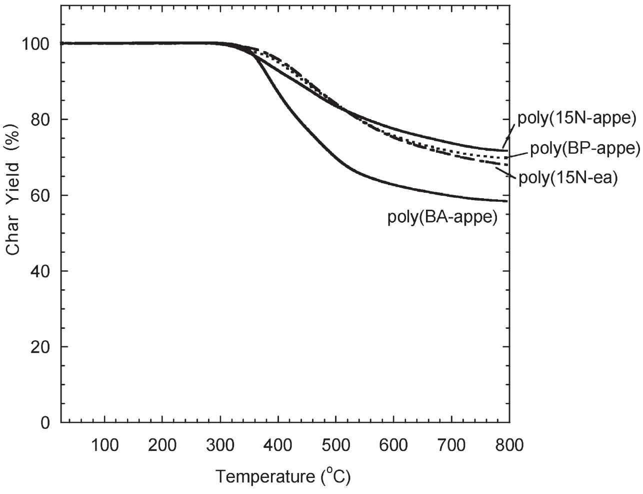


Figure 10. TGA thermograms of cross-linked poly(BA-appe), poly (BP-appe), poly(15N-appe), and poly(15N-ea).

Table 2. Thermal Stability of the Benzoxazine Polymers

	T_{d5},°C	char yield, %
poly(BA-appe)	367	59
poly(BP-appe)	401	70
poly(15N-appe)	379	72
poly(15N-ea)	409	68

based polymers (70% and 72%), despite the presence of aliphatic segments of propargyl moieties. However, the yield is slightly lower (68%) for ethynyl-based structure since only oligomers have been achieved due to extremely poor solubility of the polymer. The results indicate that diacetylene units used to form linear benzoxazine polymer afforded thermosetting polymers with exceptionally high thermal stability with good solubility in common solvents except for the case of ethynyl-based structure.

Conclusions

A series of linear, novel benzoxaine polymers containing diacetylene and oxazine groups in the main chain were successfully synthesized via an oxidative coupling approach. NMR and FTIR spectroscopy were used to confirm the structures of the polymers. A reasonably high degree of polymerization was achieved with number-average molecular weight in the range from 14 000 to 25 000 with polydispersity index in the range of 1.5−1.9 as investigated by SEC. Polymers showed unusual cross-linking behavior with the exotherm maximum below 200 °C and onset at 125 °C. Evidence of oxazine ring polymerization as low as 125 °C was obtained by FTIR, which is one of the lowest temperatures reported for benzoxazine cross-linking without addition of any catalyst or initiator. Extremely high thermal stability was confirmed by TGA. The highest char yield was 72%, and the highest temperature at 5% weight loss was above 400 °C, which is an outstanding result for thermosetting resins without addition of inorganic fillers.

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