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# Thermally Curable Acetylene-Containing Main-Chain Benzoxazine Polymers via Sonogashira Coupling Reaction

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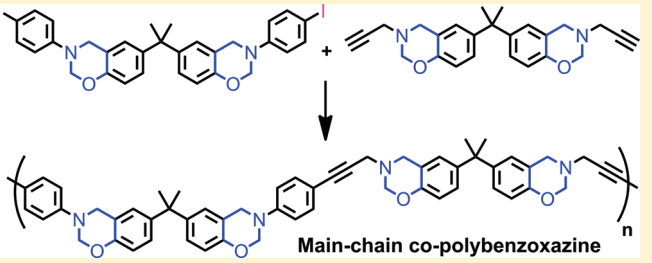
Supporting Information

**ABSTRACT:** Propargyl containing thermally curable benzoxazine precursors in the main chain have been synthesized from iodo functional bisbenzoxazine and diacetylenes by Sonogashira coupling reaction. For this purpose, 4,4′-isopropylidenediphenol (Bisphenol A) was reacted with formaldehyde and iodoaniline to form diiodobisbenzoxazine (DIBB). Sonogashira coupling reaction between DIBB and diacetylene bisether (DABE) or diacetylene bisbenzoxazine (DABB) catalyzed by palladium tetrakistriphenylphosphine yields the corresponding main-chain polybenzoxazine precursors with the molecular weights around 2300−3500 Da. The structures of the monomers and the resulting polymers are confirmed by FT-IR and $^1$H NMR spectral analysis. Curing behaviors of both the monomer and polymers were studied by differential scanning calorimetry (DSC). Thermal properties of the cured polymers were also investigated by thermogravimetric analysis (TGA).




## INTRODUCTION

The interest of academics and chemical industry in 1,3-benzoxazine chemistry is growing rapidly due to many unique properties of benzoxazines and their resins. These include near-zero volumetric change upon curing, no strong acid catalysts or additives requirement for curing, high thermal stability, good mechanical performance, low water absorption, and high char yield of the cured products.[1] Accordingly, benzoxazine resins are suitable alternative materials for applications where epoxides, bismaleimides, cyanate esters, and polyimides are used.[2] And they have capability to overcome several shortcomings of conventional novolac and resole type phenolic resins. An additional attractive feature of benzoxazine chemistry is the ease of preparation of monomers which are synthesized from inexpensive, commercially available phenols, primary amines, and formaldehyde.[3−14] Therefore, the chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility by using appropriate starting materials. The polymerization of these monomers is a thermally induced ring-opening polymerization which can be accomplished without any initiator or curative and yields polybenzoxazine networks[12,15−23] (see Scheme 1).

Many studies have been conducted in order to improve the properties of benzoxazine polymers and to expand their application scopes. However, processing of the benzoxazine monomers into thin films arising from its powder structure still remained as the major challenge for wider industrial applications. Moreover, the polymers obtained after curing are rather brittle as a result of the low molecular weight of the network structure.[24]

A recently active concept in benzoxazine resin research is based on the synthesis of telechelic, main- or side-chain polymers containing benzoxazine moieties.[25−27] At this point, the benzoxazine behaves like an ordinary thermoplastic which has good solubility and processability and also offers the ability to prepare a varnish with low solid content that forms good quality films.[24] Hence, it is expected that the cross-linked network structure, formed from polymer and polymerization of benzoxazine, will exhibit enhanced mechanical property while preserving the beneficial properties of polybenzoxazine. Thus, most efforts have focused on the preparation of benzoxazine functional polymers and polybenzoxazine precursors. The latter approach seemed to be more suitable since the obtained precursors contain benzoxazine units in every repeating unit and therefore leads to the formation of highly cross-linked network structures after thermal treatment. Ishida and Takeichi groups have independently employed monomer synthesis methodology by using bifunctional amines, bisphenol A, and formaldehyde.[28−31] Jeffamine amine-based precursors can also be prepared via similar monomer synthesis strategy.[32,33] In addition, polyphenylene and triazole type precursors have been developed via oxidative and click coupling reactions, respectively.[34−38] Polybenzoxazine precursors based on more traditional polymers such as polyesters, polyetheresters, and oligosiloxanes have also been prepared.[39−41] In those cases, appropriate functional groups incorporated to benzoxazines were conveniently used for polycondensation and Pt-catalyzed hydrosilylation reactions, respectively.

As part of our continuous interest in developing alternative methods for the production of benzoxazine resins with desired properties, we herein describe preparation and characterization

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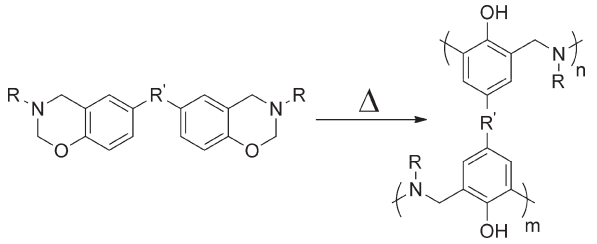
**Scheme 1. Thermally Induced Ring-Opening Polymerization of Bisbenzoxazines**



of polybenzoxazine precursors obtained by Sonogashira coupling reactions.[42,43] As will be shown below, the number of benzoxazine units per chain may be adjusted by selecting appropriate iodo and propargyl functional components. The general properties such as solubility and thermal properties are described.

## EXPERIMENTAL PART

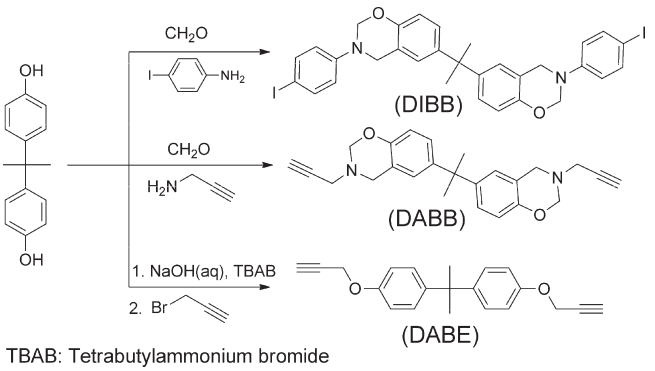
**Materials.** 4,4-Isopropylidenediphenol (Aldrich, 97%), 4-iodoaniline (Acros, 99%), paraformaldehyde (Acros, 96%), sodium hydroxide (Acros, 97+%), 1,4-dioxane (Aldrich, ≥99%), and chloroform (Acros, 99+%) were used as received. Diisopropylamine (DIPA) (Sigma-Aldrich, ≥99.5%) was dried by refluxing with $CaH_2$, and toluene (Sigma-Aldrich, ≥99.8%) was dried over sodium wire by refluxing prior to use.

**Characterization.** $^1$H NMR spectra were recorded in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard, using a Bruker AC250 instrument at a proton frequency of 250 MHz. The FTIR spectra are recorded at Perkin-Elmer Spectrum One with an ATR Accessory (ZnSe, Pike Miracle Accessory) and cadmium telluride (MCT) detector. Resolution was 4 $cm^{-1}$ and 24 scans with 0.2 cm/s scan speed. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC with a heating rate of 20 °C/min under nitrogen flow (20 mL/min). Thermogravimetric analysis (TGA) was performed on Perkin-Elmer Diamond TA/TGA with a heating rate of 10 °C/min under nitrogen flow (200 mL/min).

*Synthesis of Diiodobisbenzoxazine (DIBB).* In a 100 mL round-bottom flask, 2.65 g (88.2 mmol) of paraformaldehyde and 4.83 g (22.1 mmol) of 4-iodoaniline were dissolved with 50 mL of 1,4-dioxane. After addition of 2.50 g (11.0 mmol) of 4,4-isopropylidenediphenol, the reaction mixture was stirred at 110 °C overnight. The solvent was evaporated under vacuum, and the oily product was dissolved in chloroform. The solution was washed three times with 1 N NaOH aqueous solution, three times with saturated $CaCl_2$, and distilled water. The organic phases were dried with magnesium sulfate. The crude product was dissolved in 10 mL of tetrahydrofuran and precipitated in 200 mL of cold methanol. Brown precipitates (58%) were collected by centrifugation. $^1$H NMR ($CDCl_3$): $\delta$ = 1.56 (s, 6H, $CH_3$), 4.53 (s, 4H, Ar−$CH_2$−N), 5.27 (s, 4H, O−$CH_2$−N), 6.67−7.53 (m, 14H, Ar).

*Synthesis of Diacetylene Bisether (DABE).* DABE was synthesized according to the literature procedure.[36] 4,4-Isopropylidenediphenol (2.00 g, 8.76 mmol) was dissolved in 60 mL of 0.4 M NaOH. The mixture was heated at 70 °C until a clear solution was formed. To this solution, tetrabutylammonium bromide (0.3 g, 1.0 mmol) was added as a phase transfer catalyst. Propargyl bromide (776 $\mu$L, 9 mmol) in 20 mL of toluene was added portionwise to the reaction mixture. The solution was stirred at 90 °C overnight. It was cooled to afford solid product and filtered. In addition, the toluene layer was separated and washed with 0.1 N NaOH and neutralized with distilled water. Organic layer was dried with magnesium sulfate, and toluene was evaporated to afford extra solid. The collected crude product was recrystallized from methanol (yield: 90%). $^1$H NMR (MeOD): $\delta$ = 1.61 (s, 6H, $CH_3$), 2.90 (t, 2H, CH), 4.66 (d, 4H, $CH_2$), 6.85 (d, 4H, Ar), 7.12 (d, 4H, Ar).

**Scheme 2. Synthesis of Diiodobisbenzoxazine (DIBB), Diacetylene Bisbenzoxazine (DABB), and Diacetylene Bisether (DABE)**




TBAB: Tetrabutylammonium bromide

*Synthesis of Diacetylene Bisbenzoxazine (DABB).* DABB was synthesized according to the literature procedure.[38] In a 100 mL round-bottom flask, 2.64 g (88.0 mmol) of paraformaldehyde and 2.42 g (22.1 mmol, 2.82 mL) of propargylamine were dissolved with 50 mL of 1,4-dioxane. After addition of 5.0 g (11.0 mmol) of 4,4′-isopropylidenediphenol, the reaction mixture was stirred at 110 °C for 3 days. The solvent was evaporated under vacuum, and the oily product was dissolved in chloroform. The solution was washed three times with 1 N NaOH aqueous solution and then distilled water. Organic phases were dried with magnesium sulfate. The crude product was purified by column chromatography (silica gel, $CHCl_3$), and an oily brown product was obtained (yield: 68%). $^1$H NMR ($CDCl_3$): $\delta$ = 1.58 (s, 6H, $CH_3$), 2.29 (s, 2H, CH), 3.58 (s, 4H, C−$CH_2$−N), 4.05 (s, 4H, Ar−$CH_2$−N), 4.88 (s, 4H, O−$CH_2$−N), 6.67 (d, 2H, Ar), 6.82 (s, 4H, Ar), 6.94 (d, 4H, Ar).

*Synthesis of Polymer A.* DIBB (120 mg, 0.168 mmol) and DABE (51.1 mg, 0.168 mmol) were placed in a 50 mL dry 3-necked round-bottom flask. They were dissolved in a mixture of 8 mL of toluene and 2 mL of diisopropylamine. The reaction mixture was bubbled with nitrogen for 5 min, and 7.8 mg (6.7 $\mu$mol) of $Pd(PPh_3)_4$ and 6.4 mg (34 $\mu$mol) of CuI were added. It was stirred at 35 °C for 1 day, and solvent was removed. The crude product was dissolved in THF and filtered through a short silica gel column. The filtrate was concentrated to 7 mL and precipitated into 150 mL of cold methanol. Brown precipitates were collected by centrifugation (yield: 30%). $^1$H NMR ($CDCl_3$): $\delta$ = 1.59 (s, 12H, $CH_3$), 4.55 (s, 2H, Ar−$CH_2$−N), 4.85 (s, 4H, C−$CH_2$−O), 5.29 (s, 2H, O−$CH_2$−N), 6.66−7.53 (20H, Ar).

*Synthesis of Polymer B.* Polymer B was synthesized from DABB and DIBB in a similar manner to polymer A (yield: 35%). $^1$H NMR ($CDCl_3$): $\delta$ = 1.57 (s, 12H, $CH_3$), 3.77 (s, 2H, N−$CH_2$−C), 4.08 (s, 2H, Ar−$CH_2$−N-1), 4.54(d, 2H, Ar−$CH_2$−N-2), 4.92 (s, 2H, O−$CH_2$−N-1), 5.28 (d, O−$CH_2$−N-2), 6.66−7.53 (18H, Ar).

## RESULTS AND DISCUSSION

The transition-metal-catalyzed cross-coupling reaction of terminal alkynes with aryl halides or vinyl halides represents a powerful strategy for preparing main-chain alkyne-containing polymers. From this point, Sonogashira−Hagihara polycondensation should enable us to obtain main-chain polybenzoxazine precursors. In our study, we selected iodo functional bisbenzoxazine as thermally reactive Sonogashira reaction component since iodo-containing aromatics give high yields in the coupling process. Accordingly, diiodobisbenzoxazine (DIBB) was suc-

**Scheme 3. Synthesis of Main Chain Polybenzoxazine Precursors from Diiodobisbenzoxazine (DIBB), Diacetylene Bisbenzoxazine (DABB), and Diacetylene Bisether (DABE)**

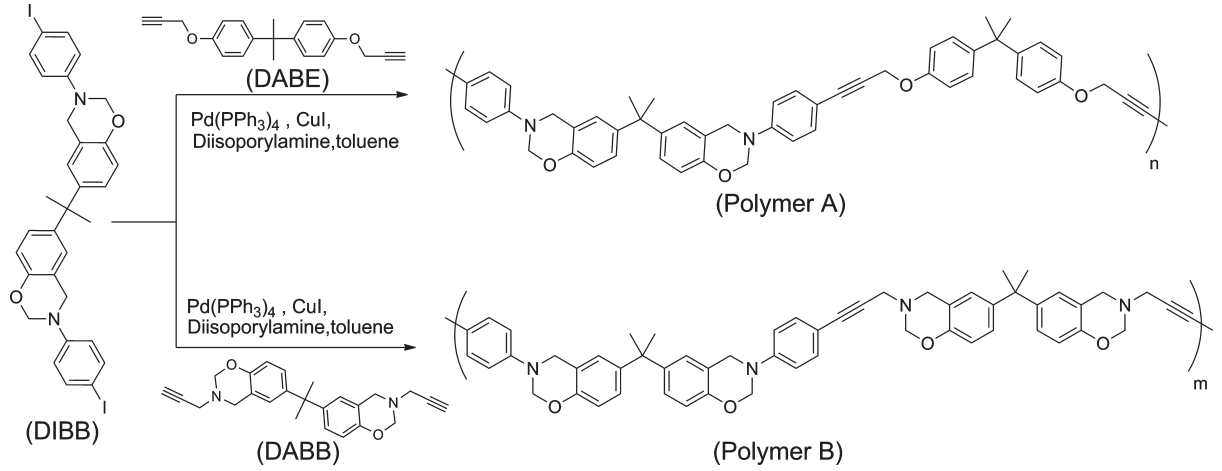



**Table 1. Molecular Weight Characteristics of Polybenzoxazine Precursors**

| polybenzoxazine precursor | iodo compound | acetylenic compound | benzoxazine group per repeating unit | $M_n$[a] (g/mol$^{-1}$) | $M_w/M_n$ |
|---|---|---|---|---|---|
| polymer A | DIBB | DABE | 2 | 2330 | 1.6 |
| polymer B | DIBB | DABB | 4 | 3497 | 1.3 |

[a] Measured by GPC according to polystyrene standards.

cessfully synthesized from bisphenol A and iodoaniline by conventional benzoxazine ring-forming reaction (Scheme 2). Diacetylene bisether (DABE) and diacetylene bisbenzoxazine (DABB) were used as acetylene-terminated monomers for the coupling reactions. Bisphenol A was converted to DABE by reacting with propargyl bromide in the presence of NaOH and tetrabutylammonium bromide as phase transfer catalyst. Moreover, for the preparation of DABB, bisphenol A was reacted with propargylamine and formaldehyde in dioxane as shown in Scheme 2.

The structures of all monomers were confirmed by $^1$H NMR and IR analyses. The spectrum of DIBB features two peaks at 4.53 and 5.27 ppm, which are consistent with the formation of benzoxazine ring (see Supporting Information). Moreover, IR spectra of DIBB reveal asymmetric stretching of C−O−C at 1228 cm$^{-1}$ and trisubstituted benzene ring modes at 950 and 1486 cm$^{-1}$ which are characteristic absorptions of benzoxazines. Similarly, spectral analyses of DABB reveal the expected structures. The $^1$H NMR spectrum shows resonances at 2.29 and 3.58 ppm which is assigned to ≡C−*H* and C*H*$_2$ of propargyl group, respectively, and oxazine ring structure was confirmed by the peaks at 4.05 and 4.88 ppm. In the IR spectrum of DABB, the characteristic absorptions of benzoxazine structure appeared at 1226 cm$^{-1}$ due to the asymmetric stretching of C−O−C, at 1492 and 931 cm$^{-1}$ due to the trisubstituted benzene ring. Additionally, the stretching vibration bands assigned to HC≡ and C≡C appeared at 3287 and 2123 cm$^{-1}$, respectively. The structure of DABE was also confirmed by the $^1$H NMR spectrum. The peaks at 2.90 and 4.66 ppm showed the formation of desired monomer. The expected bands at 3288 and 2124 cm$^{-1}$ which is assigned to ≡CH and C≡C, respectively was observed from the IR spectrum of DABE.

It is well-known that thermally activated ring-opening polymerization of 1,3-benzoxazines is an exothermic process which have maxima at around 200−250 °C depending on the functionalities of the benzoxazines. DSC thermogram of DIBB shows an exotherm with an onset at 204 °C and a maximum at 210 °C. The amount of this exotherm is 61 cal/g. Propargyl-containing benzoxazine monomer (DABB) exhibits a broader peak starting at 142 °C with a maximum at 215 °C with 153 cal/g exothermic energy. The DSC thermogram of DABE also revealed an exotherm with a maximum at 288 °C starting at 225 °C can be attributed to acetylene polymerization.

The coupling of terminal alkyne containing DABE or DABB with aryl halide functional benzoxazine (DIBB) is performed with a $Pd(PPh_3)_4$ catalyst, a copper(I) cocatalyst (CuI), and an amine base (DIPA). Henceforth, main-chain polybenzoxazine precursors were obtained as depicted in Scheme 3. Polymer A is obtained from DIBB and DABE with 2330 Da, whereas polymer B is formed from DIBB and DABB with 3497 Da. All of the obtained polymers are soluble in common solvents like chloroform, toluene, and dioxane as well as more polar solvents like dimethylformamide and dimethyl sulfoxide. Moreover, these polymers formed free-standing films by solvent casting.

Molecular weights of these polymeric precursors are obtained by gel permeation chromatography (GPC) analysis, and the results are tabulated in Table 1. As a result of condensation polymerization, polybenzoxazine precursors are obtained with different chain lengths and molecular weight distributions. However, the molecular weights of the polymers are low compared with many other Sonogashira type polymers, which is a result of the polymerization temperature used (35 °C). In the literature, the reaction of aryl iodides and acetylene derivatives is usually carried out at 50−90 °C, but we had experienced that using high temperatures resulted in insoluble products, which are forming by cross-linking of benzoxazine units in the growing polymers. Moreover, low temperature conditions are also the reason for low yield of polymerization.

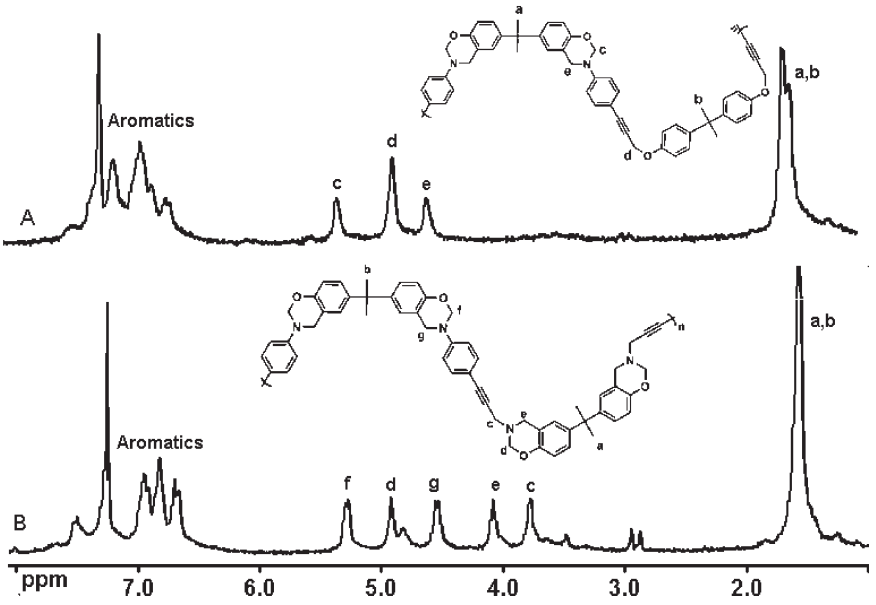



**Figure 1.** $^{1}$H NMR spectra of polymers A and B (in $CDCl_3$).

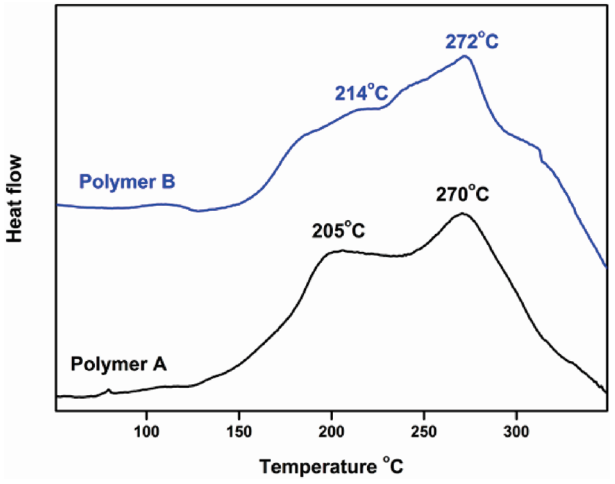
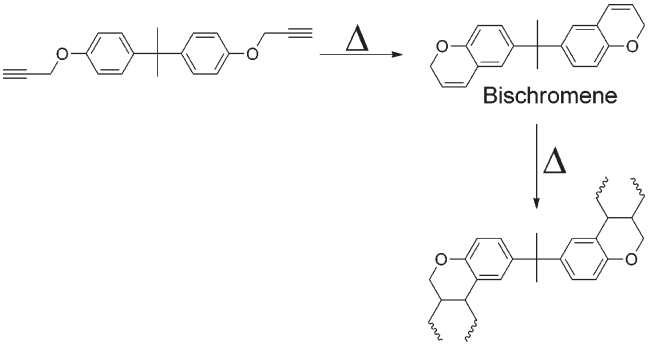



**Figure 2.** DSC thermogram of main-chain polybenzoxazine precursors.

The chemical structures of polymeric benzoxazines were confirmed by spectral analysis. As can be seen from Figure 1, the $^{1}$H NMR spectra of precursors exhibit benzoxazine structures which are identified by the presence of the characteristic chemical shifts of the methylene groups in the cyclic benzoxazine rings. Besides the chemical shifts that belong to the propargyl groups are also clearly revealed. In Figure 1A, the two resonance signals at 4.55 and 5.29 ppm are assigned to $-CH_2$ protons of oxazine ring and the signal at 4.85 ppm is due to the $O-CH_2$ protons of propargyl ether. Similarly, Figure 1B exhibits two types of oxazine ring protons at 4.08, 4.54, 4.92, and 5.28 ppm and $-CH_2$ protons of propargyl group at 3.77 ppm. Furthermore, in the FT-IR spectrum of polymer A as presented in Figures 4 and 5, $CH_2$ wagging and the asymmetric stretching vibration bands of C−O−C corresponding to benzoxazine structure at 1297 and 1228 cm$^{-1}$are observed, respectively. The bands at 956 and 1508 cm$^{-1}$ for trisubstituted benzene ring were also present in the spectrum, and the absorption band of the C≡C group in the

**Scheme 4. Thermal Formation and Curing of Bischrome**




prepolymer emerges at 2225 cm$^{-1}$. In the IR analysis of polymeric precursor derived from DIBB and DABB, the benzoxazine structure was also confirmed by the bands at 948, 123, and 1497 cm$^{-1}$, and the C≡C group was verified by the observation of the band at 2222 cm$^{-1}$.

Parts A and B of Figure 2 show the DSC profiles for the polymeric precursors polymer A and polymer B, respectively. Polymer A showed an exotherm with an onset at 125 °C and two peaks at 205 and 270 °C corresponding to the cross-linking of propargyl unit and curing of benzoxazine, respectively, with a total amount of 188 cal/g exotherm. For polymer B, these exotherms start at 150 °C with a maximum at 214 and 272 °C and 231 cal/g energy for all cross-linking reactions, which is higher than that of polymer A since every repeating unit of polymer B contains four oxazine rings.

Moreover, phenylpropargyl ethers are known to undergo Claisen type sigmatropic rearrangement to form chromenes.[44,45] The uncatalyzed rearrangements in bulk are nearly always accompanied by thermal polymerization of the formed chromene (see Scheme 4). Thus, bispropargyl ethers on uncatalyzed thermal polymerization in bulk gives cross-linked bischromenes. In this regard, the exotherm at 205 °C of polymer A can be attributed to the Claisen rearrangement and the cross-linking of

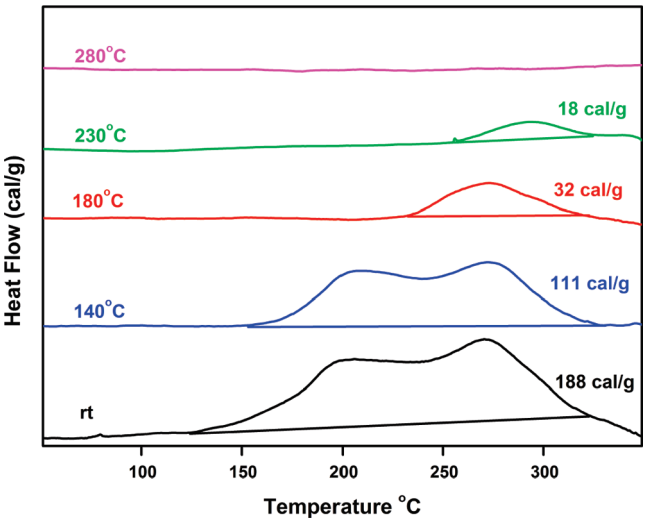



**Figure 3.** DSC thermograms of polymer A after curing at different temperatures.

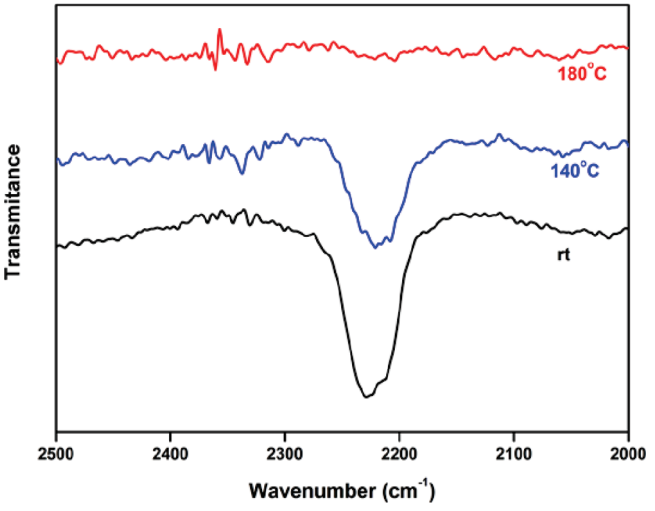



**Figure 4.** Disappearance of absorption band of C≡C bonds on polymer A after curing at 180 °C.

aryl propargyl ethers. This phenomenon is also reported by Agag et al. for benzoxazine monomers containing *p*-phenylpropargyl ethers. These monomers exhibited ring-opening and propargyl ether polymerization in the same temperature range in DSC analyses.[46] In addition to this phenomenon, it is known that three acetylene groups may readily form a benzene ring at elevated temperatures as an alternative cross-linking reaction, and the heat of this reaction can participate the exotherm of the curing. The uncatalyzed cyclotrimerization of propargyl ethers generally need higher temperatures above 220 °C; $Pd(PPh_3)_4Cl_2$ residues can also catalyze this reaction to lower the temperature of the reaction. However, in our case, it is rather difficult to provide direct evidence for such cyclotrimerization reaction, as the possible exotherm is probably shielded by that of the ring-opening reaction.

After each cure cycle of polymer A, the exotherm corresponding to curing of propargyl groups decreased constantly and disappeared after curing at 180 °C for 1 h (see Figure 3). This

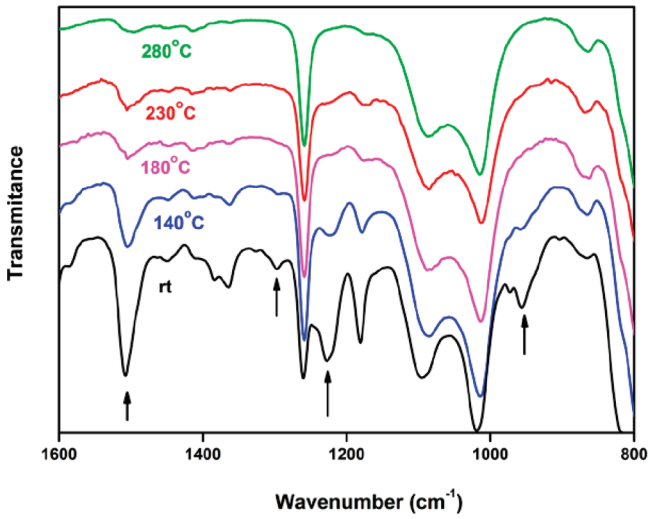



**Figure 5.** IR spectra of polymer A after curing at different temperatures.

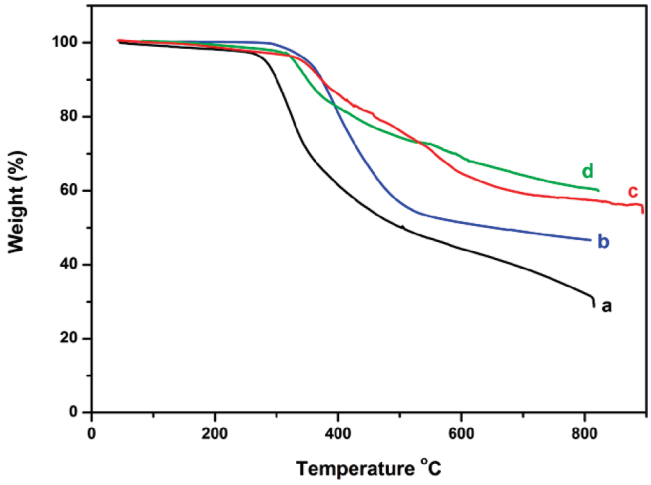



**Figure 6.** TGA thermogram of cured DIBB (a), DABB (b), polymer A (c), and polymer B (d).

issue was also monitored by the decreasing intensity and finally disappearing of C≡C band at 2225 $cm^{-1}$ in sequential FT-IR spectra in Figure 4. Moreover, in Figure 3, it is revealed that thermally induced ring-opening of benzoxazine moieties completely finished at 280 °C after 1 h curing, and these cycles were investigated by FT-IR, too. The IR spectrum taken at room temperature (Figure 5) presents the decreasing of the characteristic bands of benzoxazine at 1297, 1228, 956, and 1508 $cm^{-1}$. Disappearance of these absorptions after curing at 280 °C indicates that second exotherm belongs to ring-opening of benzoxazine moieties. Similar thermal behavior was also observed for the precursor polymer B (see Supporting Information for the DSC thermogram and FT-IR spectrum). It should be pointed out that, in this case, the polymerization of propargyl units through acetylene functionality takes place only by addition polymerization since the structure does not contain etheric groups.

Thermal stability of the polybenzoxazines was investigated by TGA under a nitrogen atmosphere. The TGA profiles of cured DIBB, DABB, polymer A, and polymer B are shown in Figure 6,


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**Table 2. Thermal Properties of the Cured DIBB, DABB, Polymer A, and Polymer B[a]**

| cured benzoxazine | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | $T_{max}$ (°C) | char % at 800 °C |
|---|---|---|---|---|
| DIBB | 283 | 300 | 320 | 32 |
| DABB | 350 | 372 | 405 | 47 |
| polymer A | 342 | 372 | 378, 555 | 58 |
| polymer B | 329 | 349 | 351, 591 | 61 |

[a] $T_{5\%}$: temperature for which the weight loss is 5%; $T_{10\%}$: temperature for which the weight loss is 10%; char %: char yields at 800 °C under a nitrogen atmosphere; $T_{max}$: temperature for maximum weight loss.

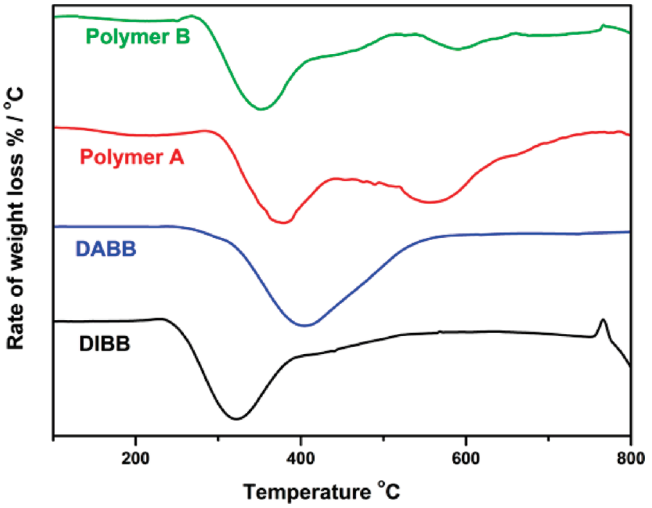


**Figure 7.** Rate of weight loss of cured polymer A, polymer B, DABB, and DIBB.

and the results are summarized in Table 2. The degradation temperatures $T_{5\%}$ and $T_{\%10}$ of cured polymer A are higher than those of polymer B, which can be possibly attributed to delayed Mannich base cleavage of the benzoxazine units. Polymer A degrades later than polymer B because its propargyl ether units prevent aniline derivatives from volatilizing as a degradation product by anchoring the aniline component through cross-linking.[47] Moreover, formed chromene groups may also contribute to the thermal stability. Hence, the higher acetylene ratio on polymer A causes the better avoidance of benzoxazine degradation compare to polymer B. Additionally, the difference of 13 °C of $T_{5\%}$ increases to 23 °C on polymers due to presence of more benzoxazine structure to degrade in a polymeric unit for polymer B. However, the weight lost becomes more significant on polymer A at ~500 °C, which corresponds to acetylenic unit degradation which is higher amount on polymer A. Finally, the char yield of polymer B at 800 °C is relatively higher than that of polymer A. Moreover, both cured polymer have comparable char yields to classical polybenzoxazines and cured DABB.

The degradation steps are presented in Figure 7 from the derivatives of the weight loss. The initial main degradation temperature ($T_{max}$) of polymer A is 27 °C higher than polymer B. This reflects the prevention of benzoxazine degradation is better on polymer A due to more acetylenic unit. In contrary, the final degradation temperature ($T_{max}$) that may correspond to acetylene is 36 °C higher on polymer B. Increased cross-linking density through additional benzoxazine units in every repeat unit of the polymer B can be an explanation for the observed enhancement in the thermal stability of polymer B other than polymer A.

## CONCLUSIONS

In conclusion, we have demonstrated that C≡C triple bonds containing benzoxazine moieties in the main chain can be prepared by Sonogashira coupling of aryl halide functional benzoxazine (DIBB) in the presence of $Pd(PPh_3)_4$ catalyst, a copper(I) cocatalyst (CuI), and an amine base (DIPA). It is clear that the process is selective, and it is possible to prepare polybenzoxazine precursors without affecting the benzoxazine moieties under polymerization conditions. Hence, the obtained polymers exhibit two different cross-linkable groups in the main chain. The benzoxazine groups were shown to readily undergo thermally activated ring-opening reaction in the absence of added catalyst and formed cross-linked networks. The polymers cured in this way exhibited comparable thermal stability to classical polybenzoxazines.

## ASSOCIATED CONTENT

**Supporting Information.** $^1$H NMR and FT-IR spectra and DSC traces for the monomers and polymer B. This material is available free of charge via the Internet http://pubs.acs.org.

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