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Synthesis of linear polymers containing benzoxazine moieties in the main chain with high molecular design versatility via click reaction

Andrey Chernykh, Tarek Agag, Hatsuo Ishida*

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

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ABSTRACT

Linear polymers with benzoxazine rings in the main chain have been synthesized applying click chemistry approach. These polymers possess molecular weights significantly higher than the benzoxazine polymers which have been chain extended via Mannich reaction. The number average molecular weight is estimated from size exclusion chromatography (SEC) to be between 20,000 and 40,000 Da. 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 crosslinking behavior of the polymers. The nature of the low temperature exotherm DSC peak observed in this work and the previous work of other authors is studied by model reactions. It is due to thermal coupling of the residual propargyl and azide end groups in the absence of active catalyst. In addition, a novel diazide-functional benzoxazine monomer has been prepared, showing a tremendous flexibility for applying click reaction to obtain various polymer architectures. Three types of polymers have been prepared from dipropargyl- and diazide-functional benzoxazine monomers. These polymers have been characterized by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

1. Introduction

Polybenzoxazines are very promising class of polymers whose properties favorably compare with epoxies, phenolics, bismaleimides, cyanate ester resins, and even polyimides. Several unique properties are observed, including near-zero shrinkage upon polymerization, low water absorption despite having hydrophilic groups, very high char yield, and fast development of properties at low conversion [1–7]. Furthermore, the flexibility in molecular design of polybenzoxazines is unmatched by any other resins. This allows designing of polybenzoxazine structures with a wide range of properties.

The current research trends on monomeric benzoxazine resins are mainly classified into three approaches, including blending or alloying with other polymers [8–11], reinforcing with inorganic particles or fibers [12–16], and designing of novel monomers with special properties [17–20]. Varieties of benzoxazine-based materials have been introduced using these approaches, showing a potential application as structural materials even for extreme environment.

A new concept of polymers containing benzoxazine moieties in the main chain has recently been developed, which leads benzoxazine technology to be much more versatile to tailor properties desired. These polymers can be processed into self-supporting flexible films. During this phase of processing, it behaves as a thermoplastic. The product prepared exhibits comparable mechanical and physical properties to ordinary thermoplastics. The product can then be partially or fully crosslinked by thermal treatment, adding typical advantages of thermosets. This novel approach is expected to expand the potential applications of polybenzoxazines into fields that low molecular weight cyclic benzoxazines cannot be used.

The first synthetic step towards this new class of materials was studied by Liu and Ishida [21,22]. Further detailed studies have recently been simultaneously reported by Takeichi et al. [23] and Ishida et al. [24] by applying polycondensation approach utilizing various diamines and bisphenols. This approach was effective in providing polybenzoxazines with unique characteristics such as high thermal stability, high T_g, and high mechanical flexibility due to the polymeric backbone. However, this approach does not allow achieving high molecular weight beyond 10,000 Da due to branching and side reactions. The condensation of aminophenols to afford polymer-containing benzoxazine in the main chain has also been reported [25]. Recently, a polyetherester containing benzoxazine units has been reported [26]. The resultant polymer showed molecular weight of ca. 34,000 Da; however, the aliphatic ether-ester groups have some drawbacks such as high water absorption and low thermal stability.

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* Corresponding author.
E-mail address: hxi3@cwru.edu (H. Ishida).

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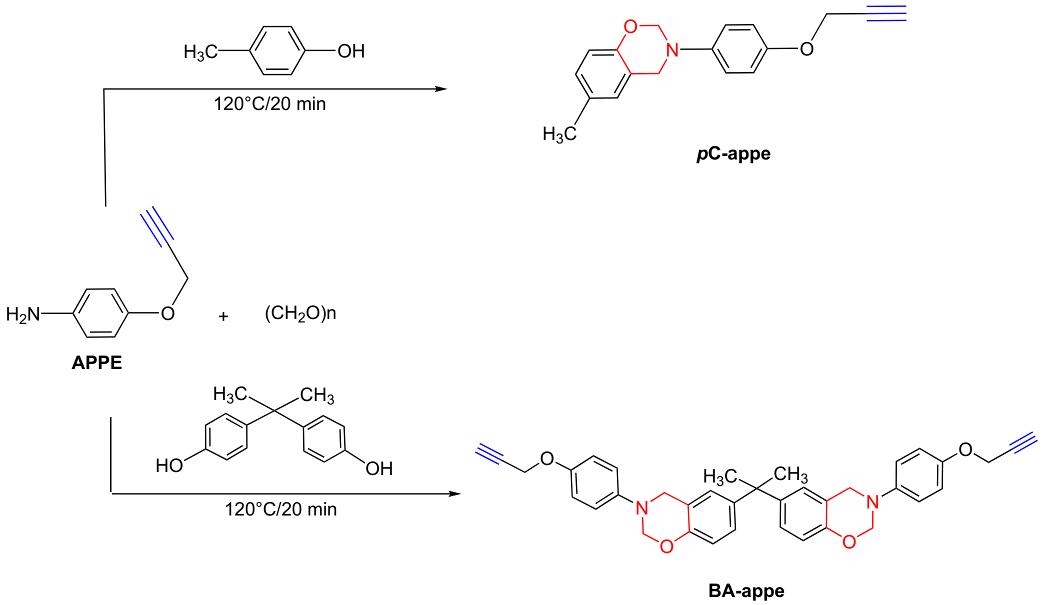


Scheme 1. Synthesis of *p*C-appe and BA-appe.

Applying different approaches in this direction would allow further increase in the molecular weight, which would lead to enhanced properties and additional potential applications. During the last several years, click chemistry has become very popular to design a variety of molecular architectures. In particular, the copper-catalyzed 1,3-dipolar cycloaddition of azides and alkynes has been intensively studied due to the number of obvious advantages. These advantages include low reaction temperature, simple and inexpensive catalyst, solvent tolerance, high selectivity, and quantitative yield of the reaction [27–29]. This method has been used as a tool for synthesizing a wide variety of linear, branched, and crosslinked polymers [30–33]. Recently, by utilizing the click reaction, polystyrene functionalized with benzoxazine has been reported as a new method for thermally curable polystyrene thermosets. It seems to be feasible to apply click reaction to prepare polymers containing benzoxazine moieties along with triazole rings that form in this reaction in the main chain [34]. The presence of thermally stable and corrosion inhibiting triazole ring in the polymer backbone will impart additional favorable characteristics to polybenzoxazine.

In this study, the preparation of linear high molecular weight polymers containing benzoxazine in the main chain was examined by applying click reaction by utilizing a novel azide-containing benzoxazine monomer. The novel monomer along with propargyl-containing benzoxazine was used for the preparation of polymers with various architectures. The structure and thermal properties of the polymers were characterized.

2. Experimental

2.1. Materials

Sodium azide, tetrabutylammonium bromide, copper iodide, and propargyl bromide were used as-received from Acros Organics. Bisphenol-A, 1,6-dibromohexane, *p*-cresol, paraformaldehyde, and 4-hydroxyphenethyl bromide were used as-received from Sigma–Aldrich. 4,4′-Diaminophenylenemethane was purchased from Johnson Matthey Catalog Company. Dimethylformamide (DMF), ethyl ether, toluene, ethyl acetate, chloroform, methylene chloride, and sodium hydroxide were obtained from Fisher. All chemicals were used as-received. Aminophenyl propargylether (APPE) was prepared following our reported method [35]. 1,6-Diazidohexane was prepared as reported elsewhere [36]. 1-Methyl-4-(prop-2-ynyloxy)benzene and 4,4′-(propane-2,2-diyl)bis((prop-2-ynyloxy)-benzene) were prepared according to the previously reported procedure [37].

2.2. 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. Polymer molecular weight was determined by size exclusion chromatography (SEC) using a Waters GPC system equipped with an 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. FTIR spectra were acquired with a resolution of 4 cm^{-1} on a Bomem Michelson MB100 equipped with a deuterated triglycine sulfide (DTGS) detector using KBr plates. Dynamic mechanical analysis was done

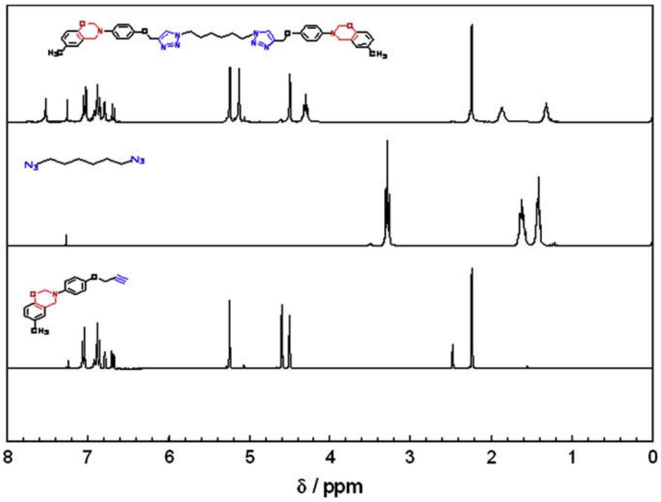
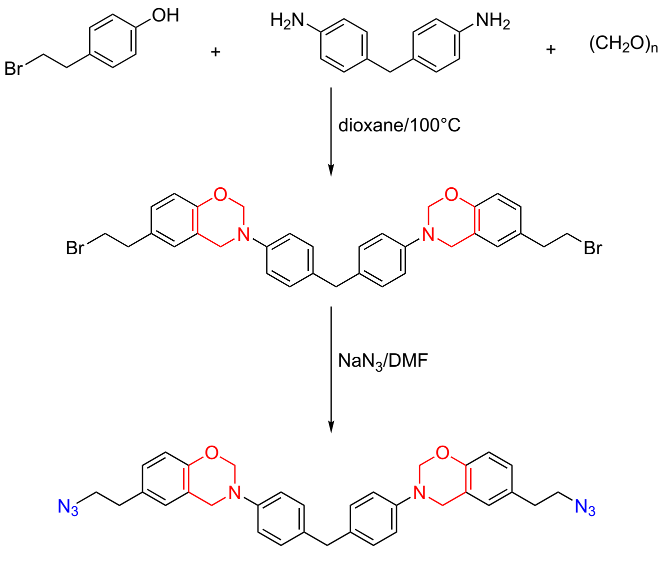


Fig. 1. ^{1}H NMR spectra of *p*C-appe (bottom), 1,6-diazidohexane (middle), and Model 1 (top).



EtAz-dapm

Scheme 2. Synthesis of EtAz-dapm.

on a TA Instruments Q800 DMA applying controlled strain tension mode with an amplitude of 10 μm, frequency of 1 Hz, and a temperature ramp rate of 3 °C/min. Thermogravimetric analysis was performed on a TA Instruments Q500 TGA with a heating rate of 10 °C/min in a nitrogen atmosphere.

*2.3. Preparation of 6-methyl-3-(4-(propargyloxy)phenyl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine (p*C*-appe)*

Into a 20 mL vial were mixed APPE (1.47 g, 10 mmol), *p*-cresol (1.08 g, 10 mmol), and paraformaldehyde (0.9 g, 30 mmol) together and heated 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 crystals with melting point 57 °C (2.29 g, 82%).

^{1}H NMR (CDCl$_3$), ppm: $\delta = 2.24$ (s, CH$_3$), 2.48 (t, ≡CH), 4.51 (s, CH$_2$, oxazine), 4.60 (d, CH$_2$), 5.25 (s, CH$_2$, oxazine), and 6.8–7.1 (7H, Ar).

^{13}C NMR (CDCl$_3$), ppm: $\delta = 51.00$ (Ar–C–N), 56.16 (O–C–C), 75.34 (C–C≡C), 78.76 (≡C), 80.44 (O–C–N).

FT-IR (KBr), cm^{-1}: 3285, 2120, 1327, 1225, 944.

*2.4. Preparation of 6,6′-(propane-2,2-diyl)bis(3-(4-(popargyloxy)-phenyl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine) (BA-appe)*

Into a 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 was further purified similar to *p*C-appe to afford a yellowish solid (4.23 g, 74%).

^{1}H NMR (CDCl$_3$), ppm: $\delta = 1.57$ (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: $\delta = 51.29$ (Ar–C–N), 56.15 (O–C–C), 75.36 (C–C≡C), 78.77 (≡C), 80.09 (O–C–N).

FT-IR (KBr), cm^{-1}: 3286, 2120, 1327, 1231, 943.

*2.5. Preparation of bis(4-(6-(2-bromoethyl)-2*H*-benzo[*e*][1,3]-oxazin-3(4*H*)-yl)phenyl)methane (EtBr–dapm)*

Into a 100 mL round-bottomed flask were mixed 4-hydroxyphenethyl bromide (4.02 g, 20 mmol), 4,4′-diaminophenylenemethane (1.98 g, 10 mmol) and paraformaldehyde (1.2 g, 40 mmol) in 25 mL of chloroform. The solution was refluxed for 8 h, followed by washing 2 times with 1 N aqueous NaOH solution and 2 times with water. The solution was dried over sodium sulfate anhydrous, followed by evaporation of chloroform under vacuum to afford yellowish solid (4.34 g, 67%).

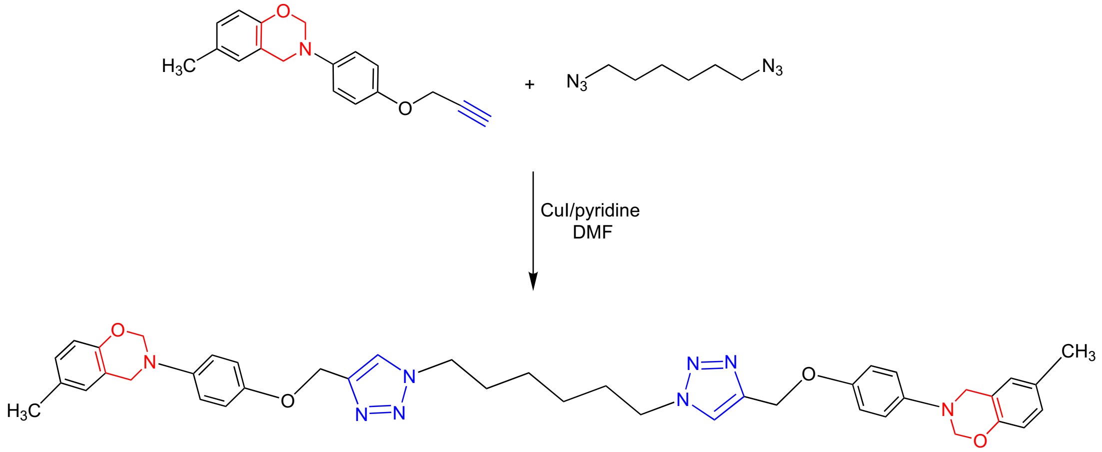
^{1}H NMR (CDCl$_3$), ppm: $\delta = 3.04$ (t, CH$_2$), 3.49 (t, CH$_2$), 3.79 (s, CH$_2$), 4.57 (s, CH$_2$, oxazine), 5.30 (s, CH$_2$, oxazine), and 6.7–7.1 (14H, Ar).

^{13}C NMR (CDCl$_3$), ppm: $\delta = 33.22$ (C–C–Br), 38.68 (Ar–C–C), 50.56 (Ar–C–N), 79.67 (O–C–N).

FT-IR (KBr), cm^{-1}: 1332, 1230, 944, 559.

*2.6. Preparation of bis(4-(6-(2-azidoethyl)-2*H*-benzo[*e*][1,3]-oxazin-3(4*H*)-yl)phenyl)methane (EtAz–dapm)*

Into a 30 mL vial was dissolved EtBr–dapm (3.24 g, 5 mmol) in 15 mL of DMF, followed by adding sodium azide (0.975 g, 15 mmol). The mixture was stirred for 10 h at 60 °C. The solution was poured into 60 mL of water, followed by extraction with ethyl acetate



Model 1

Scheme 3. Synthesis of Model 1.

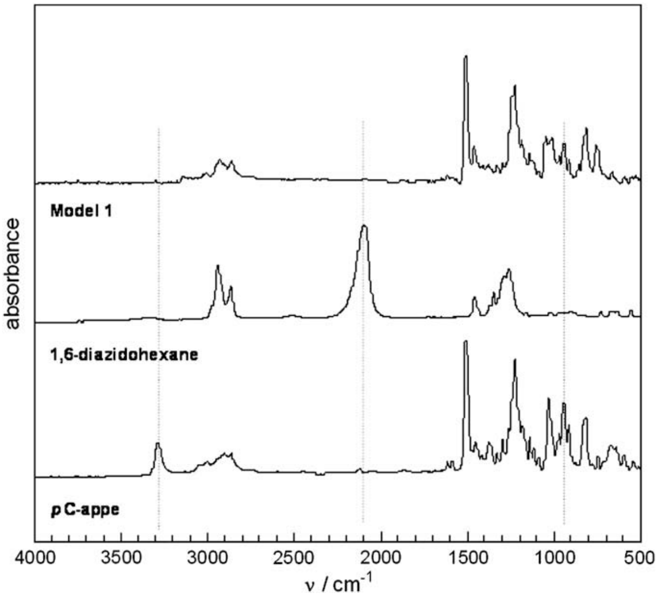


Fig. 2. FTIR spectra of *p*C-appe, 1,6-diazidohexane, and Model 1.

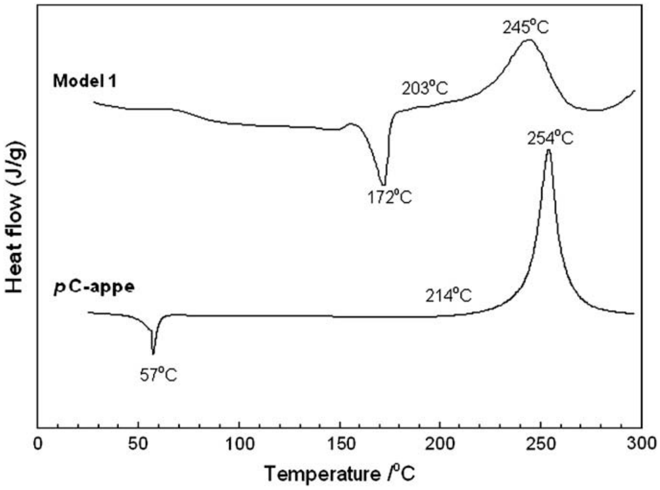


Fig. 3. DSC thermograms of *p*C-appe and Model 1.

(2 × 15 mL) and washing the ethyl acetate solution by water (2 × 20 mL). The solvent was evaporated under vacuum and the product was recrystallized from ethanol to give pale beige powder (2.18 g, 76%).

^{1}H NMR ($CDCl_3$), ppm: $\delta = 2.77$ (t, CH_2), 3.44 (t, CH_2), 3.79 (s, CH_2), 4.56 (s, CH_2, oxazine), 5.30 (s, CH_2, oxazine), and 6.7–7.1 (14H, Ar).

^{13}C NMR ($CDCl_3$), ppm: $\delta = 34.53$ (Ar–C–C), 50.52 (Ar–C–N), 52.55 (C–C–N_3), 79.70 (O–C–N).

FT-IR (KBr), cm^{-1}: 2098, 1332, 1228, 945.

2.7. *Preparation of 1,6-bis(4-((4-(6-methyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)phenoxy)methyl)-1H-1,2,3-triazol-1-yl)hexane (Model 1)*

Into a 20 mL vial were dissolved pC-appe (1.116 g, 4 mmol) and 1,6-diazidohexane (0.336 g, 2 mmol) in 2 mL of DMF. To the solution, copper iodide (38 mg, 5 mol%) and 0.5 mL of pyridine were added. The mixture was stirred at room temperature for 6 h. The mixture was poured into water and extracted with methylene chloride. The solvent, after drying over sodium sulfate anhydrous, was evaporated under vacuum to afford a solid residue which was washed with ethanol to give a beige powder (1.40 g, 96%).

^{1}H NMR ($CDCl_3$), ppm: $\delta = 1.32$ (m, CH_2), 1.87 (m, CH_2), 2.24 (s, CH_3), 4.30 (t, CH_2), 4.51 (s, CH_2, oxazine), 5.13 (s, CH_2), 5.25 (s, CH_2, oxazine), 6.7–7.1 (7H, Ar), and 7.54 (s, $=$CH).

^{13}C NMR ($CDCl_3$), ppm: $\delta = 50.98$ (Ar–C–N, oxazine), 80.50 (O–C–N, oxazine), 120.55 (C$=$C–N, triazol), 142.88 (N–C$=$C, triazol).

FT-IR (KBr), cm^{-1}: 3250 (br), 1327, 1226, 1049, 944.

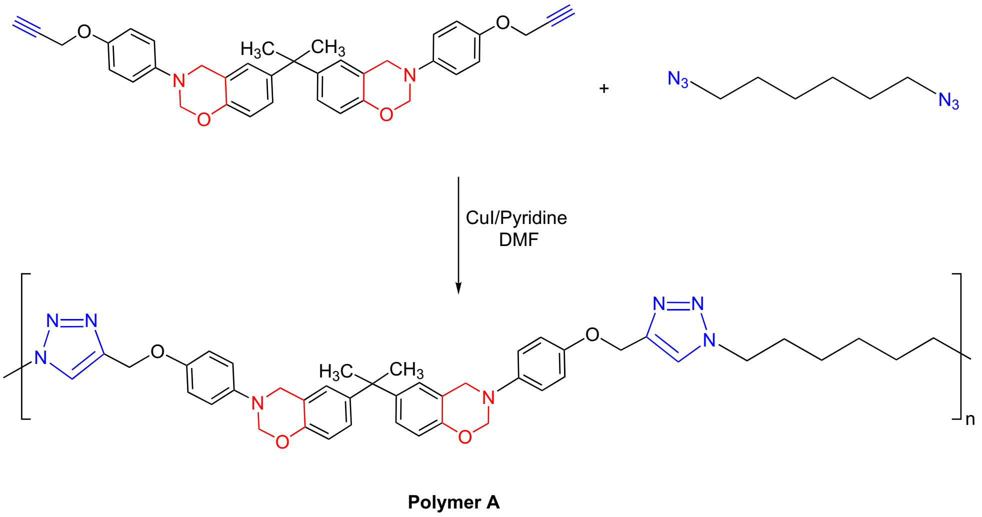
2.8. *Preparation of polymers*

2.8.1. *Polymer A*

Into a 20 mL vial were dissolved 1,6-diazidohexane (0.168 g, 1 mmol) and BA-appe (0.571 g, 1 mmol) in 4 mL of DMF. To the solution, copper iodide (20 mg, 5 mol%) and 1 mL of pyridine were added. After stirring for 16 h at room temperature, the mixture was poured into water and extracted with methylene chloride. The resultant polymer was precipitated by pouring methylene chloride solution into ethyl ether to afford a beige powder.

^{1}H NMR ($CDCl_3$), ppm: $\delta = 1.30$ (4H, CH_2), 1.57 (6H, CH_3), 1.85 (4H, CH_2), 4.28 (4H, CH_2), 4.48 (4H, CH_2, oxazine), 5.12 (4H, CH_2), 5.23 (4H, CH_2, oxazine), 6.6–7.0 (14H, Ar), and 7.54 (2H, $=$CH).

FT-IR (KBr), cm^{-1}: 3250 (br), 1327, 1232, 1050, 943.



Scheme 4. Synthesis of Polymer A.

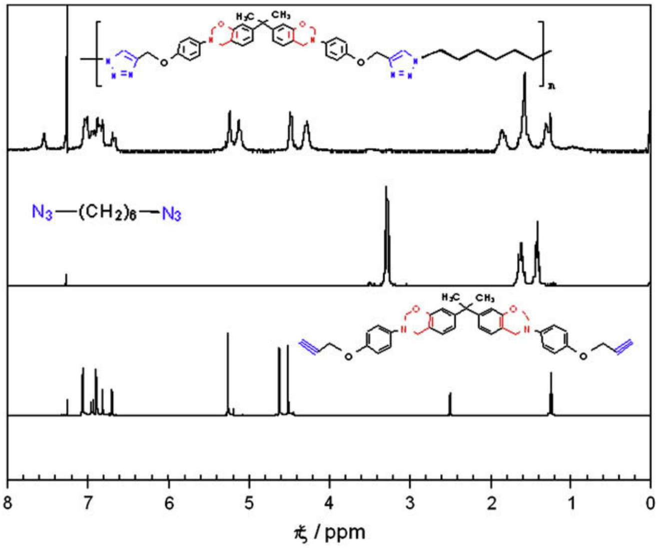


Fig. 4. ^{1}H NMR spectra of BA-appe (bottom), 1,6-diazidohexane (middle), and Polymer A (top).

2.8.2. Polymer B

Polymer B was synthesized from 4,4′-(propane-2,2-diyl)bis((prop-2-ynyloxy)benzene) and EtAz–dapm monomers in a manner similar to Polymer A.

^{1}H NMR ($CDCl_3$), ppm: $\delta = 1.60$ (6H, CH_3), 3.04 (4H, CH_2), 3.72 (2H, CH_2), 4.46 (4H, CH_2), 4.46 (4H, CH_2, oxazine), 5.09 (4H, CH_2), 5.25 (4H, CH_2, oxazine), 6.6–7.1 (22H, Ar), and 7.54 (2H, =CH).

FT-IR (KBr), cm^{-1}: 3250 (br), 1333, 1233, 1050, 944.

2.8.3. Polymer C

Polymer C was synthesized from BA-appe and EtAz–dapm monomers similar to Polymer A.

^{1}H NMR ($CDCl_3$), ppm: $\delta = 1.56$ (6H, CH3), 3.03 (4H, CH_2), 3.73 (2H, CH_2), 4.44 (4H, CH_2), 4.44 (8H, CH_2, oxazine), 5.05 (4H, CH_2), 5.20 (4H, CH_2, oxazine), 5.23 (4H, CH_2, oxazine), 6.6–7.1 (28H, Ar), and 7.54 (2H, =CH).

FT-IR (KBr), cm^{-1}: 3250 (br), 1329, 1232, 1051, 944.

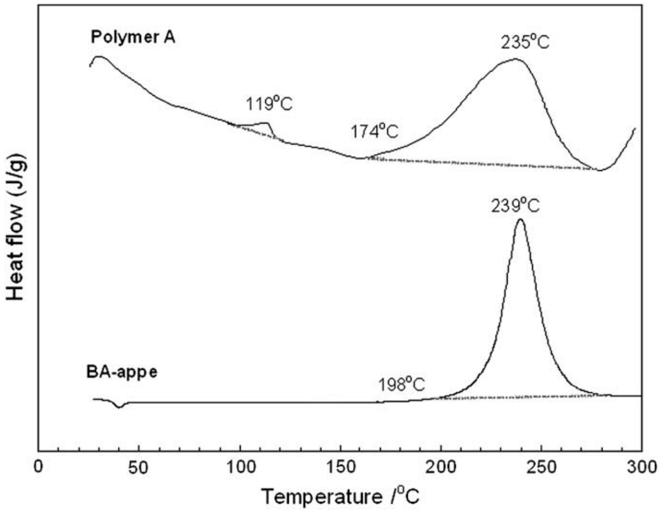


Fig. 5. DSC thermograms of BA-appe and Polymer A.

3. Results and discussion

3.1. Synthesis of monomer

Two monomers of propargyl-functional benzoxazines were prepared by modifying the reported method [35], following Scheme 1. The two monomers were designated as *p*C-appe and BA-appe.

The structure of the monomers was confirmed by ^{1}H and ^{13}C NMR and IR. ^{1}H NMR spectrum of pC-appe shown in Fig. 1a indicates the presence of propargyl group (triplet at 2.48 ppm) and benzoxazine structure (4.51 and 5.25 ppm). IR bands at 3285 and 944 cm^{-1} support the existence of propargyl and benzoxazine moieties, respectively. In addition, a novel azido-functional benzoxazine was prepared through two-step synthesis. Initially, dibromoethyl-terminated benzoxazine monomer was prepared from diaminophenylenemethane, 4-hydroxyphenethyl bromide, and paraformaldehyde in a solvent. Thereafter, the monomer was transformed into an azide-functional material using sodium azide and dimethylformamide (DMF) using a conventional method for aryl azide synthesis [35]. The monomer was designated as EtAz–dapm (Scheme 2).

NMR and FTIR results showed that benzoxazine ring remained intact in harsh conditions of azidation reaction. The NMR spectrum indicates the presence of typical benzoxazine resonances at 4.56 and 5.30 ppm and no signs of benzoxazine ring opening. Additionally, the FTIR spectrum shows the typical, characteristic azide band at 2098 cm^{-1}, confirming the transformation of bromide into azide.

3.2. Synthesis of model compound

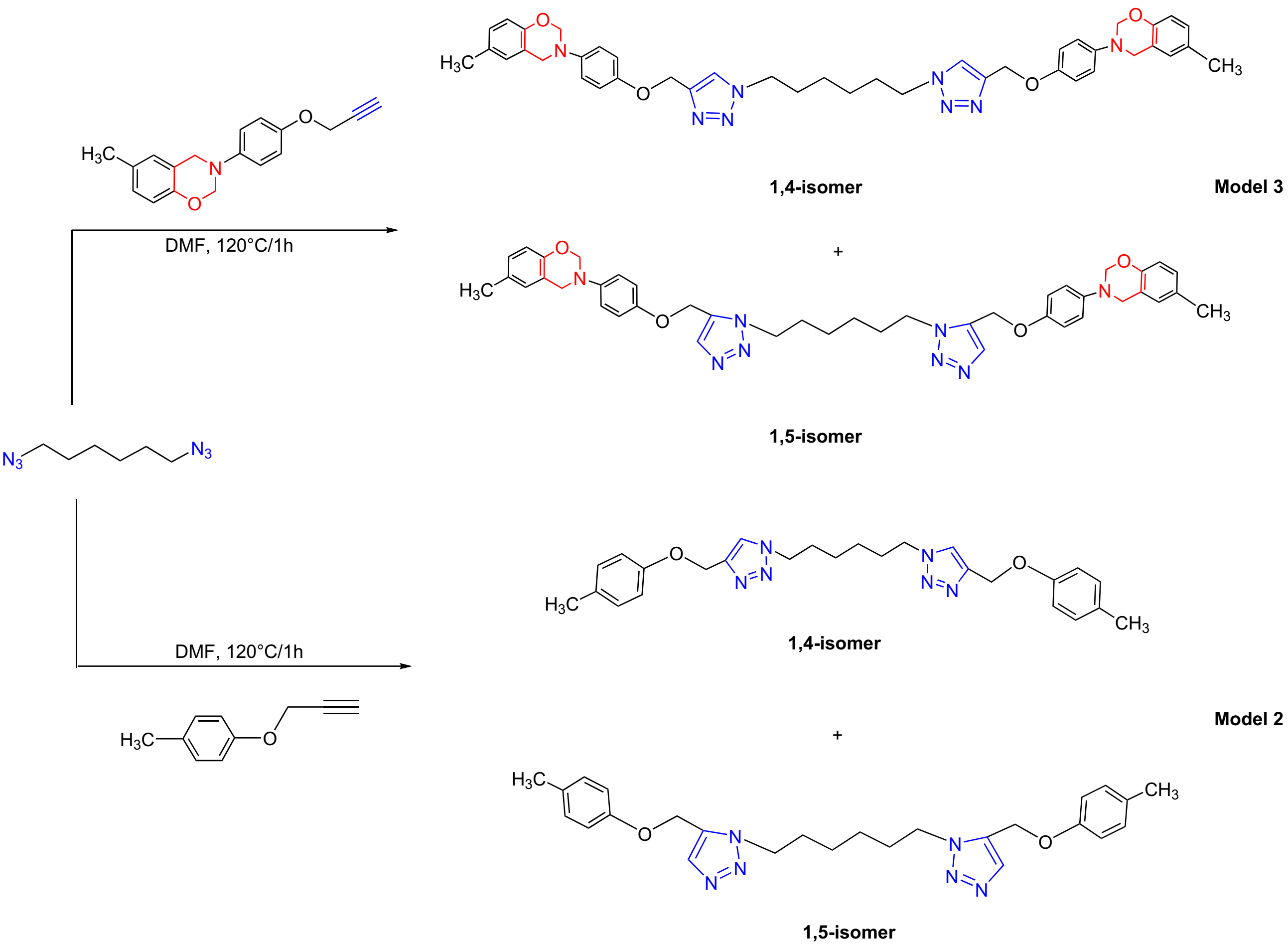
To understand click reaction in the presence of cyclic benzoxazine structure, a model compound was synthesized from monofunctional propargyl-functional benzoxazine (*p*C-appe) and 1,6-diazidohexane as shown in Scheme 3. The model reaction was carried out using 5 mol% CuI catalyst in DMF/pyridine (8:2 v/v) mixture bubbled with nitrogen. The reaction was followed by NMR, which showed that the reaction was completed after about 6 h. The product was designated as Model 1. The ^{1}H NMR spectrum of this compound shows a characteristic resonance of triazol at 7.54 ppm (=CH–) and the shift of propargyl moiety methylene peak at 5.13 ppm (Fig. 1c). The structure was further confirmed by FTIR which shows the complete disappearance of bands corresponding to propargyl (3285 cm^{-1}) and azide (2095 cm^{-1}) groups, respectively, after the reaction (Fig. 2). Also present is the typical absorption at 944 cm^{-1} attributed to the benzene ring mode of the benzoxazine group. Both NMR and IR spectra indicate that cyclic benzoxazine structure remains intact during the reaction, confirming the stability of benzoxazine at the click reaction conditions.

The effect of the presence of triazol ring on the ring opening of cyclic benzoxazine was studied by DSC. Model 1 exhibits an exothermic peak with onset at 203 °C and maximum at 245 °C which is attributed to benzoxazine polymerization. This suggests that benzoxazine cure behavior is similar to that of typical benzoxazine monomers [38].

3.2.1. Synthesis of polymers

The first polymer was synthesized by condensation polymerization of 1,6-diazidohexane and BA-appe, following Scheme 4 and is given the name Polymer A.

The reactions were carried out for 16 h until significant increase in solution viscosity was observed. The NMR spectrum presented in Fig. 4 shows characteristic resonances at 5.12 and 7.54 ppm due to triazole formation, which are analogous to those of the model compound. This suggests the formation of the corresponding



Scheme 5. Preparation of Models 2 and 3 via thermal coupling.

polymer. Also, the typical resonances due to benzoxazine structure appeared at 4.48 and 5.23 ppm, confirming that cyclic benzoxazine structure remains intact during the polymer formation reaction.

The ring opening behavior of cyclic benzoxazine structure in the main chain was studied by DSC. The typical benzoxazine polymerization exothermic peak with onset at 174 °C and maximum at 235 °C appeared on the thermogram shown in Fig. 5. In addition to this exotherm, the thermogram shows an interesting feature of low temperature exothermic peak with maximum at 119 °C (Fig. 5). This low temperature exothermic peak was also observed by Yagci et al. [34]; however, no explanation was given for this exotherm. At the same time, DSC polymerization of the model compound shown in Fig. 3 does not possess this feature. This phenomenon might be attributed to the contribution from the end groups of the polymer.

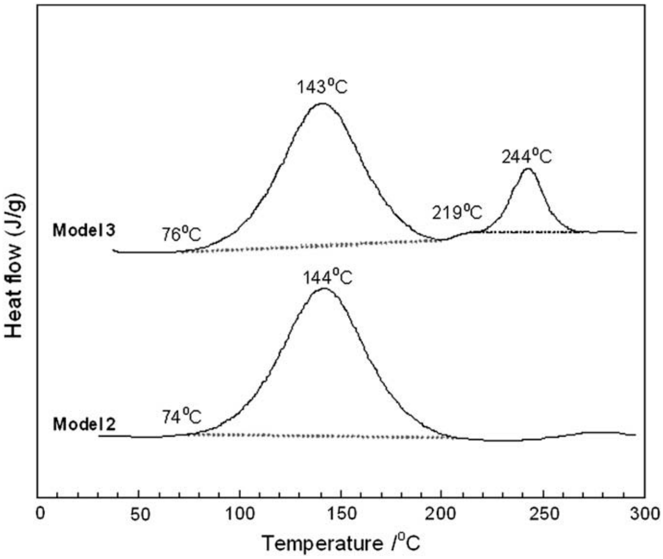


Fig. 6. DSC profiles of Models 2 and 3 formation.

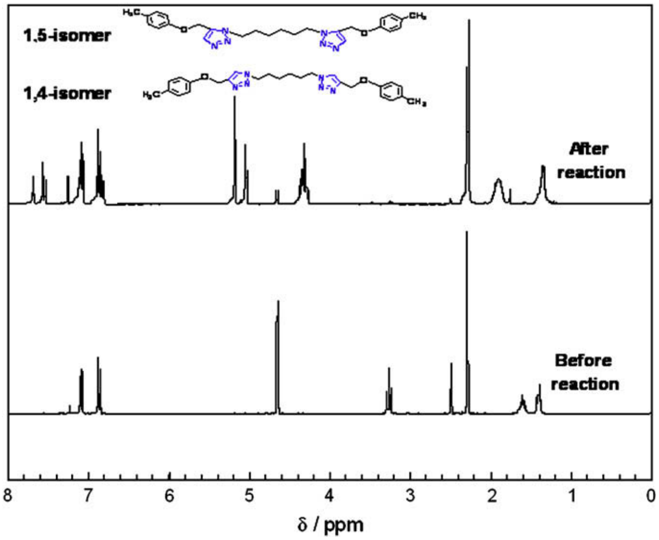
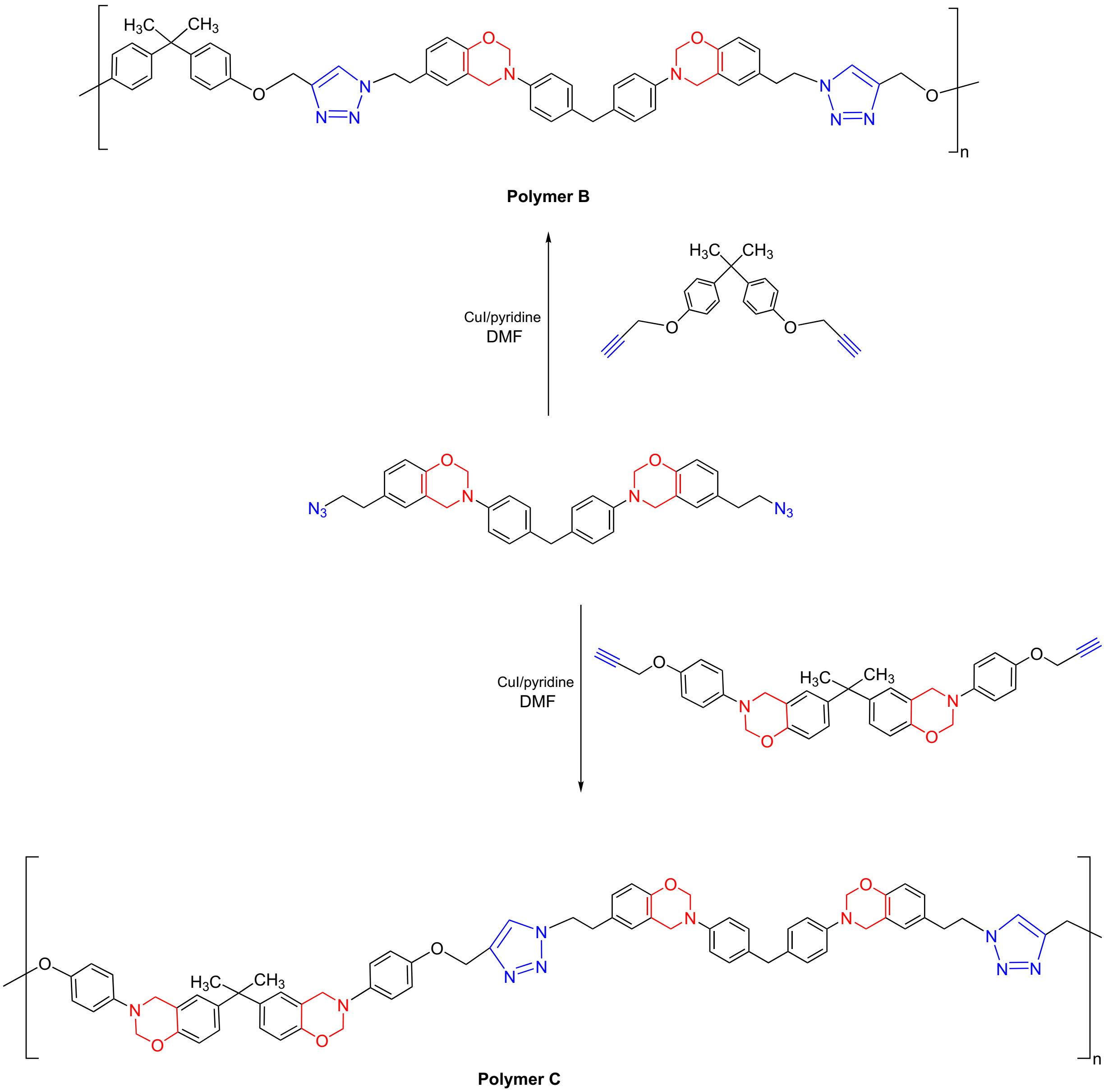


Fig. 7. ^{1}H NMR spectra of 1-methyl-4-(prop-2-ynyloxy)benzene and 1,6-diazidohexane mixture before and after reaction (Model 2).



Scheme 6. Synthesis of Polymers B and C.

To understand the reason of this first exotherm, two model reactions were performed. The model compounds, namely Models 2 and 3, were obtained via thermal coupling of 1,6-diazidohexane with both 1-methyl-4-(prop-2-ynyloxy)benzene and *p*C-appe, respectively, in the absence of a copper catalyst as shown in Scheme 5.

The thermal coupling of the mixture was firstly followed by DSC and the thermogram is shown in Fig. 6. The DSC thermogram clearly exhibits a very strong symmetric exotherm with maximum at 144 °C. This behavior was observed for both model compounds. The DSC thermogram for Model 3 also shows that the typical benzoxazine polymerization peak does not interfere with coupling reaction, suggesting the possibility of carrying out such thermal coupling at higher temperature keeping benzoxazine groups intact.

Based on the DSC results, the thermal coupling reaction was performed at 120 °C in the absence of solvent and catalyst. The reaction was followed by NMR and the spectrum is shown in Fig. 7. The resonances appeared at 7.55 and 7.67 ppm are attributed to the 1,4- and 1,5-triazole structure formation due to the thermal coupling. This result supports our early contention that the low temperature exotherm is due to the thermal coupling of the residual propargyl and azide end groups.

Additional types of polymers that contain benzoxazine in the main chain were prepared to demonstrate the molecular design flexibility by applying the click reaction. The polymers were synthesized similar to Polymer A via the coupling of EtAz–dapm with BA-prg and BA-appe following Scheme 6, and were designated as Polymers B and C, respectively.

DSC thermograms for these polymers shown in Figs. 8 and 9 possess aforementioned similar features to that of Polymer A.

The molecular weight of polymers was evaluated using SEC and the results are summarized in Table 1. The number average molecular weights (M_n) of the polymers were 26,000, 32,500 and 480,00 for Polymers A, B and C, respectively. To the authors' knowledge, this is one of the largest molecular weight ever reported on polymers containing Mannich base. This indicates that the click reaction is a useful tool to obtain higher molecular weight polymers containing benzoxazine in the main chain in comparison to our previous studies [21–25].

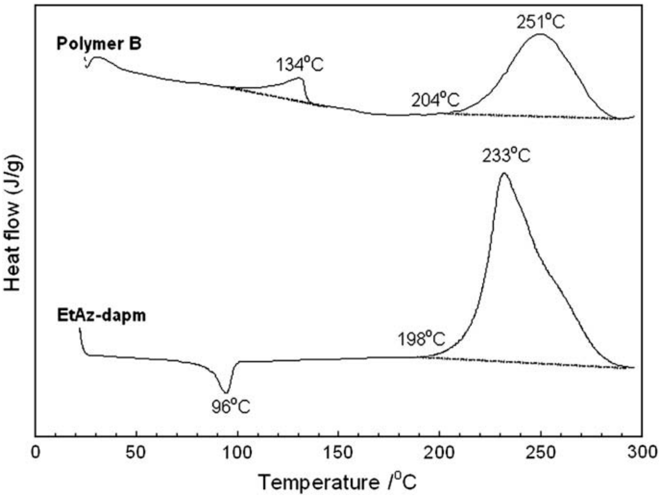


Fig. 8. DSC thermograms of EtAz–dapm and Polymer B.

To monitor the crosslinking behaviors of these polymers, self-supporting films were cast and polymerized stepwise up to 240 °C for 30 min. The reaction was followed by IR spectra shown in Fig. 10 which indicate that the bands at 1333, 1233 and 944 cm^{-1} which are related to cyclic benzoxazine structure have almost disappeared, while triazol ring absorption at 1050 cm^{-1} remained intact even after postcuring at 240 °C.

3.2.2. Thermal properties of polymers

The dynamic mechanical analysis was performed by multi-frequency strain test. The samples for testing were prepared by casting films from DMF solution and curing them for 1 h at 150 °C and 1 h at 200 °C, Polymers B and C were also postcured for 30 min at 240 °C. The storage and loss moduli temperature dependence curves are shown in Fig. 12. A very weak transition is observed around 150 °C. This is most probably not from any kind of chemical reaction since the samples were thermally treated at much higher temperatures. It has been reported that a polybenzoxazine derived from an ordinary monomeric difunctional benzoxazine resin based on bisphenol-A and aniline (BA-a) shows β-transition around 90 °C while the corresponding T_g is 170 °C [7]. As the T_gs of the current polymers studied are much higher than poly(BA-a), it is possible that the transition observed at 150 °C is due to the β-transition. The lower glass transition temperature (T_g) for Polymer A (210 °C) than the other two polymers is due to the presence of aliphatic segment in the structure and the absence of postcuring stage to avoid any decomposition. The T_gs for Polymer B and Polymer C were observed at 239 °C and 278 °C, respectively. The higher T_g for Polymer C is attributed to the presence of more benzoxazine groups per monomer unit, leading to a higher crosslink density.

Table 1
SEC data for Polymers A, B, and C.

	M_n	M_w	M_w/M_n	DP
Polymer A	25,900	49,200	1.9	35
Polymer B	32,600	61,900	1.9	37
Polymer C	47,900	100,600	2.1	41

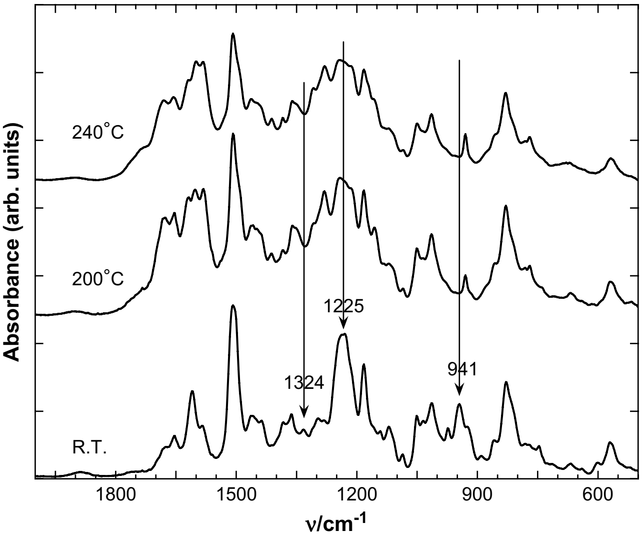


Fig. 10. FTIR spectra of Polymer B after different cure stages.

The thermal stability of the polymers was evaluated by TGA under nitrogen. TGA thermograms are shown in Fig. 11. The 5 and 10% weight loss temperatures (designated as T_{d5} and T_{d10}) are almost the same for Polymers A (324 and 348 °C) and B (323 and 347 °C) and slightly higher for Polymer C (331 and 359 °C) which can be attributed to the higher crosslinking density due to increased amount of benzoxazine groups. The char yield, as defined as the weight residue remaining at 800 °C under inert atmosphere,

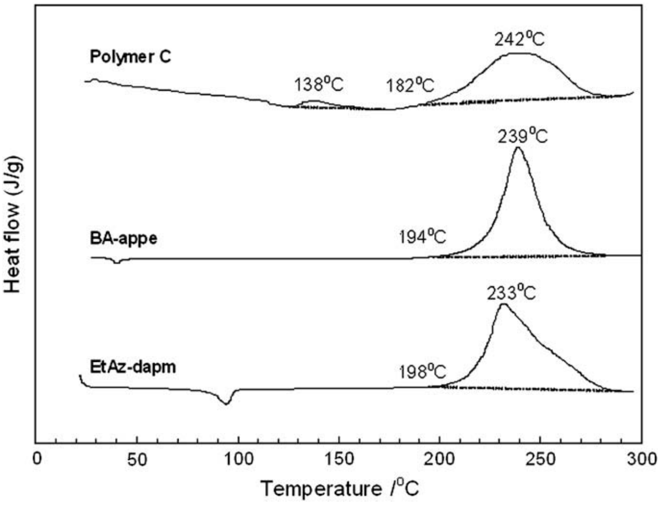


Fig. 9. DSC thermograms of EtAz–dapm, Ba-appe, and Polymer C.

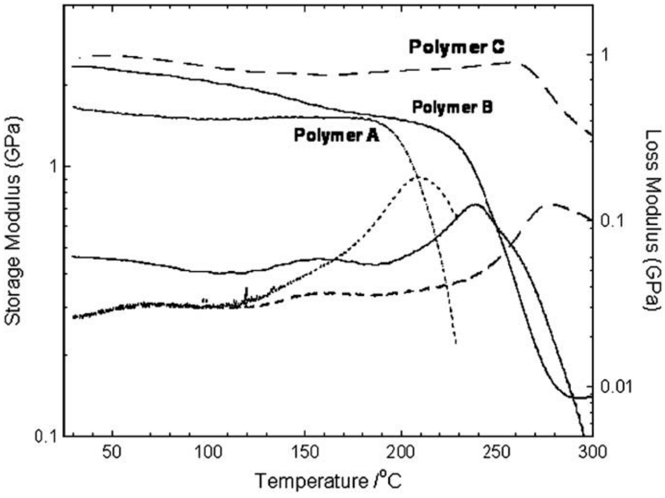


Fig. 11. DMA curves of storage and loss moduli for Polymers A, B, and C.

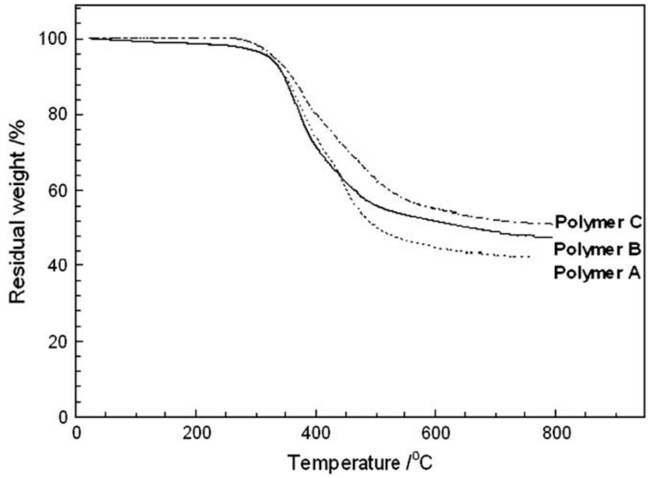


Fig. 12. TGA thermograms of Polymers A, B, and C.

for Polymer A (42%) is the lowest among all three polymers which can be explained by the presence of aliphatic segment in the backbone structure. And the char yield for Polymer C (51%) is the highest due to increased crosslinking density. This result indicates that applying click reaction afforded polymers with higher thermal stability than have been achieved in our previous work [23,24].

4. Conclusions

Linear benzoxazine containing polymers were successfully synthesized through click reaction. Two different structural approaches (azido- and propargyl-functional benzoxazines) reported in this paper offer an outstanding flexibility in future molecular design of benzoxazine containing polymers with high molecular weights. NMR and FTIR spectroscopies were used to confirm the structures of resultant polymers. DSC study showed interesting thermal behavior which was explained by the study of model reactions. The three polymers studied all showed high thermal performance exhibiting T_gs ranging from 210 °C to 278 °C. This is the first work which studies the synthesis of polymers containing benzoxazine in the main chain via click chemistry approach using variety of molecular architectures.

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