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Synthesis and thermal characterization of polybenzoxazines based on acetylene-functional monomers

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Abstract

The high thermal stability of this class of polybenzoxazines is a combined result of polymerization of acetylene terminal functional group and oxazine ring-opening polymerization. The high char yield achieved for this class of materials is in the range of 71–81% by weight at 800°C in a nitrogen atmosphere and 30% by weight at 700°C in air as it is determined by thermogravimetric analysis (TGA). Temperature at 10% weight loss ($T_{10\%}$) is in the range of 520–600°C. The polymerization and post-cure reactions of these benzoxazines are studied by differential scanning calorimetry (DSC). The char formation of the blend of an acetylene-functional benzoxazine with an analogous benzoxazine without acetylene group is also studied by TGA. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polybenzoxazine; Acetylene-functional polymer; Phenolic resin

1. Introduction

When an organic polymer is subjected to heat, it undergoes primary decomposition in the typical range of 350–550°C which produces primary char, and hydrogen-enriched volatile fragments at the polymer surface. The volatiles diffuse to the flame front and are oxidized, generating heat [1]. This heat helps further pyrolysis by carbonizing primary char into final char at temperatures above 550°C and this second pyrolysis terminates in the range of 800–1000°C [2]. This cycle can be inhibited by heat sinks, non-combustible gases, free radical acceptors, and protective liquid or char barriers. The char barrier minimizes the exposure of degradation products to the flame front and, at the same time, acts as an insulating layer which reduces heat transfer from the flame to the polymer surface [3].

Phenolic resins have been used for many years in various applications mainly because of their low flammability and relatively high char yield despite their problematic brittleness, use of strong catalyst for polymerization, and volatiles generated as a result of the condensation reaction [4,5]. To further decrease flammability, phenolic resins have been modified through esterification with boric or phosphoric acid or additives used with halogen containing compounds which release toxic gases during combustion [6]. However, with the recent development of polybenzoxazines, it is possible to synthesize inherently non-flammable materials exhibiting high char yield, superior mechanical properties and excellent processibility through molecular design, without sacrificing the advantage of conventional phenolic resins. Benzoxazines are synthesized via Mannich condensation of phenol, formaldehyde and primary amine and polymerized by ring-opening polymerization with no reaction byproducts released and no catalyst required [7–11]. The mechanism of benzoxazine ring-opening polymerization was proposed to occur via an iminium ion as an intermediate [12]. Further proposed was an ionic ring-opening mechanism coupled with the chain transfer growth step [13]. The conversion and reaction rate of polymerization of the purified monomer and as-synthesized precursors under isothermal conditions have been studied [14].

The purpose of this article is to describe the synthesis of easily processable benzoxazine monomers with an additional polymerizable side functional group, acetylene. The effect of thermal polymerization of the acetylene functional group together with the oxazine ring-opening polymerization on thermal stability and char yield, is also studied.

Much effort has been made researching thermally curable acetylene-containing materials (acetylene-terminated

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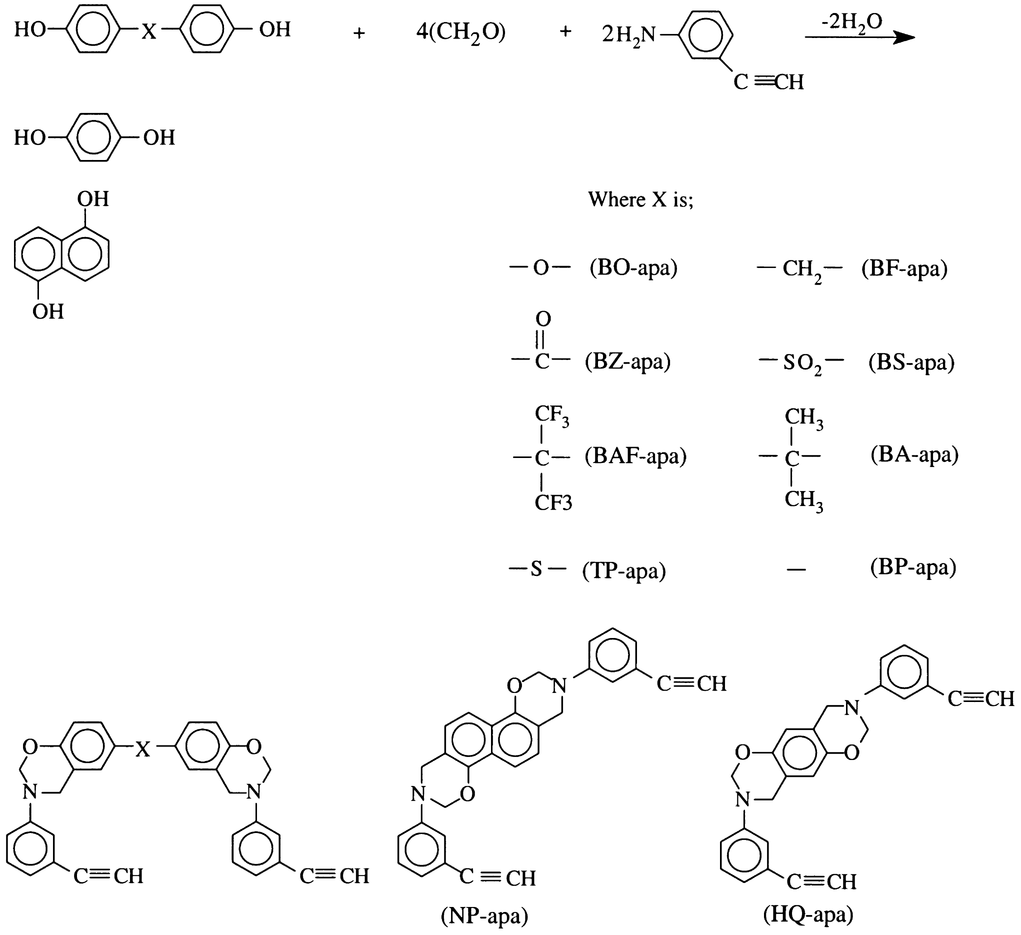
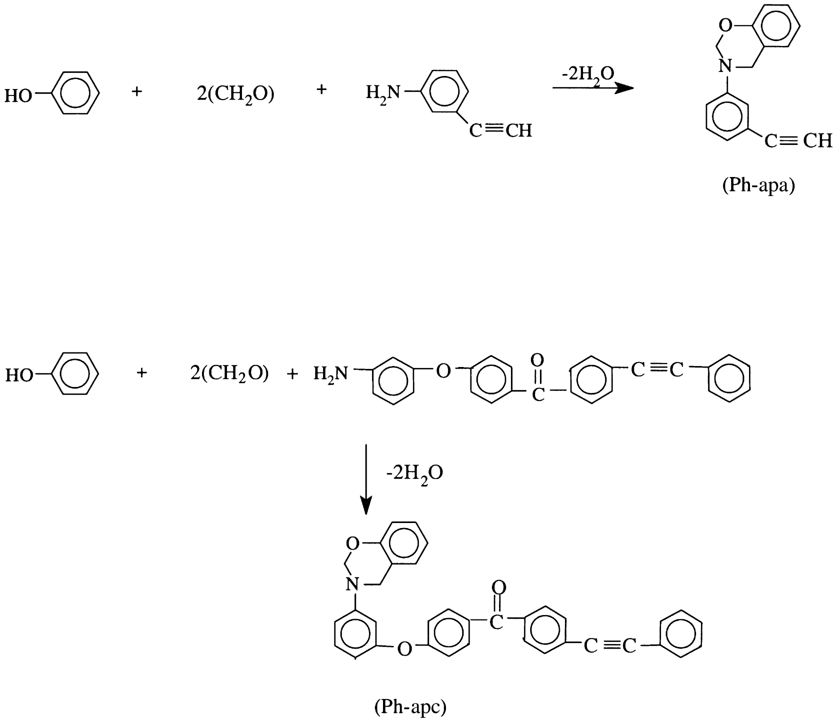


Scheme 1.

pre-polymers) because oligomers and polymers containing an acetylenic group can be polymerized under moderate conditions without the evolution of volatiles. The polymer provides many desirable properties, such as solvent resistance, moisture resistance, and good physical properties as well as high thermal stability, which makes an acetylene containing material a good candidate of matrix resin for advanced composite materials. The acetylenic group can react under cationic, coordination, free radical, photolytic and thermal inducement. The thermally induced reaction of the acetylenic group leads to chain extension, branching, or cross-linking of the polymer [15]. The products from the thermal polymerization of model diethynyl compounds show many reaction paths: forming polyenes from Strauss coupling, Diels-Alder products, trimers, tetramers, naphtalenes or conjugated polyenes [16]. An acetylene terminated imide shows that 30% of its acetylenic group undergoes trimerization, and other addition reactions consume the remainder [17].

Thermal polymerization of 4,4′-diethynyldiphenylmethane leads to a linear polymer via first order kinetics, however, during early stages of the reaction, a second, more rapid polymerization mechanism is evident. This is a formation of the cyclic trimer, which is kinetically favored but sterically prohibited as the cross-linked network grows [18]. Highly thermally stable materials can be prepared from acetylene terminated polyphenylenes that have char yields of 90% by weight at 800°C tested in the nitrogen atmosphere. However, this material is difficult to process. The char yield of the acetylene terminated polyisophthalimides is around 50–60% by weight in nitrogen at 700°C [19]. An acetylene terminated Schiff base monomer was synthesized and polymerized [20]. This polymer exhibits a high char yield of 77% by weight in nitrogen at 800°C. However, the thermo-oxidative stability is relatively poor as no char remains at 400°C in air. The thermal stability of acetylene terminated sulfone resin was also investigated and the resulting char yield at 800°C under a helium atmosphere was 65 wt.% [21]. High char yield, ease of processibility, and lower pyrolysis shrinkage are observed for polyarylacetylenes as highly-crosslinked aromatic polymers derived from the polymerization of diethynylbenzene. Typically, a pre-polymer is formed first by cyclotrimerization of diethynylbenzene using a nickel catalyst. This cyclotrimerization step liberates much of the exothermic heat of polymerization and allows controllable, safe curing [18].



Scheme 2.

2. Experimental

All chemicals were used as received. 4,4′-Isopropylene-diphenol (99%) (bisphenol-A), 4,4′-dihydroxybenzosulfone (98%) (bisphenol-S), phenol (99.9%), 2,7-dihydroxy-naphtalene (98%), 4,4’-thiodiphenol (99%) and para-formaldehyde (95%) were purchased from Aldrich. 3-Aminophenylacetylene (99%) was obtained from National Starch and Chemical Co. and Tokyo Kasei Kogyo Co. (99%). 1,4-Benzenediol (hydroquinone) was purchased from Lancaster and was 99% pure. 4,4′-Oxydiphenol (bisphenol-O) and 4,4′,-dihydroxybenzophenone were received from Ken Seika Corp. and were 99% pure. 4-(3-Aminophenoxy)-4′-phenylethynylbenzophenone was obtained from NASA-Langley Research Center.

2.1. Preparation of benzoxazine monomers and polymers

As the solubility of the majority of the bisphenols in the typical solvent used for benzoxazine synthesis is limited, a novel solventless synthesis procedure was a convenient method for preparation of this benzoxazine monomer series [22]. Stoichiometric amounts of solid bisphenol, paraformaldehyde (used in this case instead of aqueous solution of formaldehyde) and liquid 3-aminophenylacetylene were mixed together at 100°C for 15 min (reaction Scheme 1). The synthesis of monofunctional benzoxazines based on phenol is shown in reaction Scheme 2. Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (BA-a) was synthesized by the general solvent method [23]. The as-synthesized product was dissolved in chloroform and washed with 3N solution of sodium hydroxide for purification. The solvent was then evaporated by a rotary evaporator and the sample was dried in a vacuum oven overnight at 50°C. The yield of the reaction was 80–85% in terms of benzoxazine ring content and the purity of obtained benzoxazine monomer after purification was 97–99% as determined from proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and size exclusion chromatography (SEC). The purified samples were polymerized isothermally in an air circulated oven or in the furnace of thermogravimetric analyzer under nitrogen atmosphere. Homogeneous blends of BA-apa and its analogue BA-a resin (without acetylene functional group) were prepared by mixing two resins with a pre-determined mole fraction, dissolving in chloroform and mixing for several hours. The chloroform was evaporated in a vacuum oven and the blends were cured for 3 h at 190°C in an air-circulating oven.

2.2. Characterization

The benzoxazine monomers and corresponding polybenzoxazines were characterized by Fourier transform infrared spectroscopy (FT-IR) (Bomem Michelson 110 MB). One hundred co-added scans were taken at a resolution of 2 cm^{-1} using a liquid nitrogen cooled, mercury–cadmium–telluride (MCT) detector after a 20 min purge of nitrogen. Solid samples were pressed into KBr pellets or a thin film of the sample was cast from a chloroform solution on a KBr plate. To follow polymerization of the

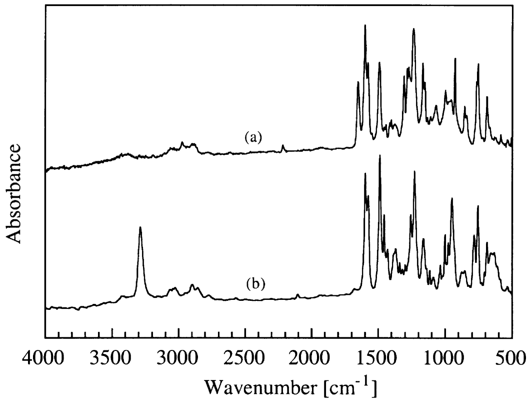


Fig. 1. Fourier transform infrared spectra of monofunctional benzoxazine monomers: (a) Ph-apc and (b) Ph-apa.

benzoxazines, the cast film on the KBr plate was isothermally cured in an oven under either circulating air or a nitrogen atmosphere. Proton nuclear magnetic resonance spectra (^{1}H NMR) were taken on a Varian Gemini-200 with a proton frequency at 200 MHz. Deuterated chloroform was used as a solvent and tetramethylsilane (TMS) was used as an internal standard. SEC was performed with a Waters 510 HPLC pump, U6K Universal Injector, Waters 440 UV detector fixed at 254 nm and used with HPLC grade tetrahydrofuran as the eluent.

Thermogravimetric analysis (TGA) of polybenzoxazines was performed on the TA Instruments thermogravimetric analyzer, High Resolution TGA 2950, with 1 μg sensitivity of the balance and an evolved gas analysis (EGA) furnace. Nitrogen and air were used as purge gases for the testing. A heating rate of 20°C/min was used for all the tests. Differential scanning calorimetry (DSC) was performed on TA Instruments Modulated DSC 2920 with a heating rate of 10°C/min using a nitrogen purge and an empty aluminum pan as a reference. Hermetic pans were used for all tests.

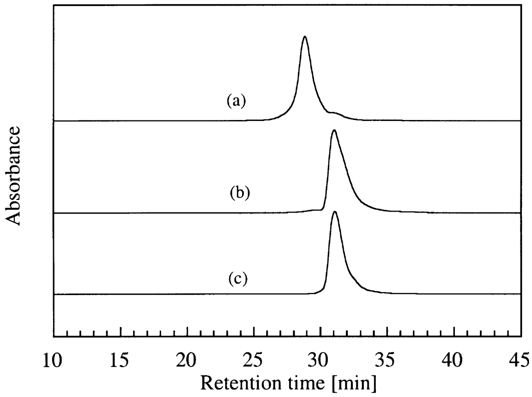


Fig. 2. SEC chromatograms of benzoxazine monomers: (a) BZ-apa; (b) HQ-apa and (c) Ph-apa.

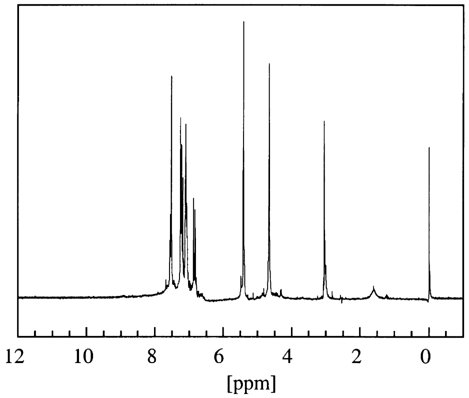


Fig. 3. ^{1}H NMR spectra of benzoxazine monomer BZ-apa.

3. Results and discussion

3.1. Characterization of benzoxazine monomers

FT-IR spectra of purified monofunctional benzoxazine monomers, 3-phenylacetylene-3,4-dihydro-2H-1,3-benzoxazine (Ph-apa) and 3-phenylacetylene-3,4-dihydro-3-phenylphenoxy-2H-1,3-benzoxazine (Ph-apc) are shown in Fig. 1. Vibrational assignments of model compounds of similar benzoxazines have been reported [24]. In-plane carbon–carbon stretching vibrations (aromatic modes 19a and 19b) determined from the 1, 2 and 4 substitution of a benzene ring of the benzoxazine molecule appear at 1496 cm^{-1} (mode 19b) for Ph-apa, BA-apa and BP-apa [25]. The tetrasubstituted benzene ring present in the HQ-apa shows the position of this vibration shifted to a lower frequency at 1486 cm^{-1} (not shown here). Another characteristic band is the antisymmetric C–O–C stretch at 1233 cm^{-1} for all the compounds studied. The band at 933–935 cm^{-1} is assigned to the C–H out-of-plane deformation (vibrational mode 10a) [24]. This vibration is strong and its frequency is unchanged in the spectra of all monomers. The aforementioned vibrational assignments confirm that oxazine ring formation indeed occurred.

The characteristic band at 3282 cm^{-1} is assigned to the C–H stretching vibration of the monosubstituted acetylene functional group whereas the bending mode can be found in the region of 630–640 cm^{-1}. These bands are absent in the spectrum of Ph-apc as a result of the substitution of acetylenic hydrogen with phenyl group. The low intensity band at 2104 cm^{-1} is attributed to the carbon–carbon triple bond stretching mode and is present also in the spectrum of Ph-apc.

FT-IR spectra of purified bifunctional benzoxazine monomers bis(3-phenylacetylene-3,4-dihydro-2H-1,3-benzoxazinyl)sulfone (BS-apa), bis(3-phenylacetylene-3,4-dihydro-2H-1,3-benzoxazinyl)ketone (BZ-apa), bis(3-phenylacetylene-3,4,-dihydro-2H-1,3-benzoxazinyl)hexafluoropropane (BAF-apa) and bis(3-phenylacetylene-3,4,-dihydro-2H-1,3-benzoxazinyl)ether (BO-apa) exhibited additional

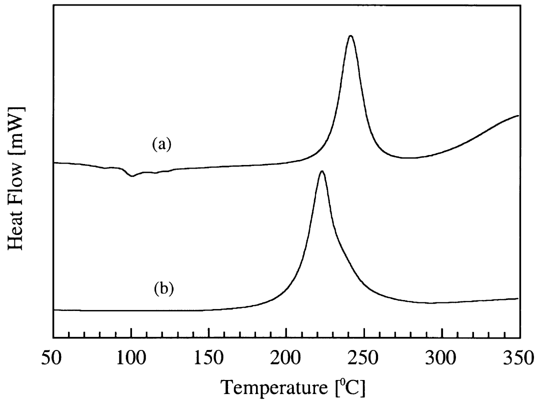


Fig. 4. DSC thermograms of monofunctional benzoxazine monomers: (a) Ph-apc and (b) Ph-apa.

characteristic bands due to the presence of a central group in the benzoxazine molecule (not shown here). BS-apa has characteristic bands at 1144 and 1304 cm^{-1} which are assigned to the symmetric and antisymmetric stretch of the SO_2 functional group. BAF-apa has a CF_3 functional group which absorbs strongly in the range of 1250–1150 cm^{-1}. The characteristic C=O stretching mode from the bisphenol derivative of BZ-apa appears at 1642 cm^{-1}.

Fig. 2 shows SEC chromatograms of the representative compounds. The purity of the compounds is determined to be 97–99%. As expected, the longest retention time (31 min) corresponding to the smallest hydrodynamic volume, is observed for monofunctional benzoxazine monomer, Ph-apa. Hydroquinone based benzoxazine monomer (HQ-apa) shows the same retention time (31 min), suggesting a similar hydrodynamic volume. The largest hydrodynamic volume at a retention time of 28 min corresponds to the bifunctional benzoxazine monomer, BZ-apa.

The proton NMR spectra of the representative compound are shown in Fig. 3. The resonance of the acetylenic protons is found at about 3.0 ppm. The resonances at 4.56 and 5.32 ppm are assigned to the protons in the methylene bridges of the oxazine ring. The peaks in the region 6.6–7.6 ppm are attributed to the phenyl protons of benzoxazine monomer, BZ-apa.

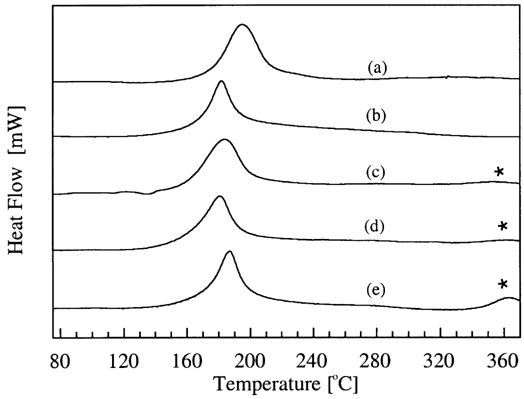


Fig. 5. DSC thermograms of bifunctional benzoxazine monomers: (a) BP-apa; (b) BZ-apa; (c) HQ-apa; (d) BS-apa and (e) BA-apa.

3.2. Thermal analysis of related polybenzoxazines

The non-isothermal DSC thermograms of monofunctional resins are presented in Fig. 4. The Ph-apa resin has the oxazine ring polymerization exotherm highly overlapped with the acetylene polymerization exotherm at the temperature range of 220–235°C. However, Ph-apc shows two well resolved exotherms for both processes. The sharp exotherm at 230°C is attributed to the benzoxazine polymerization, and the broad exotherm at the much higher temperature of 350°C is because of the acetylene polymerization. These assignments are supported by the FT-IR studies of the polymerization of this compound [26]. It was also reported that polymerization of disubstituted arylacetylenic monomers occurs at the higher temperature of 350°C, as identified by DSC [27]. As Ph-apa and Ph-apc are viscous liquids at room temperature, no melting endotherm was observed in DSC thermograms of these compounds.

The non-isothermal DSC thermograms of bifunctional monomers are presented in Fig. 5. The samples were examined by DSC to determine the reaction exotherms of oxazine ring-opening polymerization and acetylene functional group. Exotherms at the temperature range from 180 to 200°C observed in all DSC curves suggest primary polymerization of both functionalities—oxazine ring and acetylene functional group [26]. Also shown is the small post-cure exotherm around 360°C (designated by asterisks). The extent of this process greatly depends on the molecular structure of the monomer. The highest exotherm of this reaction was observed for BA-apa benzoxazine containing an isopropyl central group and no clear exotherm was observed for the monofunctional benzoxazine, Ph-apa. This phenomenon can be attributed to the steric hindrance effect of the central linking group of bisphenol derivative during polymerization.

Char yield was determined from TGA curves as a solid residue remained at 800°C in nitrogen and at 700°C in an air atmosphere. The data of char yield as well as the temperature at 5% and 10% weight loss tested in nitrogen atmosphere for all synthesized compounds are summarized in Table 1. The char yields of polybenzoxazines from purified monomers were 5–10% lower than the char yield of resins from as-synthesized monomers. The char yields of these polybenzoxazines in air are shown in Table 2. The highest char yield of 81 wt.% was achieved for polybenzoxazines, Ph-apa, Ph-apc, HQ-apa, and BZ-apa. The high char yield of 79 wt.% was achieved for acetylene-functional benzoxazines containing thermally stable linking species such as sulfone, thio, and methylene.

The monofunctional acetylenic benzoxazines, Ph-apa and Ph-apc, showed high char yield although monofunctional benzoxazines containing unreactive amine (e.g. aniline) do not cross-link, but form only low molecular weight

Table 1
Degradation temperature and char yield of polybenzoxazines

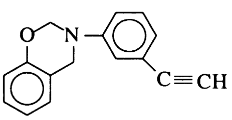
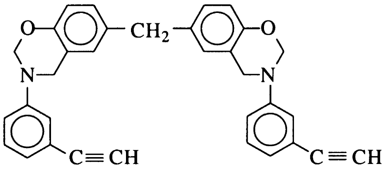
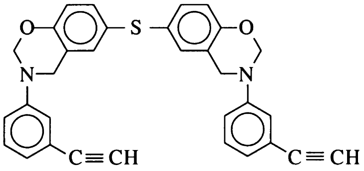
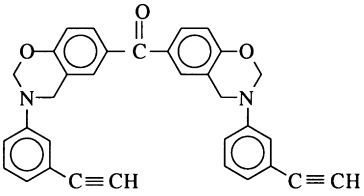
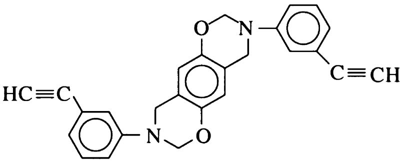
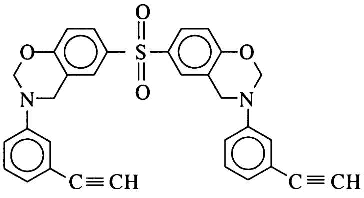
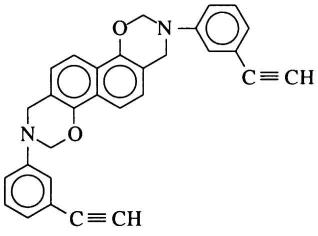
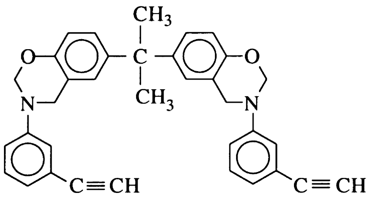
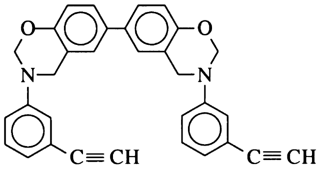
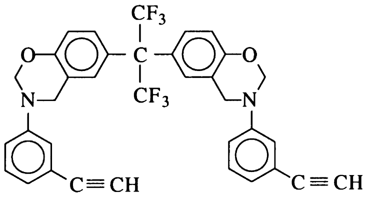
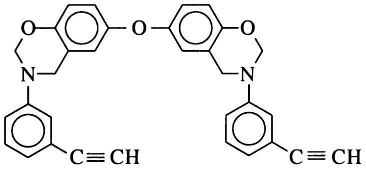
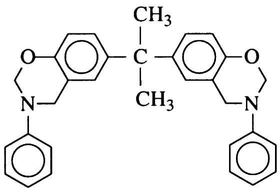
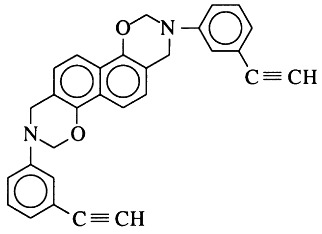
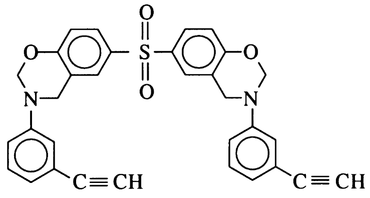
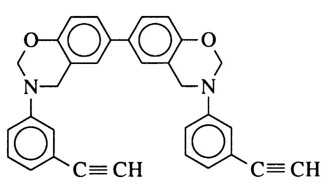
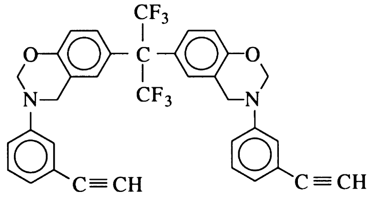
Monomer unit	$T(°C)_{5\%}/N_2$	$T(°C)_{10\%}/N_2$	Char (%)/N_2 at 800°C
 Ph-apa	491	592	81
 BF-apa	470	575	78
 TP-apa	489	592	79
 BZ-apa	478	547	80
 HQ-apa	488	573	81
 BS-apa	440	540	78
 NP-apa	380	428	76
 BA-apa	458	524	74
 BP-apa	462	492	73
 BAF-apa	494	539	71
 BO-apa	415	513	75
 BA-a	390	425	32

Table 2
Degradation temperature and char yield of polybenzoxazines in air

Monomer unit	$T(°C)_{5\%}$/air	$T(°C)_{10\%}$/air	Char (%)/air at 700°C
 NP-apa	377	437	30
 BS-apa	378	422	28
 BP-apa	452	494	19
 BAF-apa	427	454	19

oligomers. Introducing another polymerizable functional group, acetylene, polymerization of the oxazine ring and acetylene triple bond resulted in a cross-linked network and exhibited high char yield upon thermal degradation. Another notable result is the char yield of 74 wt.% for BA-apa-based polybenzoxazine. The char yield of the analogous compound (BA-a) containing aniline instead of 3-aminophenylacetylene is 32 wt.%. This is the highest increase in char yield by about 40 wt.% due to the contribution of acetylene group cross-linking. Side phenyl groups present in the structure of polybenzoxazines from unfunctionalized monomers (BA-a) can easily be volatilized during thermal degradation [26]. It is presumed that linking these weak side phenyl groups by introducing polymerizable acetylene group contributed to improve the thermal stability and to increase the char yield. The thermo-oxidative stabilities of acetylene functional polybenzoxazines in air dramatically decreased at 800°C. However, reasonably high char yield for the representative compounds was achieved at 700°C (Table 2).

Fig. 6 displays thermogravimetric curves of the aforementioned compounds, Ph-apa, Ph-apc, HQ-apa, BA-apa, and BZ-apa, which were polymerized at optimum conditions. These compounds were polymerized in an air-circulating oven and tested under nitrogen. Additionally, these polybenzoxazines exhibit very high glass transition temperatures (T_g) in the range 320–370°C and high values of shear modulus (G'), up to 2.3 GPa, as it was determined by the dynamic mechanical analysis [28].

3.3. The effect of polymerization environment on thermal properties

Degradation temperature as well as char yield of polybenzoxazines from acetylene-functional monomers depends greatly on the atmosphere used for polymerization of these resins [26]. In order to study the effect of a nitrogen environment, Ph-apa was polymerized in a TGA furnace under nitrogen environment prior to the tests (Fig. 7). A significant drop in char yield was observed for this polymer, and even higher polymerization temperature did not significantly affect the char yield when polymerized in nitrogen. The HQ-apa polymer resulted in the smallest 4 wt.% reduction in char yield when polymerized in nitrogen. The BZ-apa polymer also showed a small reduction in char yield by 6 wt.% but exhibited the largest difference in the initial temperature of decomposition to 300°C from 420°C for the samples polymerized in nitrogen and air, respectively. The char yield of the BA-apa polymer was reduced significantly by 23 wt.%. However, the analogous polybenzoxazine based on bisphenol-A and unsubstituted amine (BA-a) resulted in the char yield of 30 wt.% regardless of the polymerization environment, even though the rate oxazine ring-opening polymerization was significantly affected by the polymerization environment [26]. These differences in char yield and thermal stability of the polymers are likely

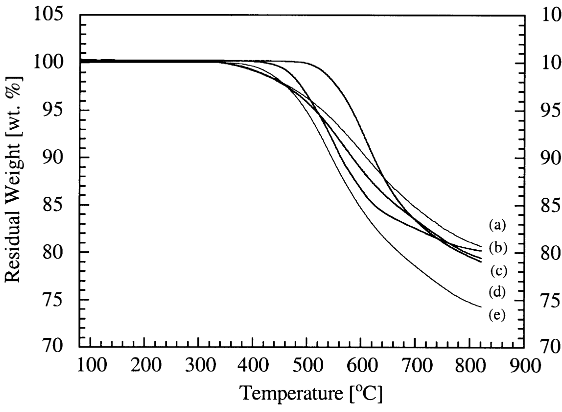


Fig. 6. TGA curves of polybenzoxazine from: (a) HQ-apa; (b) BZ-apa; (c) Ph-apc; (d) Ph-apa and (e) BA-apa, polymerized for 3 h at 190°C in air.

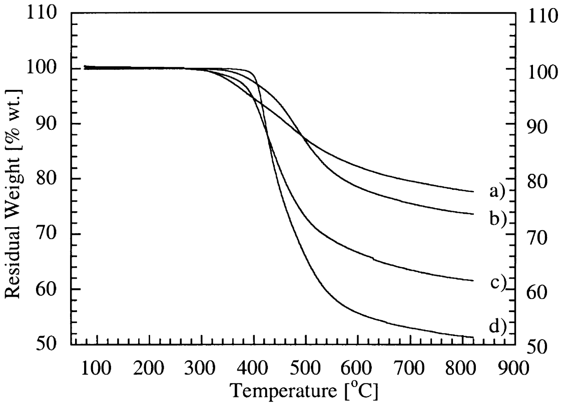


Fig. 7. TGA curves of polybenzoxazines from: (a) HQ-apa; (b) Ph-apa; (c) BZ-apa; and (d) BA-apa, polymerized for 3 h in N_2.

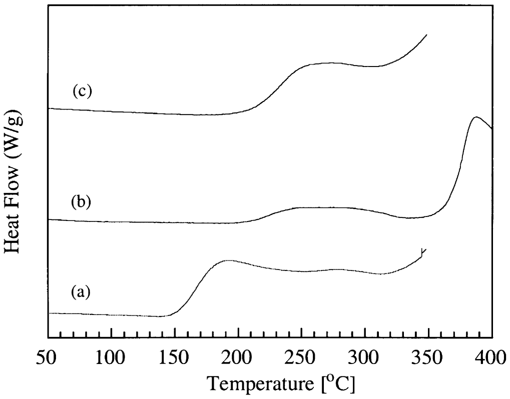


Fig. 9. DSC thermograms of BA-apa, polymerized for 3 h in air: (a) 160°C; (b) 180°C and (c) 190°C.

due to the structural differences and different relative concentration of the networks formed from the polymerization of acetylene triple bond and oxazine ring under different polymerization environments.

During the TGA experiment, the polymerized material is exposed to higher temperatures gradually in an inert atmosphere. Thus, the mobility of the partially cross-linked benzoxazine portion of the polymer increases, and further development of the cross-linked structure either from polybenzoxazine or polyene is possible until degradation temperature is reached. In spite of this fact, cross-linked networks are not developed to the same degree, which can be observed for the same samples polymerized in air, as shown by the difference in char yield. This phenomenon was further investigated by DSC with BA-apa benzoxazine.

Fig. 8 shows the non-isothermal DSC thermograms of BA-apa bezoxazine polymers which are polymerized in nitrogen at 160, 180 and 190°C. From the DSC thermogram (a), the exotherm centered at 175°C is attributed to the residual polymerization of oxazine ring and acetylene group. Also the following small but broad exotherm is attributed mainly to the secondary reaction of the acetylene group and residual oxazine ring polymerization. The exotherms at 300 and 375°C are the post-cure reaction and they can be related to the structural changes of the already reacted acetylene group. As thermal degradation starts from a temperature above 400°C as seen in Fig. 6, these exotherms cannot be related to thermal degradation. The same post-cure behavior was also found in acetylene terminated imide [29]. While DSC results indicate similar thermograms in both air and nitrogen atmosphere (Figs. 8 and 9), FT-IR and TGA results show substantial differences in these environments.

4. Thermal stability of blends

Fig. 10 shows the char yield of copolymers obtained from the benzoxazine resins, BA-apa and BA-a. The char yield was not improved proportionally to the mol% of the added BA-apa material. Adding 10 mol% of BA-a to BA-apa dramatically decreased the char yield of the copolymer by more than 20 wt.%. This suggests that high char yield of BA-apa material was mainly determined by the structure formed by acetylene polymerization. Any defects or impurity made the cross-linked network vulnerable to thermal degradation and brought a catastrophic drop in the char yield.

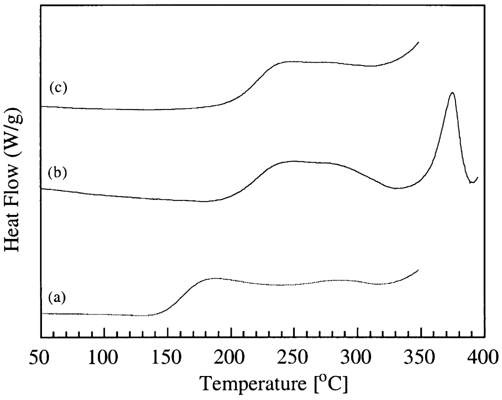


Fig. 8. DSC thermograms of BA-apa, polymerized for 3 h in N_2: (a) 160°C; (b) 180°C and (c) 190°C.

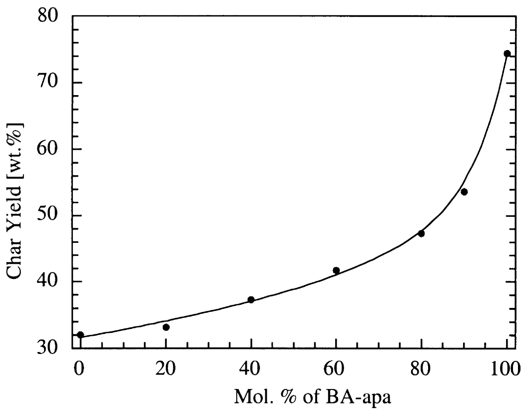


Fig. 10. Char yield versus composition of BA-apa and BA-a mixture.

5. Conclusion

It was shown that acetylene functional group polymerization in addition to oxazine ring-opening polymerization forms highly thermally stable cross-linked network. Polymerization in the nitrogen resulted a significant decrease in the degradation temperature as well as the char yield of acetylene functional benzoxazines. The study of the char formation in the form of mixtures of BA-apa and BA-a confirmed the major contribution of acetylene polymerization to the highly thermally stable structure of BA-apa polybenzoxazine.

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