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Molecular characterization of the polymerization of acetylene-functional benzoxazine resins

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Abstract

High char yield polybenzoxazines are obtained from acetylene-functional benzoxazine monomers. Polymerization of acetylene functional group, in addition to oxazine ring opening polymerization, contributes greatly to the exceptional thermal stability. A significant change in char yield is found for these polybenzoxazines by different polymerization environments. The polymerization behaviour of these compounds under air and nitrogen atmosphere has been studied by Fourier transform infra-red spectroscopy, ultra-violet–visible spectroscopy, differential scanning calorimetry and proton nuclear magnetic resonance spectroscopy. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polybenzoxazine; Acetylene-functional polymer; Phenolic resin

1. Introduction

A recent development of a family of benzoxazine-based phenolic resins made it possible to combine thermal properties and flame retardance of phenolic resin with mechanical performance and molecular design flexibility of epoxy resin. The inherently nonflammable polybenzoxazine resins exhibited high char yield, superior mechanical properties and excellent processability through flexible molecular design, without sacrificing the advantage of conventional phenolic resins [1]. Conventional phenolic resins have been used for many years in various applications, including aircraft interiors, mainly because of their low flammability with relatively high char yield, in spite of brittleness, volatiles generating during curing, and use of catalyst for polymerization [2,3]. As benzoxazine resins react through ring-opening polymerization, no reaction byproducts are released, which eliminates the formation of voids. This makes the newly developed polybenzoxazines ideally suited for matrices for high performance composite applications [4].

To further improve the thermal stability of polybenzoxazines, a polymerizable side functional group, acetylene, was introduced into a series of benzoxazine monomers [5]. Because acetylene terminated resins polymerize into three-dimensional void-free networks without the evolution of volatiles, and the cured products show high thermo-oxidative stability, solvent resistance and moisture resistance, and good mechanical properties [6], these resins can be considered as good candidates for high performance resins for aerospace applications. Those easily processable acetylene functional benzoxazines were polymerized in the range of 190–220°C and resulted in char yield up to 81 wt% at 800°C under nitrogen atmosphere [5].

As the final properties depend on the degree of polymerization, it is essential to understand the polymerization of these resins to define the final properties and processing conditions. Therefore, the purpose of this paper is to study the effect of the environment on the thermally induced polymerization of these acetylene-functional benzoxazines and the resulting char formation.

The mechanism of benzoxazine ring opening polymerization has been investigated and it has been proposed to occur via an iminium ion as an intermediate [7]. Also, ionic ring opening mechanism coupled with the chain transfer growth step was proposed for benzoxazine ring-opening polymerization [8]. The conversion and rate of polymerization of the purified monomer were compared to those of as-synthesized precursors under isothermal conditions [9]. All these studies were performed with regular benzoxazines without any polymerizable side functional groups. It has been known that acetylenic group can react under cationic, coordination,

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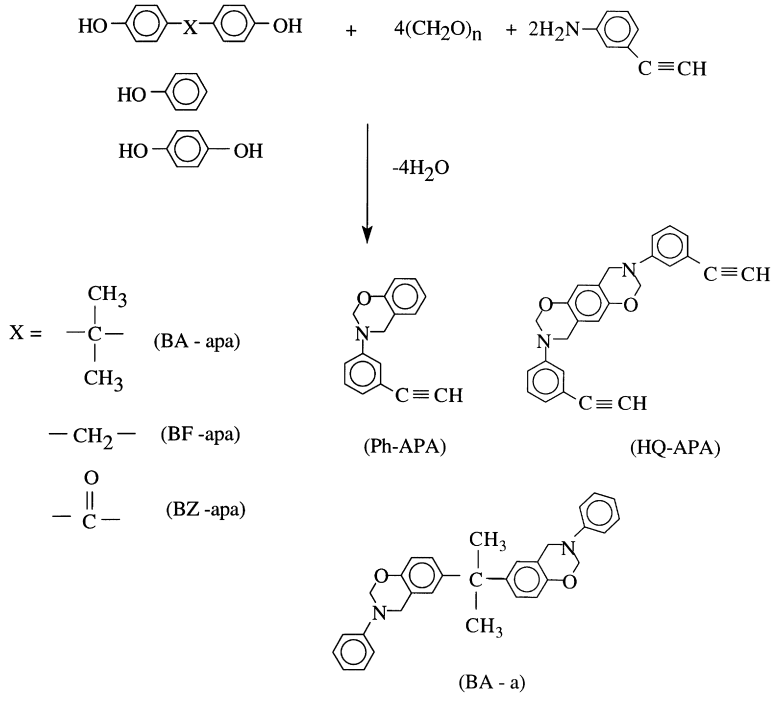
free radical, photolytic, and thermal inducement. The reaction of the acetylenic group leads to chain extension, branching, or crosslinking of the polymer by thermal inducement [6]. It has been reported by many researchers that the acetylene group undergoes complex reactions such as Glaser coupling, Strauss coupling, and Diels–Alder reaction of the Strauss or Glaser product [10–19].

For acetylene-functional bezoxazines, two types of thermally initiated polymerizations occur during the thermal curing process: polymerization of the acetylene-functional group; and oxazine ring-opening polymerization. In differential scanning calorimetry (d.s.c.) experiments with acetylene-functional benzoxazine resins, the reaction exotherm of acetylene polymerization broadly overlaps with the reaction exotherm of benzoxazine ring-opening polymerization [5]. Fourier transform infra-red (*FT*i.r.) is a convenient method for this study to follow these two different polymerization reactions simultaneously occurring in the same molecule.

2. Experimental

A novel solventless synthesis procedure [20] was used for preparation of benzoxazine monomers, 3-phenylacetylene-3,4-dihydro-2H-1,3-benzoxazine (Ph-apa), bis(3-phenylacetylene-3, 4-dihydro-2H-1, 3-benzoxazinyl)isopropane (BA-apa), 3-phenylacetylene-2,3,5,6-hexahydro-bis-*m*-oxazine (HQ-apa), and bis(3-phenyl-acetylene-3,4-dihydro-2H-1,3-benzoxazinyl) ketone (BZ-apa) (Scheme 1). Details of the synthesis and characterization of these monomers have been discussed in a previous paper [5]. Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (BA-a) was synthesized by the method utilizing a solvent [21].

The polymerization of benzoxazine monomers was followed by using a Michelson 110 MB *FT*i.r. spectrometer. After 20 min purge with nitrogen, 100 coadded scans were taken at a resolution of 2 cm^{-1} using liquid-nitrogen cooled mercury–cadmium–telluride (MCT) detector. The monomers used for *FT*i.r. analysis were dissolved in tetrahydrofuran (THF) at a concentration of 10 wt% and the solution was cast on a KBr plate using a spin coater. The KBr plate was spun at a speed of 2000 rpm for 2 min in order to obtain a sufficiently thin and uniform film. The solvent was removed by placing the coated KBr plate in a vacuum oven overnight at 40–50°C. The coated benzoxazine monomers on KBr plates were isothermally polymerized in an oven under either circulating air or nitrogen atmosphere. Proton nuclear magnetic resonance (^{1}H n.m.r.) spectra were taken on a Varian Gemini-200 with a proton frequency of 200 MHz. Deuterated chloroform was used as a solvent and tetramethylsilane (TMS) was used as an internal standard. D.s.c. was performed on a TA Instruments Modulated DSC 2920 with a heating rate of 10°C min^{-1} using nitrogen purge and an empty aluminum pan as a reference. A sealed pan was used for all tests. Thermogravimetric analysis (t.g.a.) was conducted using a TA Instruments thermogravimetric analyser, High resolution TGA2950 equipped with 1 μg sensitivity balance and an evolved gas analysis (EGA) furnace. Nitrogen was used as a purge gas and a heating rate of 20°C min^{-1} was used for all tests. Ultra-violet–visible (u.v.–vis) spectra were obtained on a Hewlett-Packard



Scheme 1.

8452A diode-array spectrophotometer in the wavelength range of 190–820 nm with a single deuterium lamp light source. The polybenzoxazine samples were taken from the cast film on quartz plate.

3. Results and discussion

It was found that polymerization environment (air or nitrogen) greatly affects the thermal stability as well as the char yield of polybenzoxazines from acetylene functional monomers. Through d.s.c. and t.g.a. studies, it was found that the concentration and structure of polyene chains as well as the extent of oxazine ring opening polymerization are affected by different polymerization environments [5]. The polymerization was monitored by *FT*i.r. for monofunctional and bifunctional acetylene-functional benzoxazines, in both air and nitrogen.

3.1. Polymerization of monofunctional benzoxazine with acetylene-functional group Ph-apa benzoxazine

*FT*i.r. spectra of Ph-apa polymerized in nitrogen atmosphere at 210°C for different times are shown in Fig. 1. The polymerization of the acetylene groups can be followed by the change of the intensity of the band at 3286 cm^{-1} (designated by asterisks) [22], which is associated with the acetylenic C–H stretch. The significant intensity decrease of the bands at 1486 cm^{-1}, 1233 cm^{-1} and 952 cm^{-1}, which are attributed to the benzoxazine ring [23], indicates that the ring-opening reaction has occurred. This is also confirmed by the appearance of new bands at 3300–3500 cm^{-1}, which are assigned to the hydrogen-bonded hydroxyls of open oxazine ring species. New bands at 1640–1680 cm^{-1} can also be observed in the spectra of the polymerized samples. Schiff base, –N=CH–, which is a possible intermediate of oxazine ring-opening polymerization [7], usually absorbs in this region. However, this band can overlap with the C=C stretching vibration of polyenes formed upon acetylene polymerization which also absorbs in this region. Conjugation [22], which weakens the C=C force constant, lowers this frequency by 10–50 cm^{-1} and there is a new band at 1605 cm^{-1} also observed in the spectra of polymerized samples, suggesting the presence of conjugated species. The ratios of integrated intensities of the bands at 3286 and 952 cm^{-1} to the integrated intensity of the internal standard band are plotted against heating time as shown in Fig. 2 for the samples isothermally polymerized at 210°C under air and nitrogen. The band at 755 cm^{-1}, which is assigned to the C–H out-of-plane bending of meta-disubstituted benzene ring, was chosen as an internal standard. Oxazine ring-opening polymerization proceeds faster than acetylene triple bond polymerization, as shown in this plot.

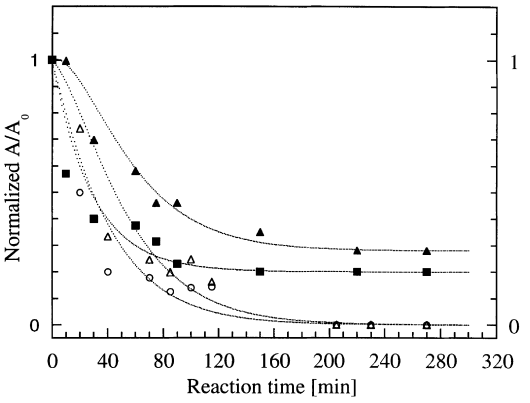


Fig. 2. Normalized A/A_0 versus reaction time of Ph-apa polymerization in air and nitrogen for peak at 3286 and 755 cm^{-1}: ▲, 3286 cm^{-1}/N_2; ■, 945 cm^{-1}/N_2; △, 3286 cm^{-1}/air; ○, 945 cm^{-1}/air.

Acetylene and oxazine polymerizations of Ph-apa in air at 210°C were also monitored by *FT*i.r. It is obvious that under these conditions both processes proceed much faster than in nitrogen. Both functionalities, the acetylene group and the oxazine ring, were consumed quickly at the beginning of heating as indicated by a significant decrease in the intensity of the bands at 3286 and 952 cm^{-1}. Acetylene polymerization is very likely affected by oxidation reaction during this thermally induced uncatalysed process.

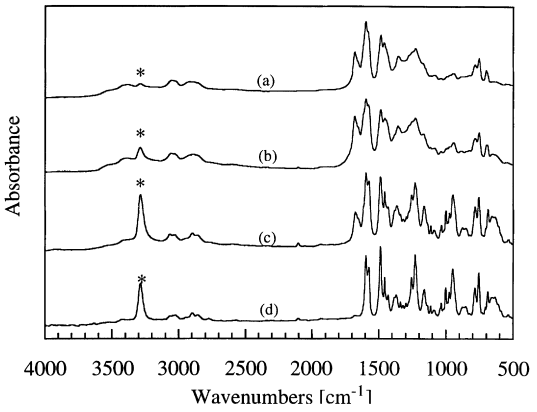


Fig. 1. *FT*i.r. spectra of Ph-apa polymerization in nitrogen at 210°C: polymerized for (a) 270 min, (b) 100 min, (c) 30 min, and (d) monomer.

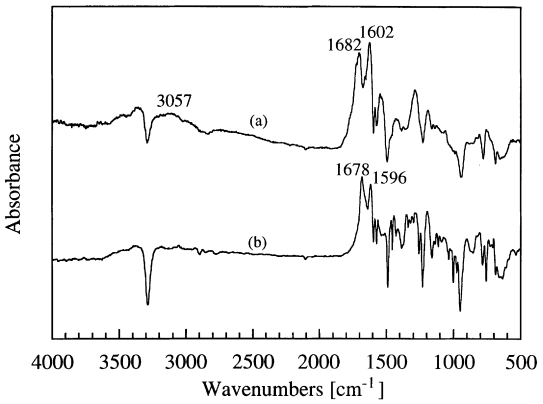


Fig. 3. Difference spectra of Ph-apa from the samples polymerized at 210°C: (a) in air; and (b) in nitrogen.

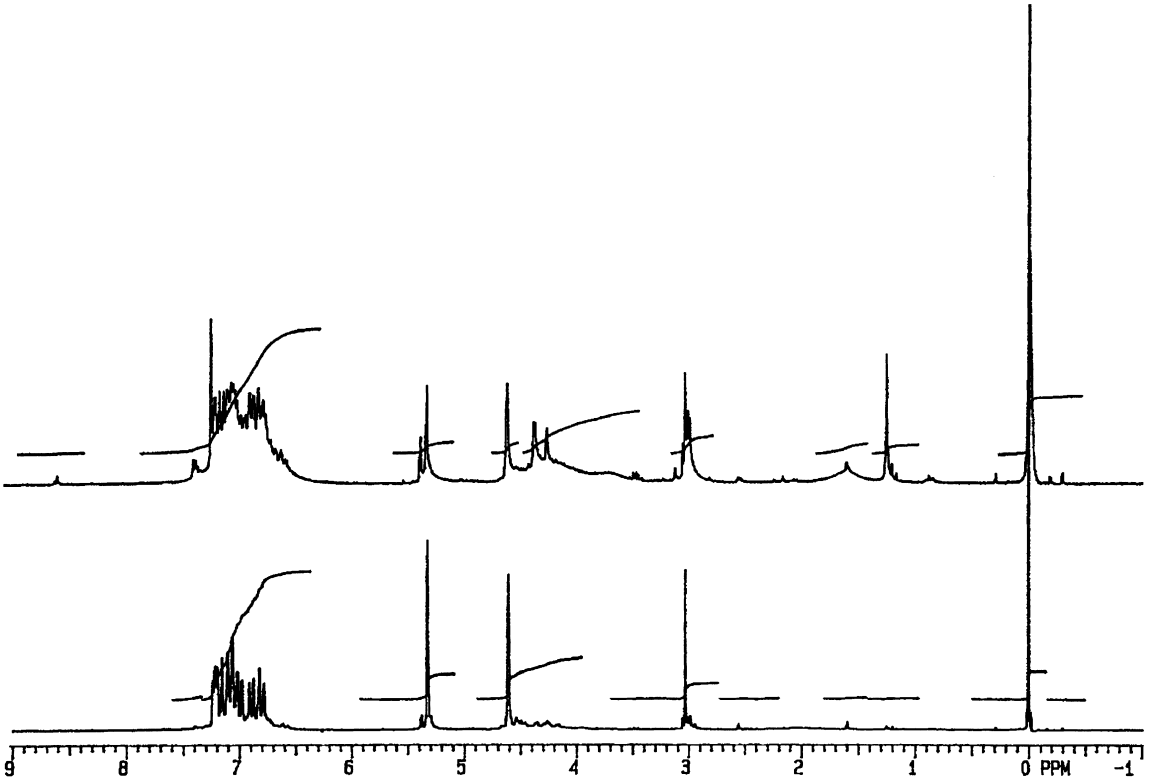
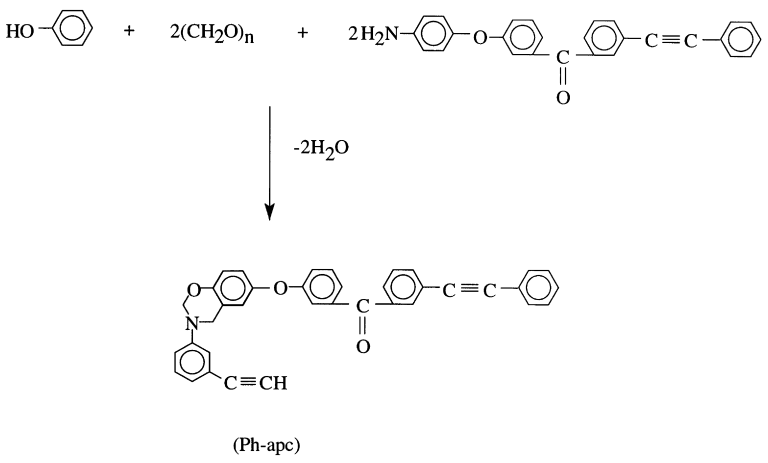


Fig. 4. ^{1}H n.m.r. spectra of Ph-apa, from top to bottom, polymerized for 10 min in air and in nitrogen.

From the difference spectrum in Fig. 3, the presence of conjugated double bonds can be identified, which are formed upon polymerization of acetylene for the samples cured under inert and air atmosphere at 210°C. The difference spectra were obtained from the fully polymerized samples at the end of the reaction and the samples polymerized near the gel point. New bands at 1600 and 3045 cm^{-1} in the spectra of these samples are attributed to the structures formed upon polymerization of acetylene triple bond. The band at 3045 cm^{-1} is usually attributed to the C–H stretching adjacent to the double bond, and the band at 1600 cm^{-1} is attributed to the C=C stretching. It is possible that the band at 1680 cm^{-1}, which is assigned to the secondary amide is overlapped with the band assigned to the C=N stretching of the Schiff base.

3.1.1. ^{1}H n.m.r. study of polymerization

^{1}H n.m.r. spectra shown in Fig. 4 were taken from the Ph-apa samples partially polymerized at 190°C for 10 min in air and nitrogen environments. These curing conditions were chosen due to the solubility limitation of heated Ph-apa. Also, the effect of the environment on polymerization of this monomer was the most distinguishable at the beginning of the reaction below gel point, as shown by *FT*i.r. In the



(Ph-apc)

Scheme 2.

4.1–4.3 ppm region, new resonances with low intensity were observed in the spectrum of the sample polymerized in nitrogen, as compared with the spectrum of the monomer. These chemical shifts are usually associated with the proton resonances of methylene units of the Mannich bridges, which resulted from oxazine ring polymerization. The extent of this reaction is very small, corresponding to approximately 10% conversion of oxazine rings as determined from the relative intensities of these peaks. The intensity of the protons associated with the acetylenic protons remains unchanged. The fact that no decrease in the intensity of this peak was observed in the n.m.r. spectra, contrary to the *FT*i.r. results, can only be explained by the physical effect rather than by chemical reaction. The spectrum of the sample heated under the same conditions but in air shows significant structural difference as compared to the sample heated in nitrogen. The polymerization of both functionalities in air proceeded to much higher extent than the polymerization in nitrogen. New chemical shifts in the 4.1–4.3 ppm region exhibit greater intensity than they were for the samples heated in nitrogen. The new peak at 8.6 ppm is assigned to the resonance of the iminium ion or Schiff base, –CH=N–. The proton resonances of the shorter polyene chains are usually found in the 6.2–6.5 ppm region. Interestingly, a new peak appears at 1.1 ppm, which is a characteristic resonance of a hydroperoxide proton possibly formed by the reaction of acetylenic hydrogen with oxygen. This peak is absent in the spectrum of the same sample polymerized in a nitrogen environment.

3.2. Ph-apc benzoxazine

The d.s.c. thermogram of phenylacetylene-functional benzoxazine, Ph-apc (Scheme 2), revealed two separate polymerization exotherms at 240 and 350°C [5]. These two temperatures were chosen to monitor isothermal polymerization of this monomer by *FT*i.r. (Fig. 5). Arylacetylene functional group is represented by the band at 2200 cm^{-1}, which is assigned to the C ≡ C stretching. No effect of curing environment was observed for this compound and, for simplicity, *FT*i.r. spectra were obtained from the samples polymerized under nitrogen. Due to the complexity of the structure of this monomer, it was difficult to find a band characteristic to the oxazine ring. As the spectra taken at lower temperature of 230°C show, there is an intensity increase of the OH bands at 3300–3400 cm^{-1}, confirming oxazine ring polymerization. The complete polymerization of the arylacetylene portion of the monomer happens at the higher temperature of 350°C as shown by the disappearance of the band at 2200 cm^{-1}.

3.3. Polymerization of bifunctional benzoxazine with acetylene-functional group

To investigate the effect of the environment on the polymerization of acetylene functional group and oxazine ring, isothermal polymerization of BA-apa benzoxazine at 190°C was monitored by *FT*i.r. under air and nitrogen. The C–H out-of-plane deformation [23] of tri-substituted benzene at 952 cm^{-1} was selected to monitor the polymerization of oxazine ring. The band at 2976 cm^{-1}, which is assigned to the C–H stretching of methyl group [22], was used as an internal standard. Within 40 min of heating in air, the bands due to the acetylene and oxazine groups decreased significantly. Heating for 360 min nearly completely consumed both acetylene and oxazine groups. The same polymerization experiments were repeated but in nitrogen, and Fig. 6 shows normalized integrated intensity, A/A_0, as a function of heating time. The oxazine ring polymerization shows about 7% difference by the environment of polymerization. Compared to the oxazine ring, the polymerization reaction of acetylene triple bond did not show much difference. And the oxazine ring polymerization proceeded much slower than that of the acetylene-functional group in nitrogen. Even though no significant difference was found on the reaction of acetylene triple bond under different polymerization environments, it is possible that the secondary reaction of the already opened acetylene triple bond can

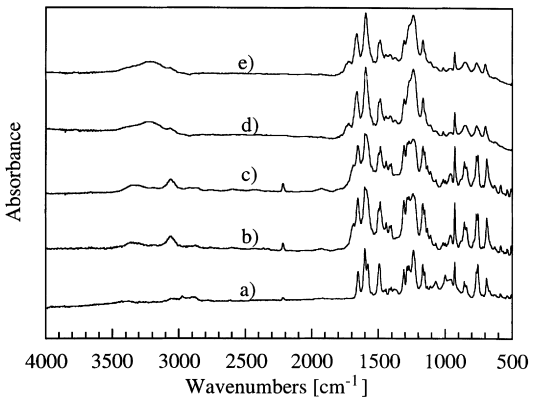


Fig. 5. *FT*i.r. spectra of Ph-apc: (a) monomer; (b) polymerized at 230°C for 60 min; (c) polymerized at 230°C for 240 min; (d) polymerized at 350°C for 60 min; (e) polymerized at 350°C for 240 min.

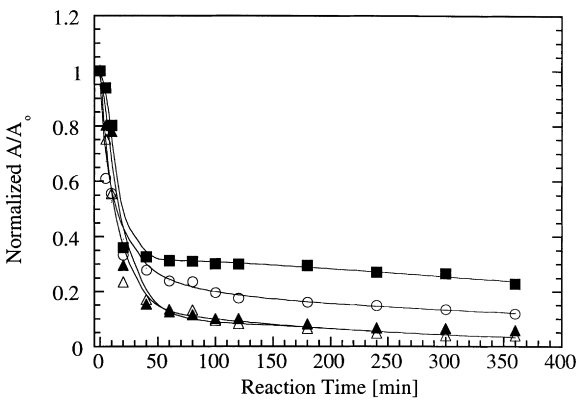


Fig. 6. Normalized A/A_0 versus reaction time of BA-apa polymerization at 190°C in air and nitrogen for oxazine ring and acetylene group: ■, 953 cm^{-1}/N_2; ○, 953 cm^{-1}/air; ▲, 3283 cm^{-1}/N_2; △, 3283 cm^{-1}/air.

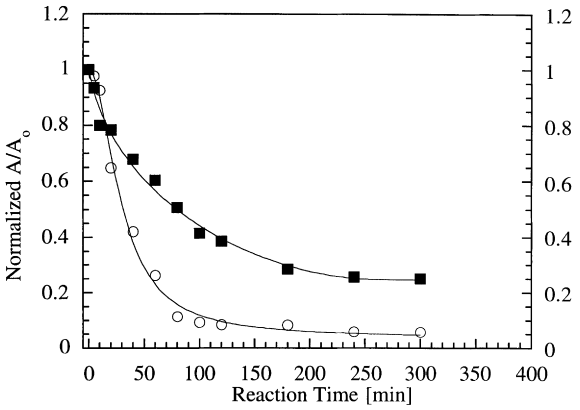


Fig. 7. Normalized A/A_0 versus reaction time of oxazine ring polymerization of BA-a at 190°C: ■, 950 cm^{-1}/N$_2$; ○, 950 cm^{-1}/air.

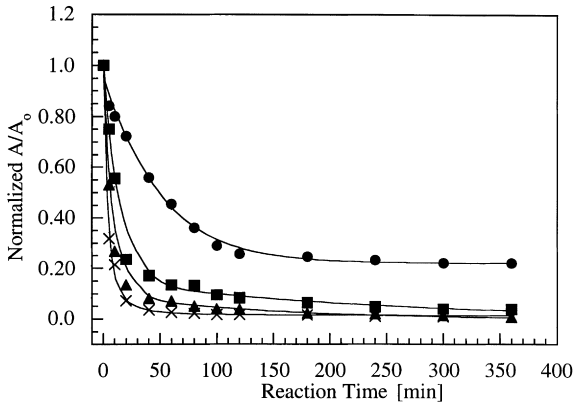


Fig. 9. Normalized A/A_0 versus reaction time of acetylene group polymerization of BA-apa at: ●, 160°C; ■, 190°C; ▲, 200°C; × 220°C.

be affected. This was suggested in the d.s.c experiment by the shift towards a higher temperature and the increased extent of exotherm assigned to post-cure reaction, which comes from the reaction of already polymerized acetylene group [5].

The same experiments in air and nitrogen were done with BA-a benzoxazine, which does not have acetylene triple bond in the amine portion (Fig. 7). After 6 h at 190°C, about 94% of the reaction was completed in air compared to 75% in nitrogen. This result suggests that the polymerization of the oxazine ring depends on the polymerization environment.

To further investigate the polymerization behaviour of oxazine ring and acetylene group, the polymerization of BA-apa benzoxazine at four different temperatures with varying polymerization time was monitored by *FT*i.r. Plots are made as a function of polymerization time at different temperatures at 160°C, 190°C, 200°C and 220°C in air, to follow polymerization of the oxazine ring (Fig. 8) and the acetylene triple bond (Fig. 9). These figures, which show the initial very steep decrease of A/A_0, followed by a gradual decrease with reaction time, suggest that the polymerization is dependent on the viscosity of the medium. This phenomenon can be seen in the diffusion controlled curing process in which the curing reaction is controlled by the increased viscosity of the medium [24]. At elevated temperatures, these plots showed accelerated rate of polymerization above 190°C for acetylene group and above 220°C for the oxazine ring. At 190°C and the above, the reaction of the acetylene triple bond proceeded faster and to a greater extent than the oxazine ring. At 190°C and above, the reaction of the acetylene group proceeded very fast and these groups were consumed almost completely within 120 min of polymerization.

The *FT*i.r. experiment of 3 h of polymerization can be related to the d.s.c. experiment. For the oxazine ring, 80% of reaction at 160°C and 85% at 190°C were achieved for 3 h of polymerization in air while 75% at 160°C and 93% at 190°C were achieved for the acetylene group (Figs 8 and 9). For these reasons, the first exotherm centered at 188°C disappeared when the polymerization temperature was increased from 160°C to 190°C by further polymerization of the acetylene group. Even though no difference was found on the reaction of the acetylene triple bond under different cure environments, the secondary reaction of already reacted acetylene triple bonds can be affected. This result can also be related to the d.s.c. thermogram of polymer heated at 190°C, which showed a decrease of the

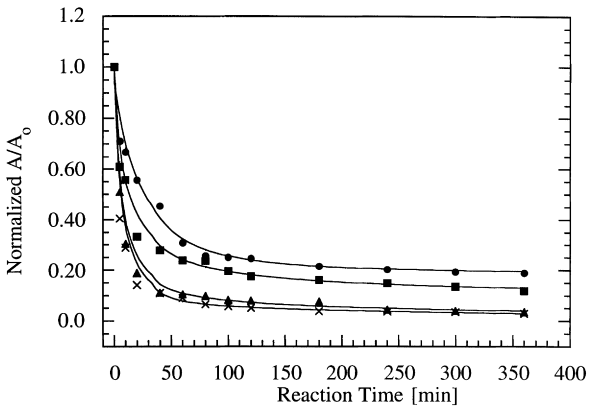


Fig. 8. Normalized A/A_0 versus reaction time of oxazine ring polymerization of BA-apa at: ●, 160°C; ■, 190°C; ▲, 200°C; × , 220°C.

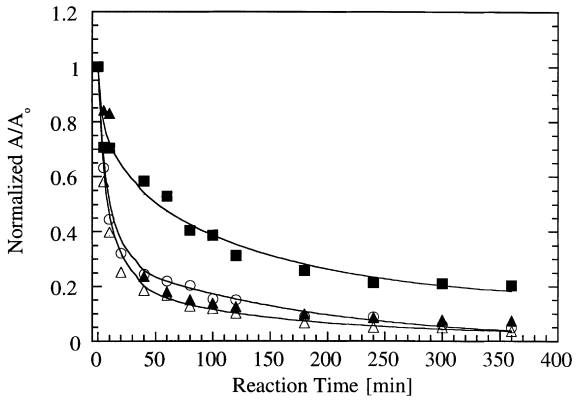


Fig. 10. Normalized A/A_0 versus reaction time of BZ-apa polymerization in air and nitrogen for the peak at: △, 3286 cm^{-1}/air; ○, 950 cm^{-1}/air; ▲, 3280 cm^{-1}/N$_2$; ■, 950 cm^{-1}/N$_2$.

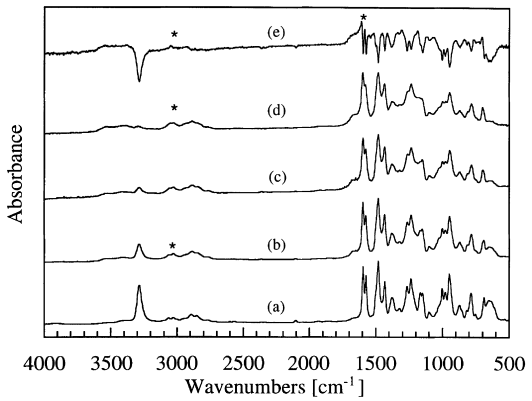


Fig. 11. *FT*i.r. spectra of HQ-apa polymerization at 190°C in nitrogen and the difference spectrum: (a) monomer; (b) 30 min; (c) 90 min; (d) 6 h; (e) subtracted.

first exotherm but a significant increase of the post-cure reaction by changing cure environment[5].

In order to verify whether this difference is common to other acetylene-functional benzoxazines, the polymerization of BZ-apa and HQ-apa benzoxazines was monitored in both air and nitrogen. A similar tendency has been observed as in the polymerization of BA-apa. As seen from the relative integrated intensities of the oxazine ring and the acetylene group for BZ-apa (Fig. 10), polymerization of the oxazine ring was greatly affected by the different polymerization environments, while the reaction of the acetylene triple bond showed some differences at the initial polymerization stage. Also, the polymerization of the oxazine ring group proceeded faster and to a larger extent in air than in nitrogen. Polymerization of HQ-apa was monitored in both air (Fig. 11) and nitrogen, and a similar tendency as in the previous case has been observed (Fig. 12).

Polyene, a part of the crosslinked structure which is formed upon thermal polymerization of acetylene functionalities, was further investigated for this system by FTIR. The acetylenic groups of acetylene-terminated benzoxazine resins can polymerize via a number of possible routes [10–19]. As shown in Fig. 11, the intensity of the band at 2104 cm^{-1} decreased with increasing reaction time and no new band at a lower frequency is observed, which reduces the possibility of the formation of –C≡C–C≡C– by the Glasser coupling. The difference spectrum in Fig. 11 of the fully polymerized sample and sample polymerized to gel point shows an increase of the intensity of the band at 3050 cm^{-1}, which is assigned to the C–H stretching adjacent to a double bond (designated by asterisks). This suggests a possible formation of the cyclic trimer, 1,3,5-trisubstituted benzene ring, via free radical or cycloaddition reaction. The difference spectrum also shows significant increase in the intensity of the bands or possibly formation of new bands in the 1611–1660 cm^{-1} region, which indicates the presence of new carbon–carbon double bonds of polyene conjugated linear or branched chains. To evaluate in more detail the formation of cyclic trimer or linear, branched structure upon thermal polymerization of acetylene terminal units of benzoxazines, HQ-apa and BZ-apa, another technique has to be used.

3.4. U.v.–vis study of HQ-apa resin

U.v.–vis spectra of HQ-apa and related polybenzoxazines, which are heated in air at 190°C, are shown in Fig. 13. For comparison, the spectrum of 3-aminophenylacetylene is also displayed. This technique was used to investigate the extent and length of conjugation of polyenes in this system formed upon thermally induced free radical polymerization of the acetylene functional group. It is well known [25] that bathochromic shift and a hyperchromic effect are observed in the u.v.–vis spectra of conjugated polyenes as the length of the conjugated chain increases. The band at 250 nm, which is attributed to –C≡CH, can be observed in both HQ-apa and 3-aminophenylacetylene spectra. This band disappears upon polymerization for 1 h, which suggests that all acetylene functionalities were consumed. This is in agreement with the *FT*i.r. study of this

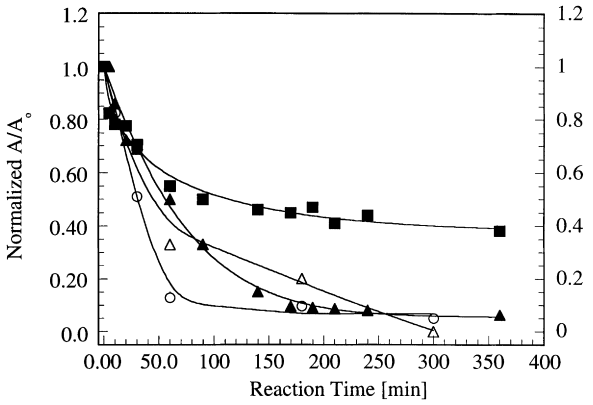


Fig. 12. Normalized A/A_0 versus reaction time of HQ-apa polymerization at 190°C for the peak at: ○, 950 cm^{-1}/air; ■, 950 cm^{-1}/nitrogen; △, 3286 cm^{-1}/air; ▲, 3286 cm^{-1}/nitrogen.

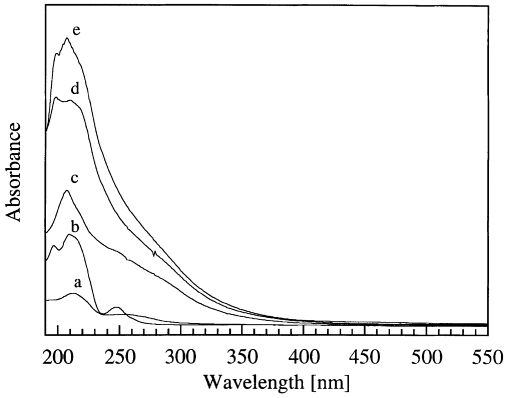


Fig. 13. U.v.–vis spectra of 3-aminophenylacetylene and HQ-apa polymer: (a) 3-aminophenylacetylene; (b) HQ-apa monomer; (c) HQ-apa polymerized at 190°C in air for 1 h; (d) HQ-apa polymerized at 190°C in air for 3 h; (e) HQ-apa polymerized at 190°C in air for 6 h.

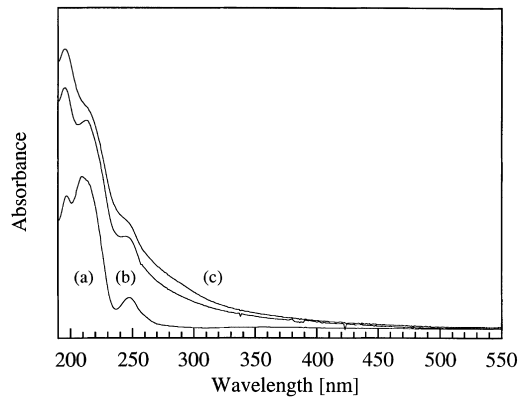


Fig. 14. U.V.–vis spectra of HQ-apa: (a) HQ-apa monomer; (b) polymerized at 190°C in nitrogen for 1 h; (c) polymerized at 190°C in nitrogen for 3 h.

compound. New broad bands that are shifted to a longer wavelength are observed in the 250–350 nm range. These bands are usually the $\pi \rightarrow \pi^*$ transition of short conjugated polyenes. Major structural changes are also observed in the aromatic region of 190–230 nm which is accompanied by a hyperchromic effect. HQ-apa monomer exhibits two overlapped bands around 230 nm. As the polymerization time increases, a third band at 200 nm occurs as it is expected for polynuclear aromatic structures resulting from oxazine ring-opening polymerization.

U.v.–vis spectra of HQ-apa heated in nitrogen are shown in Fig. 14. As compared to the spectra of the same compound heated in air, the acetylene band at 250 nm decreases more slowly and still remains even after 3 h of heating. New broad bands appear in the spectra of cured resin at the wavelength 250–350 nm region, which can be attributed to short polyene chains. These bands are less intense as they are compared to the u.v.–vis spectra of the same compound cured in air. These results are in agreement with *FT*i.r. curing study, where the acetylene triple bond did not disappear completely even after 6 h of heating. The difference in the hyperchromic effect for the samples polymerized in nitrogen suggests different extents of conjugated double bonded species with similar length as compared with the spectra of samples heated in air. A hyperchromic effect in the region of 220 nm can be due to the increasing chain length of benzoxazine oligomers and/or due to the formation of 1,3,5-trisubstituted benzene, formed upon polymerization of acetylenic group. Judging from the low frequencies of these bands, short polyene chains are formed upon polymerization of acetylene triple bond, but the possibility of cyclic trimerization of this functional group cannot be excluded.

4. Conclusion

Acetylene-functional benzoxazines polymerized in air resulted in higher char yield and thermal stability than those polymerized under inert atmosphere, due to the different concentration and structure of newly formed polyene chains by acetylene group polymerization, and due to the different extent of ring opening polymerization. Polymerization of both oxazine and acetylene groups proceeds faster and to a greater extent under air environment. Both polymerization processes occur almost simultaneously when performed in air, at a relatively low temperature of 190°C without any added catalyst. U.v.–vis spectra revealed that acetylene functional group on the oxazine ring form short chains of conjugated polyenes.

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