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Novel benzoxazine monomer containing diacetylene linkage: An approach to benzoxazine thermosets with low polymerization temperature without added initiators or catalysts

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ABSTRACT

A novel benzoxazine monomer containing diacetylene linkage has been synthesized by applying an oxidative coupling approach. The structure is confirmed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. Differential scanning calorimetry (DSC) is used to study crosslinking behavior of synthesized material. The benzoxazine monomer exhibits unexpectedly low exothermic peak with the onset around 140 °C, which is significantly lower than conventional benzoxazines or benzoxazines containing additional crosslinking sites. Benzoxazine polymerization at this low temperature is also confirmed by FTIR. The initial model studies are made in order to understand this phenomenon and preliminary explanation is given. High thermal stability of the crosslinked thermoset was confirmed by thermogravimetric analysis (TGA).

1. Introduction

Benzoxazine resin is a recently developed class of thermosetting resins which received drastically increased attention in the past several years. These materials attract much interest because they possess all the advantages of traditional phenolic resins such as excellent mechanical and thermal properties along with added unique advantages such as near-zero shrinkage upon curing, low water absorption and remarkable molecular design flexibility [1–6]. All these advantages make the polybenzoxazines very promising material for various high-performance applications. However, some applications call for more ductility and low polymerization temperature.

The approach to increase toughness of benzoxazine resins comprises manufacturing of polymer alloys including the use of elastomers [7–14], fiber composites [15–17], and nanocomposites with inorganic additives [18–22]. Another effective pathway which has been utilized recently is introducing additional polymerizable groups into benzoxazine, such as nitrile [23], acetylene [24], propargyl [25], allyl [26], maleimide [27] or epoxy [28] functionalities. This approach allows increasing crosslinking density and minimizing dangling side groups, thus, leading to improved toughness and thermal properties.

A typical crosslinking procedure for benzoxazine resins includes heat treatment at 200 °C [29] or in some cases up to 250 °C [4], and it would be highly advantageous for many applications to decrease the crosslinking temperature. A number of initiators and/or catalysts have been added to benzoxazine systems to decrease the polymerization temperature. The systems studied include acids and phenols [30] or cationic initiators [31]. Furthermore, catalyzing groups such as carboxylic acids [32] or phenols [33] were incorporated into benzoxazine molecules. All these approaches, although can be used successfully, usually lead either to incomplete polymerization at lower temperature or to different crosslinked network structure.

Propargyl containing benzoxazine monomers have been synthesized by Agag and Takeichi [25]. The monomers are attractive since they can be synthesized with high yields from inexpensive materials unlike typical acetylenes. The thermosets obtained by polymerizing these monomers showed improved thermal and mechanical properties. Acetylene functional groups can react together via oxidative coupling in the presence of various metallic catalysts in an oxygen atmosphere to give diacetylene structure with a quantitative yield [34–37].

Diacetylene monomers are well known to be polymerized topochemically in solid state by UV [38,39], gamma radiation [40,41] or thermal annealing [42,43] to give crystalline conjugated polymers. However, diacetylene moieties often do not undergo polymerization in crystalline phase due to unfavorable relative orientation of monomers although they readily react at the

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temperatures above melting point in isotropic melt [44,45]. Taniguchi and his colleagues [46] in the study on thermal reactivity of diacetylenes suggested, based on the obtained results, that the monomers were loosely preorganized for the 1,4-addition to occur in the liquid state.

Assuming some kind of local order is possible even in the melt, it is interesting to see how the polymerization kinetics depends on molecular organization. The well defined example of ordering in the melt is formation of the liquid crystalline phase. The published results on kinetics of polymerization in liquid crystalline state appear to be quite controversial. In some cases, drastic increase in the rate of polymerization was reported [47–52], and, in other reports, no change in the rate of polymerization was observed [53,54]. Hoyle et al. [55] demonstrated that overall polymerization rate was increased because of strong suppression of the rate of termination while the propagation rate remained unchanged. Thus, it is an open question how polymerization kinetics of additional crosslinkable groups in monomers containing diacetylene moiety changes.

In this study, we report an unusual polymerization behavior without having any additives on the novel class of benzoxazine monomer containing diacetylene linkage. The monomer containing diacetylene linkage was synthesized via oxidative coupling from propargyl-functional benzoxazine. The polymerization behavior of the monomer along with model diacetylene compound was studied and discussed.

2. Experimental

2.1. Materials

p-Nitrophenol, tetrabutylammonium bromide, propargyl bromide, and tin(II) chloride dihydrate were used as received from Acros Organics. *p*-Cresol, paraformaldehyde, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, and copper(I) chloride were purchased from Sigma–Aldrich. Dimethylformamide (DMF), pyridine, ethyl acetate, toluene, dioxane, dichloromethane, methanol, hydrochloric acid, and sodium hydroxide were obtained from Fisher. All chemicals were used as received. 1-Methyl-4-(prop-2-ynyloxy)benzene was prepared according to the previously reported procedure [56]. 4-Propargyloxyphenyl-3,4-dihydro-2*H*-1,3-benzoxazine (*p*C-appe) was prepared following our reported method [57]. 6,6′-(Propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine) (BA-a) was synthesized by the solventless method followed by conventional benzoxazine purification [58].

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. Spectra were averaged from 32 transients for ^{1}H NMR and 2500 transients for ^{13}C NMR. FTIR spectra were acquired at a resolution of 4 cm^{-1} with co-addition of 32 scans on a Bomem Michelson MB100 equipped with a deuterated triglycine sulfide (DTGS) detector using KBr plates. Thermal behavior was analyzed with a TA Instruments 2920 differential scanning calorimeter using a heating rate of 10 °C/min in a nitrogen atmosphere. Thermogravimetric analysis was performed on a TA Instruments Q500 TGA with a heating rate of 10 °C/min under nitrogen at a flow rate of 40 mL/min.

2.3. Synthesis

2.3.1. Preparation of 1,6-bis(4-(6-methyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)phenoxy)hexa-2,4-diyne (pC-da)

In 40 mL vial was dissolved *p*C-appe (1.77 g, 6 mmol) in 4 mL of DMF. To the solution, copper(I) chloride (30 mg, 5 mol%), 0.1 mL of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, and 1 mL of pyridine were added. The mixture bubbling with oxygen was stirred at room temperature for 6 h. 30 mL of DMF was added and mixture was filtrated through a short silica column to remove copper. The filtrate was poured into 100 mL of water; the resultant precipitate was filtered, washed with water, and dried under vacuum to afford beige powder (yield: 1.66 g, 94%).

^{1}H NMR ($CDCl_3$), ppm: $\delta = 2.25$ (s, CH_3), 4.52 (s, CH_2, oxazine), 4.66 (s, CH_2), 5.26 (s, CH_2, oxazine), and 6.7–7.1 (14H, Ar).

^{13}C NMR ($CDCl_3$), ppm: $\delta = 50.97$ (Ar–C–N, oxazine), 56.65 (O–C–C≡), 70.90 (C≡C–C≡), 74.73 (C–C≡C–), 80.41 (O–C–N, oxazine).

2.3.2. Preparation of 1,6-bis(p-tolyloxy)hexa-2,4-diyne (model-da)

In 40 mL vial was dissolved 1-methyl-4-(prop-2-ynyloxy)-benzene (0.88 g, 6 mmol) in 4 mL of DMF. To the solution, copper(I) chloride (30 mg, 5 mol%), 0.1 mL of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, and 1 mL of pyridine were added. The mixture bubbling with oxygen was stirred at room temperature for 6 h. The crude product was further purified similar to pC-da to afford light beige powder (yield: 0.84 g, 97%).

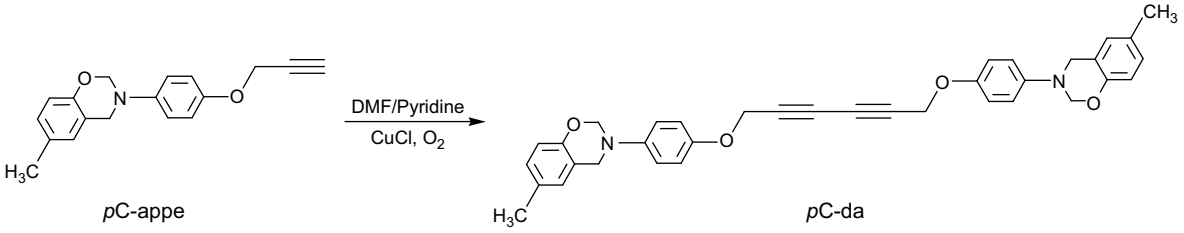
^{1}H NMR ($CDCl_3$), ppm: $\delta = 2.29$ (s, CH_3), 4.71 (s, CH_2), 6.84 (d, Ar), and 7.09 (d, Ar).

^{13}C NMR ($CDCl_3$), ppm: $\delta = 56.29$ (O–C–C≡), 70.90 (C≡C–C≡), 74.70 (C–C≡C–).

3. Results and discussion

3.1. Preparation of diacetylene benzoxazine monomer (pC-da)

Diacetylene benzoxazine monomer, 1,6-bis(4-(6-methyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-yl)phenoxy)hexa-2,4-diyne, designated as *p*C-da, was prepared via oxidative coupling from previously reported [57] propargyl-functional benzoxazine monomer, 4-propargyloxyphenyl-3,4-dihydro-2*H*-1,3-benzoxazine (*p*C-appe) according to Scheme 1. The structure of the monomer was confirmed by ^{1}H and ^{13}C NMR and FTIR. ^{1}H NMR spectrum of *p*C-da indicates the presence of characteristic benzoxazine resonances at 4.52 and 5.26 ppm, and the complete disappearance of the propargyl proton resonance of *p*C-appe at 2.48 ppm (Fig. 1). Also, the



Scheme 1. Synthesis of *p*C-da.

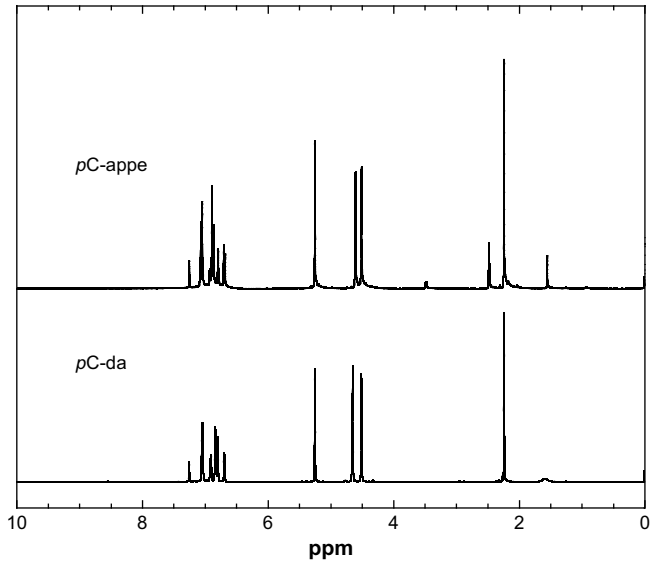


Fig. 1. ^{1}H NMR spectra of *p*C-appe and *p*C-da.

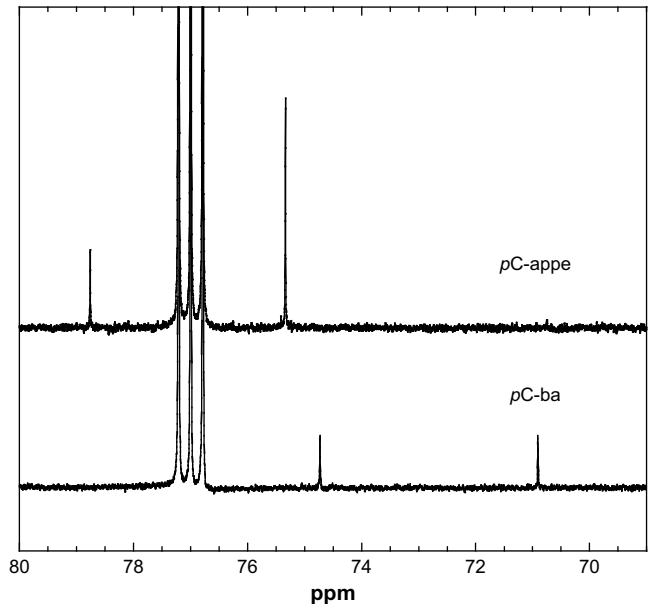


Fig. 2. ^{13}C NMR spectra of *p*C-appe and *p*C-da.

shift of ^{13}C NMR resonances of propargyl ether group from 75.34 and 78.76 ppm to 70.90 and 74.73 ppm is typical for diacetylene formation [56] (Fig. 2). IR spectrum shows the presence of the characteristic absorption band at 944 cm^{-1} due to the benzene ring to which oxazine ring is attached; however, the diacetylene bands at approximately 2150 and 2250 cm^{-1} [56] are extremely weak due to the symmetry of the molecule and are of little analytical use.

In order to understand the thermal crosslinking behavior of the synthesized monomer, a model diacetylene monomer without benzoxazine structure is synthesized following Scheme 2. The

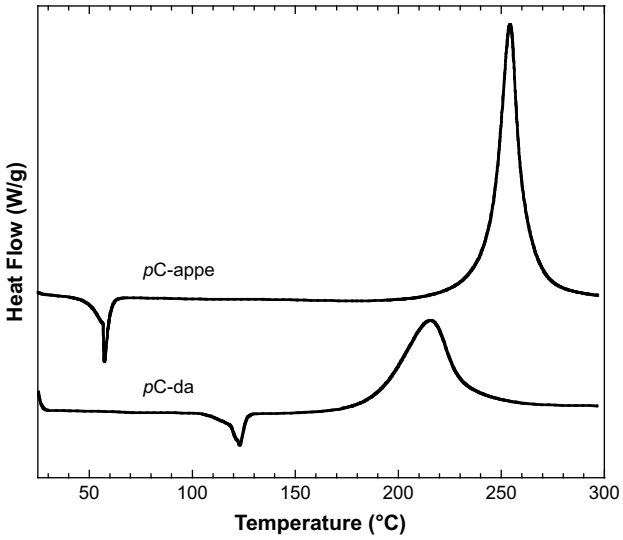


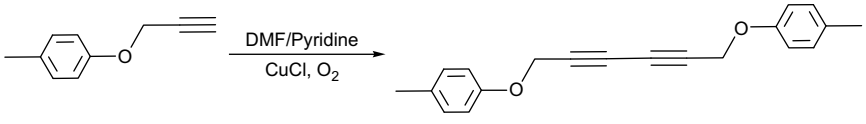
Fig. 3. DSC thermograms of *p*C-appe and *p*C-da.

formation of diacetylene was confirmed by the presence of ^{13}C NMR resonances at 70.90 and 74.70 ppm and the absence of propargyl proton resonance at 2.48 ppm.

3.2. Polymerization behavior of diacetylene monomers

Polymerization of a diacetylene-functional benzoxazine monomer was examined by DSC. Fig. 3 shows the DSC thermograms of *p*C-da in comparison with *p*C-appe. *p*C-appe showed two overlapping exotherms which reflect the crosslinking of propargyl group and the polymerization of oxazine ring starting at 191 °C with a maximum at 235 °C. However, a drastic change in the polymerization behavior of the monomer was observed due to the presence of diacetylene linkage. Surprisingly, DSC thermogram for *p*C-da was shifted to lower temperature and demonstrated an exothermic peak with onset and maximum at 140 °C and 215 °C, respectively. The integration of exothermic peak gives the value of 340 kJ/mol, which is the sum of polymerization enthalpies obtained separately for the model diacetylene monomer and a typical benzoxazine such as BA-a [58], 207 and 149 kJ/mol, respectively. Another interesting feature of *p*C-da is that a single, nearly symmetric exothermic peak was observed. This is contrary to many benzoxazine systems with additional polymerizable groups for which separable peaks are observed. For better understanding of this phenomenon, the thermal polymerization of model diacetylene monomer which has no oxazine group was studied. DSC thermogram for model monomer showed exotherm with the maximum at 211 °C and onset at 140 °C (Fig. 4) which matches well with the position of *p*C-da exotherm.

In order to confirm benzoxazine polymerization in this relatively low temperature exothermic process, IR experiment was conducted for a *p*C-da film cast on a KBr crystal from chloroform and thermally treated at different temperatures. As shown in Fig. 5, the characteristic benzene ring mode of benzoxazine at 944 cm^{-1} quickly disappears already at 150 °C meaning oxazine ring opening, which is quite unlike all the reported benzoxazine monomers.



Scheme 2. Synthesis of model-da.

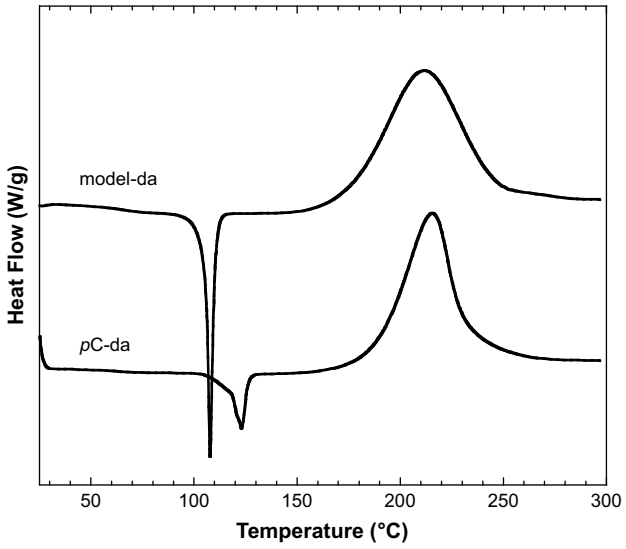


Fig. 4. DSC thermograms of model-da and *p*C-da.

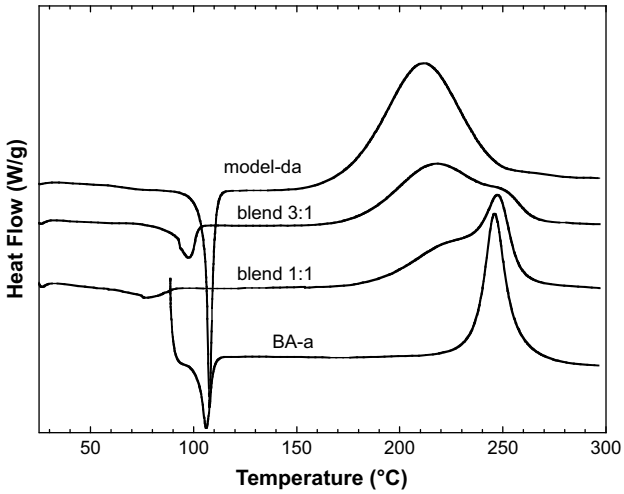


Fig. 6. DSC thermograms of model-da, BA-a, and melt blends of model-da/BA-a with ratios 3:1 and 1:1.

The low polymerization temperature and the appearance of the single, nearly symmetric polymerization exotherm made us think about two possible reasons for such a unique behavior. One possibility is thermal initiation of benzoxazine polymerization assisted by the diacetylene crosslinking exothermic heat. Another possibility is the topochemical effect on the polymerization kinetics. It is possible that local alignment of benzoxazine groups might facilitate the ease of benzoxazine polymerization, due to the presence of diacetylene group. In order to investigate the validity of these hypotheses, the mixtures of model diacetylene monomer and BA-a at different ratios (0.5:0.5 and 0.25:0.75) were prepared by dissolving in chloroform. After drying the solutions, DSC experiments were conducted and the thermograms obtained are shown in Fig. 6. Neat BA-a demonstrated a typical exotherm at 246 °C; whereas the model diacetylene monomer showed the maximum at 211 °C, as described above. For the blends, two polymerization peaks at 218 and 247 °C that correspond to the neat materials were observed. This experimental result contradicts the hypothesis that heat of diacetylene reaction initiates benzoxazine polymerization.

It is now possible to concentrate ourselves on the topochemical reasons. For the topochemical effect, there are two possible causes for the oxazine local alignment. The first cause might be the liquid-crystal like order in the melt due to the rigidity of the diacetylene group. It should be cautioned that it is not necessary to observe packing of many chains like liquid crystal forming molecules to observe topochemical effect on polymerization kinetics. It suffices to have two molecules aligned in a favorable orientation rather than random direction of a true liquid. The second cause is the alignment induced by the polymerization of the diacetylene group. As the diacetylene groups polymerize to form polydiacetylene, the benzoxazine group will become the side chain with constant chain length from the polydiacetylene main chain. This favorable position could facilitate polymerization of oxazine rings. Either way, we do not have means to verify these hypotheses and further detailed study will be needed.

We have found that this effect of exotherm temperature reduction was even more pronounced for the main chain benzoxazine polymers containing diacetylene linkage [59]. Statistically, once a favorable interaction is formed, the neighboring groups will have a better chance to align which might take place in polymeric system.

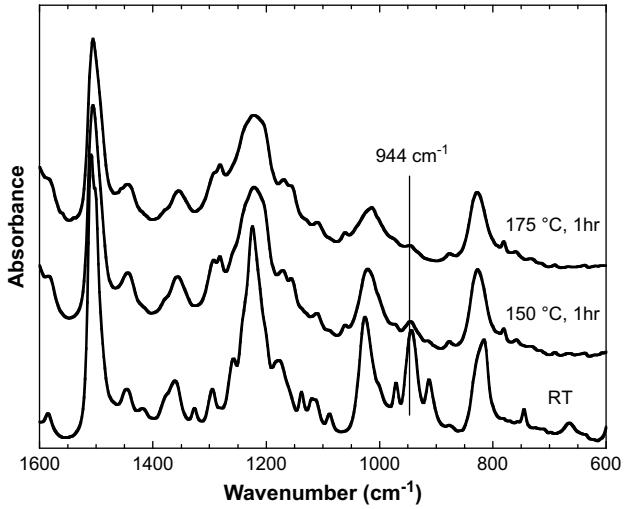


Fig. 5. FTIR spectra of *p*C-da at different stages of polymerization.

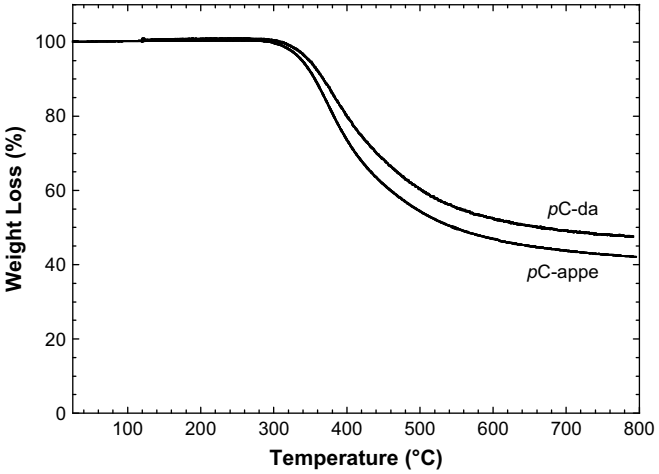


Fig. 7. TGA thermograms of polymerized *p*C-appe and *p*C-da.

3.3. Thermal stability

The thermal stability of the crosslinked diacetylene benzoxazine monomer in comparison with its propargyl precursor (*p*C-appe) polymerized under the same conditions was investigated by TGA under nitrogen and the thermograms are shown in Fig. 7. The 5 and 10% weight loss temperatures are 339 °C and 356 °C for *p*C-appe, and 349 °C and 368 °C for *p*C-da, respectively. The char yield at 800 °C is 42% for propargyl and 48% for diacetylene monomers. These results reveal high thermal stability of diacetylene benzoxazine, although the thermoset is derived from the monomer containing methyl group, which is thermally unstable and is blocking possible benzoxazine crosslink site. Higher stability in comparison with propargyl monomer can be attributed to the improved amine anchoring [25] and higher thermal resistance exhibited by the crosspolymerized diacetylene structure than by structure formed by condensation polymerization of propargyl group.

4. Conclusions

Novel benzoxazine monomer containing diacetylene group as an additional crosslinkable site was successfully synthesized. As a result of introduction of diacetylene structure, benzoxazine monomer demonstrated unique polymerization behavior. DSC study showed a single exothermic peak for benzoxazine and diacetylene polymerizations with onset at 140 °C and maximum at 215 °C, which was significantly lower than for any of the previously synthesized benzoxazines. It made it possible to completely polymerize benzoxazine group already at 175 °C without addition of catalyst. Model studies were conducted to determine the mechanism which led to such unique thermal behavior. The possibility of the exothermic heat accelerating polymerization of oxazine rings was shown to contradict the observed results. Local alignment of benzoxazine groups in the melt that plays an important role in lowering the polymerization temperature was suggested. Along with lower crosslinking temperature, the monomer containing diacetylene demonstrated high thermal stability with char yield of 48% and 349 °C at 5% weight loss which is comparable to the high performance thermosets.

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