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Synthesis and characterization of thermally curable polyacetylenes by polymerization of propargyl benzoxazine using rhodium catalyst

Baris Kiskan, Yusuf Yagci*

Istanbul Technical University, Department of Chemistry, Maslak 34469, Istanbul, Turkey

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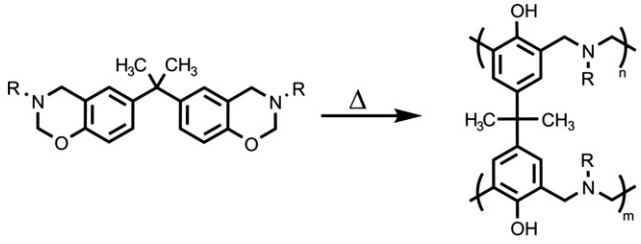
ABSTRACT

A novel acetylene monomer containing benzoxazine group was synthesized and polymerized with [(norbornadiene)rhodium(I) chloride]$_2$ ([(nbd)RhCl]$_2$) to give the corresponding polymer. The effect of triethylamine as co-catalyst in the polymerization was investigated. The spectral and thermal analyses confirmed the presence of benzoxazine functionality in the resulting polymer. It is shown that polyacetylene containing benzoxazine side groups undergoes irreversible *cis–trans* isomerization and thermally activated curing in the absence of any catalyst forming polyacetylene thermoset with high thermal stability.

1. Introduction

In the past ten years, polybenzoxazines have gained immense interest in the field of polymer research from both industrial and academicals point of view. This is undoubtedly due to not only the bulk properties of polybenzoxazines such as thermal and chemical stability, low flammability, stable dielectric constant, low water absorption, and high dimensional stability, but also due to their formation via thermal ring opening of the corresponding benzoxazines without any catalyst and generating any by-products [1–5] (Scheme 1).

Additionally, benzoxazines exhibit molecular design flexibility that allows the properties of the cured materials to be tailored for wide range of applications. Thus, many benzoxazine monomers with specific functional groups were synthesized, and their cure reactions and properties were studied [1,6–15]. However, cured benzoxazine materials are brittle and processing into thin films from monomers is rather difficult. Over the years, several approaches for overcoming these limitations have been implemented. For example, incorporation of benzoxazine structures to the other conventional polymers is an attractive approach to combine the properties of both classes of polymers and develop materials with high thermal stability and easy process ability. Most of the reported examples involved the use of macromonomers that contain one or two benzoxazine functionalities per chain which were cured with low molar mass benzoxazines to yield cross-linked polybenzoxazines with dangling polymer chains [16–19].



Scheme 1. Thermally activated polymerization of difunctional benzoxazine monomers.

During the past few years, considerable attention has been devoted to the incorporation of benzoxazines as a thermally reactive group into the backbone of conventional polymers [20–23]. In these cases, polymers contained higher number of benzoxazine units per chain and upon curing the polymer segments chemically anchored to the network. However, the preparation of the corresponding side chain polymers has scarcely been dealt with. The only previous report concerns the preparation of side chain benzoxazine polymers from poly(*p*-hydroxy styrene) by applying usual benzoxazine synthesis [24]. We have reported an alternative route by copolymerizing maleimide benzoxazine with styrene [25]. A recent report from our laboratory suggested that side chain benzoxazine polymers could also be obtained by a simple a click reaction route. Typically, polystyrene and PVC were functionalized with benzoxazine groups using click reaction of propargyl benzoxazine with azido-containing polystyrene [26] and PVC [27]. In

* Corresponding author. Tel.: +90 212 285 3241; fax: +90 212 285 6386.
E-mail address: yusuf@itu.edu.tr (Y. Yagci).

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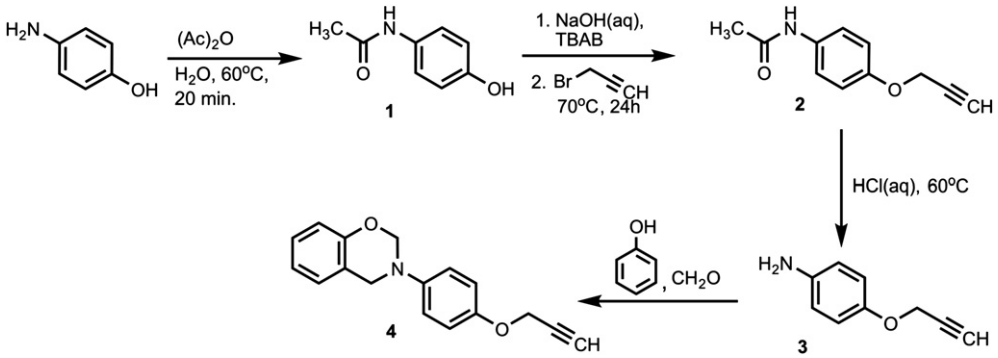


Scheme 2. Synthesis of propargyl benzoxazine.

these click reactions, one of the components is terminal acetylene, which can also be used in various other reactions. It is known that transition metal catalyzed polymerization of substituted acetylenes has been subject of substantial interest, owing to the unique physical and chemical characteristics of the materials thus obtained [28,29]. Accordingly, significant amount of research effort is directed to design and prepare catalyst systems to polymerize acetylene derivatives [29,31]. Among these catalysts, rhodium polymerizes substituted acetylenes like phenylacetylene [32,33], *N*-propargylamides [34–36], *N*-propargylcarbamates [37], propiolic esters [38,39] efficiently initiate the polymerization through an insertion mechanism [37,40]. The resulting polymers are stereoregular with generally *cis–transoidal* main chain structures, which give rise to helical conformations. Another important feature of the rhodium catalyst is related to its tolerance to various solvents and functional groups. For example, protic solvents as amines, alcohols, and even water can be used for such polymerization systems [31,33,41].

In this study, propargyl ether group containing benzoxazine was synthesized and polymerized with Rh catalyst alone and in the presence of triethylamine co-catalyst to yield helical polymers with thermally curable side chain benzoxazines. The structures of the intermediate compounds, monomer and the resulting polymers were characterized. The thermal properties of the cured structures were also investigated and compared with that of typical polybenzoxazines.

2. Experimental

2.1. Materials

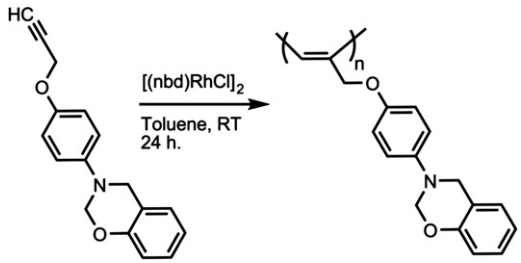
Ethanol (≥99.5%, Aldrich), HCl (37%, Sigma–Aldrich), 1,4-dioxane (≥99.0%, Sigma–Aldrich), chloroform (≥99%, Sigma), acetic anhydride (≥99%, Sigma–Aldrich), sodium hydroxide, (≥97.0%, Sigma–Aldrich), toluene (99.9%, Acros), [(norbornadiene)rhodium(I) chloride]$_2$ [(nbd)RhCl]$_2$ (≥98%, Fluka), triethylamine (99.7%, Acros), anhydrous magnesium sulfate (99%, Sigma–Aldrich), phenol (~99%, Sigma–Aldrich), paraformaldehyde (95%, Sigma–Aldrich), diethylether (≥98%, Sigma–Aldrich), methanol (+99%, Acros Organics), *p*-aminophenol (99%, Acros Organics), propargyl bromide (~80 vol.% in toluene, Fluka) were used as-received.

2.2. Preparation of 3-(4-(prop-2-ynyloxy)phenyl)-3,4-dihydro-2H-benzo[e][1,3] oxazine (4)

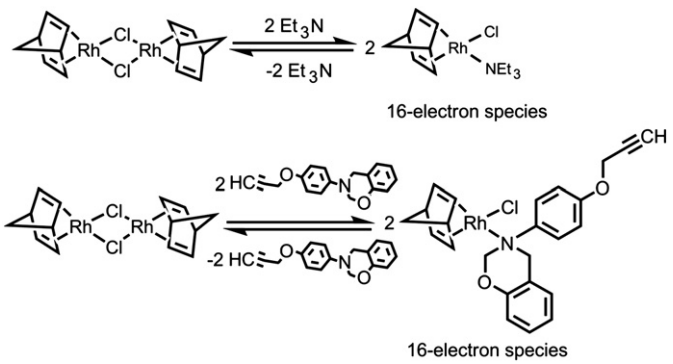
The monomer, 3-(4-(prop-2-ynyloxy)phenyl)-3,4-dihydro-2*H*-benzo[e][1,3] oxazine was synthesized as described previously [26].

2.3. Polymer synthesis

Into a 20 mL Schlenk tube with a sidearm was added 0.85 mmol of propargyl benzoxazine. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. Toluene (3 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving [(nbd)RhCl]$_2$ (10 μmol) in 2 mL of toluene with one drop of TEA, which was transferred to the monomer solution using a syringe. The reaction mixture was stirred at room temperature under nitrogen for 24 h. The mixture was then diluted with 3–5 mL of toluene and the solution filtered for insoluble products. Then the solution was added drop wise to methanol (100 mL) under stirring. The precipitate was collected by filtration and dried under vacuum at room temperature to a constant weight. The polymeric product was isolated as powder with a moderate yield (26%). Additionally, the insoluble product was obtained with an 18% yield. (*Note*: Polymerization without co-catalyst yielded 25% soluble and 16% insoluble products.)



Scheme 3. Polymerization of propargyl benzoxazine with [(nbd)RhCl]$_2$ in the presence of co-catalyst.



Scheme 4. Formation of active species in the [(nbd)RhCl]$_2$/Et$_3$N and [(nbd)RhCl]$_2$/propargyl benzoxazine systems.

Table 1
Polymerization of propargyl benzoxazine with $[(nbd)RhCl]_2$ in the presence and absence of co-catalyst

Polymer	Co-catalyst	Yield (%)	M_n	PDI
PBA-1	Et_3N	26	3450	2.56
PBA-2	–	25	<1000	–

Polymerizations were performed under N_2 at ambient temperature for 24 h.

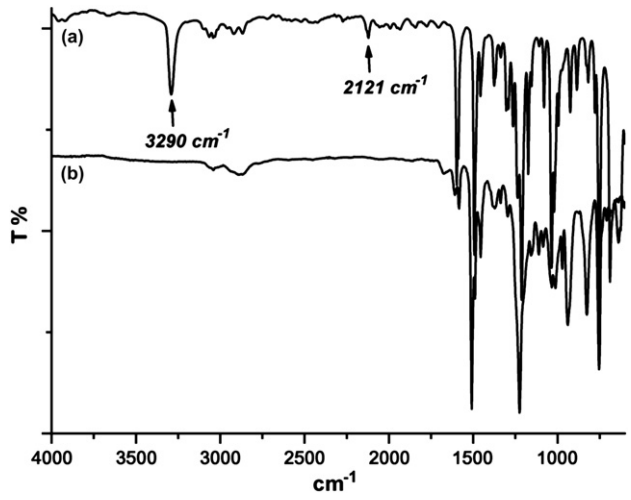


Fig. 1. FT-IR spectra of propargyl benzoxazine (a) and PBA-1 (b).

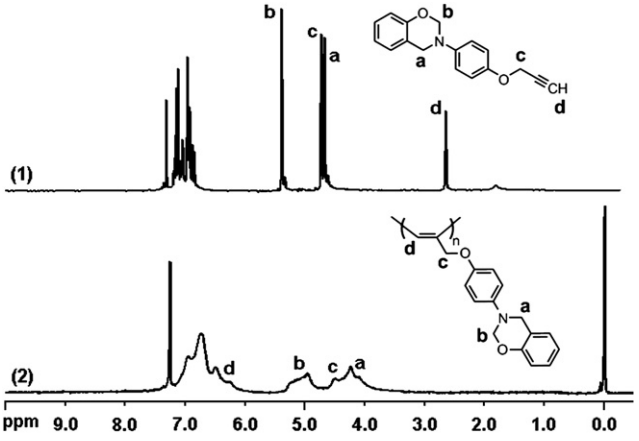


Fig. 2. ^1H NMR spectra of propargyl benzoxazine (1) and PBA-1 (2).

2.4. Characterization

^1H NMR spectra were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. FT-IR spectra were recorded on a Perkin–Elmer FTIR Spectrum One spectrometer. Differential Scanning Calorimetry (DSC) was performed on Perkin–Elmer Diamond DSC with a heating rate of 10 °C/min under nitrogen flow. Thermal gravimetric analysis (TGA) was performed on Perkin–Elmer Diamond TA/TGA with a heating rate of 10 °C/min under nitrogen flow (200 mL/min). Molecular weights were determined by gel-permeation chromatography (GPC) instrument equipped with Waters styragel column (HR series 2, 3, 5E) with THF as the eluant at a flow rate of 0.3 mL/min and a Waters 410 Differential Refractometer detector. UV–vis spectra were recorded in a quartz cell (thickness: 1 cm) JASCO V-530 UV–vis spectrophotometer.

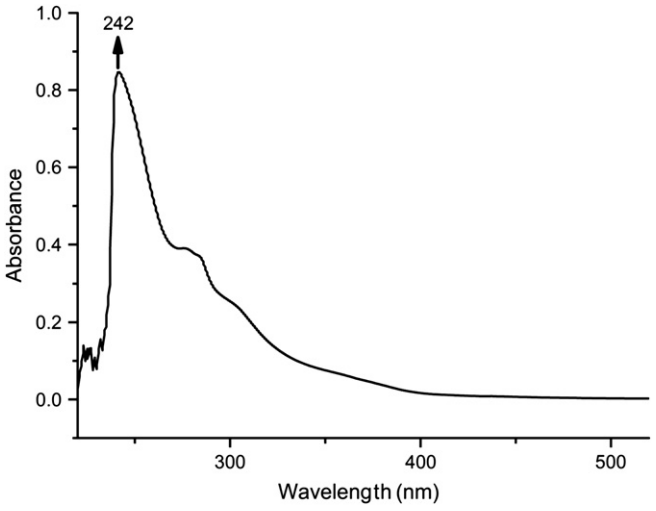


Fig. 3. UV–vis spectrum of PBA-1 in $CHCl_3$.

3. Results and discussions

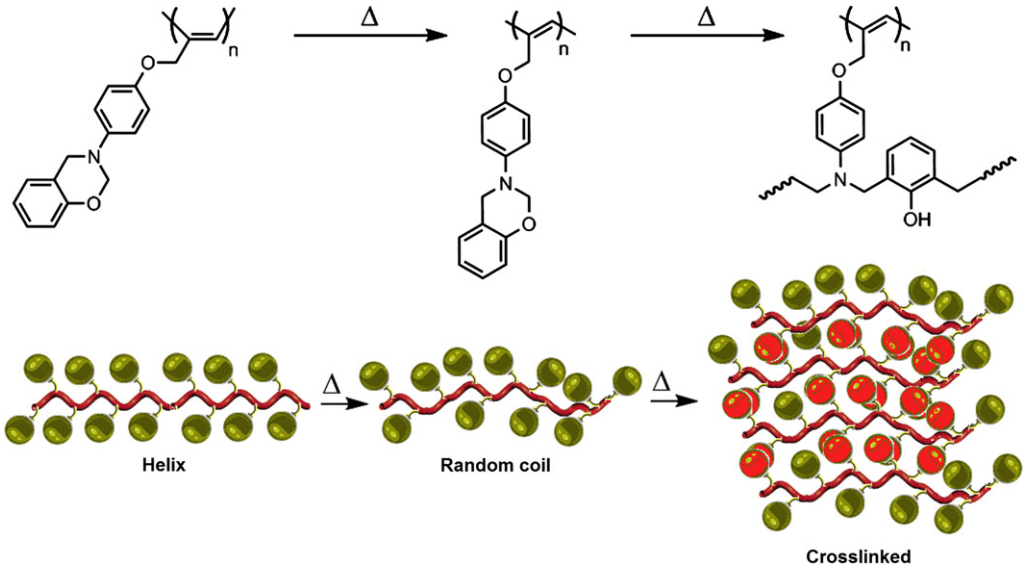
In this study, propargyl benzoxazine was selected as thermally reactive and transition metal catalyst polymerizable monomer, which was prepared as described previously [26] (Scheme 2).

Propargyl benzoxazine is expected to yield polymers upon transition metal catalyst polymerization as it contains terminal acetylene group in its structure (Scheme 3). The Rh-catalyzed reaction in toluene proceeded smoothly at ambient temperature for 24 h and gave the expected light gray poly(acetylene benzoxazine) (PBA), after precipitation in MeOH. In this reaction, Rh(I) was selected as the polymerization catalyst due to its widespread use in related polymerizations.

Although moderate yields were attained, limited chain growth was occurred. This is probably due to the partial activity of the $[(nbd)RhCl]_2$ as catalyst in the polymerization. It is demonstrated that this catalyst does not display a good catalytic activity by itself [30,32]. However, in the presence of Et_3N as co-catalyst, its catalytic activity considerably increases by the loss of symmetry of the 2,5-norbornadiene ligand in the initiating species with the formation of a 16-electron Rh complex $[(nbd)Rh(Et_3N)Cl]$. In our case, trisubstituted amine structure present in the propargyl benzoxazine would presumably act as co-catalyst [41,42] (Scheme 4). The results of polymerizations in the absence and presence of triethylamine are given in Table 1. The pronounced effect of triethylamine in the molecular weight is noted.

Table 2
Spectral characterization of propargyl benzoxazine and PAB-1

Compound	^1H NMR δ (ppm)	^{13}C NMR δ (ppm)	FT-IR ν (cm^{-1})	UV λ_{max} (nm)
Propargyl benzoxazine	2.48 (t, J = 2.4, 1H), 4.55 (s, 2H), 4.61 (d, J = 2.3, 2H), 5.29 (s, 2H), 6.78–7.14 (aromatics, 8H)	51.0, 56.3, 75.4, 78.9, 80.5, 114.4, 116.9, 120.4, 120.8, 126.8, 127.9, 128.5, 143.2, 152.9, 154.4	3290, 3094, 3060, 3036, 2919, 2867, 2121, 1598, 1494, 1213, 1035, 1020, 924, 885, 818, 752	244
PAB-1	4.23 (br s, 2H), 4.48 (br s, 2H), 4.95 (br s, 2H), 6.26 (br s, 1H), 6.48–6.95 (aromatics, 8H)	21.1, 25.6, 50.6, 67.9, 69.7, 80.2, 115.5, 116.8, 120.0, 120.8, 126.7, 127.8, 129.4, 142.3, 153.4, 154.3	3041, 2937, 2893, 1584, 1508, 1489, 1456, 1225, 1034, 1012, 972, 939, 826, 753	242



Scheme 5. Transformation of helical PBAs to random coil and thermally activated cross-linking.

Table 3
DSC characteristics of PBA-1, PBA-2 and propargyl benzoxazine

Polymer	T_g (°C)	Isomerization onset (°C)	Isomerization maximum (°C)	Onset of curing (°C)	Maximum curing (°C)	Heat of exotherm (J/g)
Propargyl benzoxazine	–	–	–	225	240	772
PBA-1	104	140	170	188	221	130
PBA-2	–	–	–	162	192	222

DSC experiments were performed with a heating rate of 10 °C/min under nitrogen flow.

The chemical structure of the PBA obtained was confirmed by both FT-IR and ^{1}H NMR spectral analyses. In the FT-IR spectrum (Fig. 1b), the disappearance of the acetylenic ≡C–H and C≡C stretching vibrations at 3290 cm^{-1} and at 2121 cm^{-1}, respectively, was clearly noted. Additionally, the observation of C=C stretching vibration bands at 1674 cm^{-1} indicates the formation of polyacetylene backbone. The remaining bands of the benzoxazine group, such as aromatic C=C stretching vibrations and C–O–C symmetric and asymmetric vibrations are detected from the FT-IR.

Further analysis of PBA-1 via ^{1}H NMR (Fig. 2.2) showed the disappearance of ≡C–*H* at 2.5 ppm after polymerization. Additionally, appearance of =C–*H* proton at 6.2 ppm indicates the polyacetylene formation with *cis* conformation. As far as the subsequent use of the resulting polymer (PBA) in thermal curing is concerned, the effect of Rh catalyst polymerization reaction on the stability of benzoxazine ring was an important issue. Thus, O–C*H*$_2$–N and Ar–C*H*$_2$–N protons of the oxazine structure appearing at 5.1 ppm and 4.2 ppm, respectively, clearly indicate the retention of the benzoxazine ring during the polymerization reaction. Spectral characteristics of the compounds are tabulated in Table 2.

However, after polymerization in the presence of triethylamine, some insoluble products (PBA-2, see Table 1) were formed, which were still containing oxazine ring as confirmed by FT-IR and DSC analyses. It should also be mentioned that phenolic OH stretching vibrations are detectable in the FT-IR spectra of insoluble PBA-2, which is evidencing the presence of ring opened benzoxazine structures in the polymer.

The absorption spectrum of the PBA-1 is shown in Fig. 3. PBA-1 displayed a strong band of the phenyl chromophore at 242 nm. Little absorption was observed in the long wavelength region,

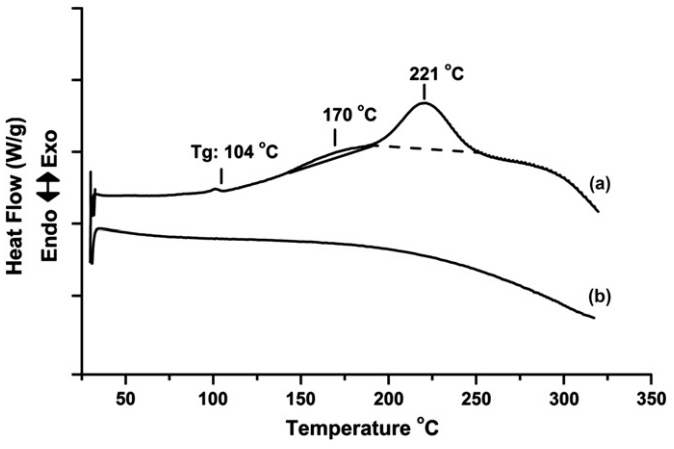


Fig. 4. DSC curves of PBA-1 (a) first and (b) second run 30–320 °C.

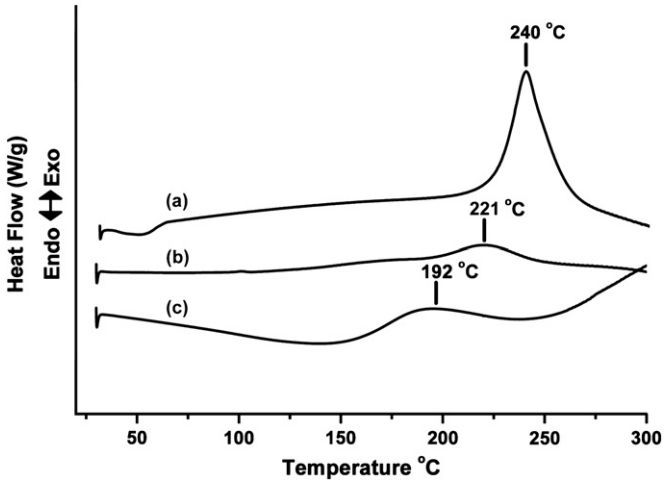


Fig. 5. DSC curves of propargyl benzoxazine (a), PBA-1 (b), and PBA-2 (c), at 30–300 °C.

suggesting that the polymer possesses a short persistence length of backbone conjugation [39] and lack of enough stereo-regularity. It was previously reported that the electronic absorption of a polyacetylene chain increases with its stereo-regularity [43]. Moreover, the steric requirements of aromatic substituents may enforce a planar conformation of polyacetylene backbone, which allows better conjugation of the alternating double bonds and hence makes the polymer absorptive in the longer wavelength region [44]. In our case, however, such steric effect is not valid and as a consequence longer wavelength absorption is not detected.

The ring strain of oxazine allows benzoxazines to undergo ring-opening polymerization under thermally activated reaction conditions. Because of the multifunctional nature, PBAs were expected to form cross-linked networks upon heating (Scheme 5).

The thermally activated cure behavior of PBAs and precursor propargyl monomer were studied by Differential Scanning Calorimetry (DSC) and the results are summarized in Table 3. In Fig. 4, the non-isothermal DSC thermograms of PBA, first (a) and second runs (b), are plotted. As can be seen from Fig. 4a, the polymer exhibits a glass transition temperature (T_g) at 104 °C. The exothermic peak with a maximum of 221 °C was assigned to the ring-opening polymerization of benzoxazine moieties. It is known that the helical structure is deformed by external stimuli such as heat and polar solvents [45]. In the thermogram the *cis*-to-*trans* isomerization of the polymer, starting from ca.140 °C with a maximum at 170 °C is detectable [46,47]. Further heating results in the conversion to a random coil structure. In the second run, however, no thermal transition is observed (Fig. 4b). The fixed random coil form retains its configuration after cross-linking. In Fig. 5, DSC thermograms of propargyl benzoxazine (a), PBA-1 (b), PBA-2 (c) are overlaid. The maximum curing temperatures of PBA-1 and PBA-2 are less than that of propargyl benzoxazine. This behavior can be attributed to the neighboring effect of any ring opened benzoxazine. When phenolic structures, formed from the partial ring opening, are in close proximity, they trigger further ring opening process and reduce the curing temperature. In another words, partially ring opened structures play a catalytic role in the curing process. Consequently, the maximum curing temperature of PBA-2 is lower than PBA-1. This behavior also accounts for the onset curing temperature and heat exotherm. The broad exothermic interval observed in the case of PBA-2 (Fig. 5, curve c) may be due the irreversible *cis*-to-*trans* transition merged with and/or hidden beneath the latter ring opening exotherm. DSC characteristics of PBA-1, PBA-2 and propargyl benzoxazine are expressed in Table 3.

Thermal stability of the cured PBA was investigated by thermogravimetric analysis (TGA) under nitrogen exposure. The TGA

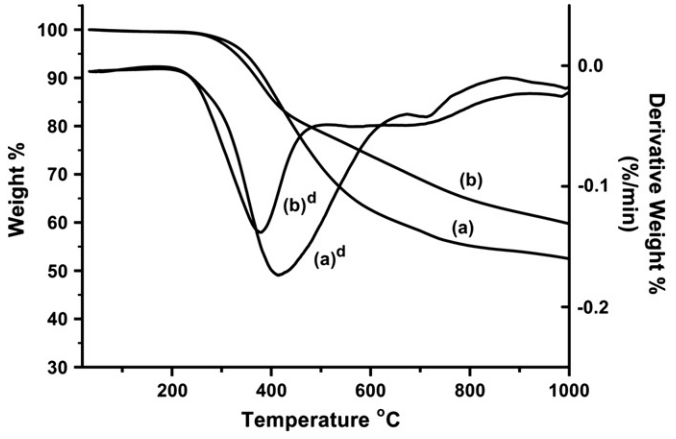


Fig. 6. TGA thermograms and their derivatives of cured propargyl benzoxazine (a), (a^d) and cured PBA-1 (b), (b^d).

Table 4
TGA analysis of cured propargyl benzoxazine and PBA-1

Cured product	$T_{5\%}$ [a] (°C)	$T_{10\%}$ [b] (°C)	T_{max} [c] (°C)	Y_c [d] at 800 °C (%)
Propargyl benzoxazine	348	386	414	55
PBA-1	330	371	380	65

TGA analysis was performed with a heating rate of 10 °C/min under nitrogen flow (200 mL/min).
[a] $T_{5\%}$: the temperature for which the weight loss is 5%.
[b] $T_{10\%}$: the temperature for which the weight loss is 10%.
[c] $T_{max.}$: maximum weight loss temperature.
[d] Y_c: char yields.

and derivate profiles of cured propargyl benzoxazine (a), (a^d) and cured PBA (b), (b^d), respectively, are shown in Fig. 6 and the results are summarized in Table 4. It can be seen that the char yield at 800 °C of the cured PBA is significantly higher than the cured propargyl benzoxazine. This behavior can be attributed to the constructive effect of the molecular weight on the thermal stability which may be explained in terms of more favored intramolecular besides intermolecular cross-linking. However, the initial weight loss temperature of cured PBA is slightly lower than the cured propargyl benzoxazine.

In conclusion, we have synthesized and polymerized benzoxazine based acetylene monomer to obtain thermally activated self-curable polymers. Upon heating benzoxazine acetylene polymers undergo irreversible *cis–trans* isomerization followed by random coil formation and finally intra- and intermolecular curing. Further studies are now in progress to increase yield and molecular weight by using other catalysts together with a search for possible ways for retaining the helical structure in the network for the formation of nano-tunnels.

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