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Synthesis and properties of a new crosslinkable polymer containing benzoxazine moiety in the main chain

Andrey Chernykh, Jinping Liu, Hatsuo Ishida*

Case Western Reserve University, Department of Macromolecular Science and Engineering, 10900 Euclid Avenue, Cleveland, OH 44106-7202, United States

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Abstract

Using difunctional phenolic and amine compounds, a new polymer with benzoxazine groups in the main chain has been synthesized through the Mannich reaction of a phenol, formaldehyde, and an amine. ^{1}H and ^{13}C nuclear magnetic resonance spectroscopies, Fourier transform infrared spectroscopy, size exclusion chromatography, and elemental analysis are used to characterize the resulting polymer. Polymer with molecular weight of approximately 10,000 Da is obtained. The resultant polymer has a moderately broad polydispersity index. The thermal properties of the polymer have also been studied by differential scanning calorimetry and thermogravimetric analysis.

Keywords: Polybenzoxazine; Crosslinkable polymer; Main chain benzoxazine

1. Introduction

Polybenzoxazines have recently been developed for many fields such as the electronics and aerospace industries because they possess various unique properties. Among them are nearly zero shrinkage upon curing [1], thermal stability [2], and chemical resistance. Conventionally, benzoxazine monomers are synthesized from a phenolic derivative, a primary amine, and formaldehyde [3]. Various types of phenols and amines have been utilized for the synthesis of benzoxazine. Initially, variety of difunctional phenolic compounds and monofunctional amines were used [4,5]. Recently difunctional aliphatic amines were studied in connection with monofunctional phenols and exhibited outstanding mechanical properties [6].

In the past, all benzoxazine studies were reported using preformed benzoxazine monomer as the precursor for the polymerized benzoxazines. It has been reported that monofunctional benzoxazine molecules do not form large molecular weight polymers despite the possibility of forming a linear polymer [7]. Under mild polymerization conditions, chain growth can terminate at the dimer length due to hydrogen bond formation at the growth front [8]. To overcome this problem, many difunctional benzoxazines are used to obtain crosslinked polymers with useful properties. While molecular connectivities have been improved, interference with chain growth by hydrogen bond formation has not changed. This leads us to hypothesize that there might be nanoscale aggregates that are loosely connected even for a homopolymer. If, however, a polymer that has benzoxazine rings in the main chain is developed, the molecular connectivity among these hypothesized, nanoscale aggregates might be dramatically improved, leading to better mechanical and physical properties. There are some applications where polymeric precursors are preferred over monomeric precursors for further polymerization. The possibility of adjusting polybenzoxazine properties due to a rich design flexibility of molecular architectures opens wide opportunities to further enhance the properties over the monomeric benzoxazine resins. Polymeric precursors offer the ability to prepare a varnish with low solid content that forms good quality films.

Initially, we hypothesized that if we use a diamine with both ortho positions occupied, it would be possible to

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

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minimize the formation of branches. The influence of various kinds of reaction conditions on the reaction pathway was explored using the combination of 4,4′-methylene-bis-(2,6-dimethylaniline), formaldehyde and bisphenol-A [9,10]. Thus, a novel linear polybenzoxazine molecule with oxazine rings in the main chain was synthesized for the first time. However, insolubility of the products due to extreme rigidity resulted in a low molecular weight and broad polydispersity, although the choice of solvent was not rigorously optimized. An attempt to overcome this difficulty using a flexible and thus more soluble segment, namely an aliphatic amine, will be attempted in this work. Initial synthetic steps toward higher molecular weight polybenzoxazine with oxazine rings in the main chain and its characterization, which will set up the basis for future research, will be investigated in this paper.

2. Experimental

Chemicals purchased from Aldrich included paraformaldehyde (95%) and bisphenol-A (99+%). 1,6-Diaminohexane (99+%) was obtained from Fluka. Chloroform was used as solvent for polymerization. All chemicals were used as received.

The benzoxazine polymer was synthesized from bisphenol-A, 1,6-diaminohexane and paraformaldehyde by the following procedure (Scheme 1). Using a 1:1:4 molar ratio of the reactants, 1,6-diaminohexane (0.58 g, 5 mmol) and paraformaldehyde (0.6 g, 20 mmol) were stirred in 60 ml of chloroform at room temperature for 30 min, followed by the addition of 1.14 g (5 mmol) of bisphenol-A. The solution was then refluxed for 20 h in a flask equipped with a condenser.

In order to remove the initial reactants and fractionate the higher molecular weight polymer, the chloroform polymer solution was poured into an excess amount of cold methanol. The precipitates were dried for 2 days under vacuum at room temperature.

White powder. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 1.38, 1.60 (8H, $CH_2{-}CH_2{-}CH_2$), 1.60 (6H, Ar−C−CH_3), 2.69, 2.72, 2.75 (4H, N−CH_2), 3.92 (4H, Ar−CH_2−N), 4.81 (4H, O−CH_2−N), 6.62−6.95 (6H, Ar−H). ^{13}C NMR (600 MHz, $CDCl_3$, 298 K): δ 27.48 (2C, C−C−C), 28.41 (2C, C−C−C), 31.39 (2C, C−C−Ar), 41.98 (C, Ar−C−Ar), 50.94 (2C, Ar−C−N), 51.70 (2C, N−C−C), 82.54 (2C, O−C−N), 116.00 (2C, Ar), 119.65 (2C, Ar), 125.66 (2C, Ar), 126.51 (2C, Ar), 143.17 (2C, Ar), 152.19 (2C, Ar). Anal. Found: C, 75.60; H, 7.48; N, 6.87. Calcd. For $(C_{25}H_{32}N_2O_2)_n$: C, 76.53; H, 8.16; N, 7.14.

The structure of the purified compound was verified by proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopies using a Varian Inova NMR spectrometer at a proton frequency of 600 MHz and the corresponding carbon frequency. Deuterated chloroform was used as a solvent for obtaining NMR spectra. Spectra were averaged from 256 transients for ^{1}H NMR and from 10,000 transients for ^{13}C NMR to yield spectra with sufficient signal-to-noise ratio even for the end-group analysis. A relaxation time of 10 s was used for the integrated intensity determination of ^{1}H NMR spectra.

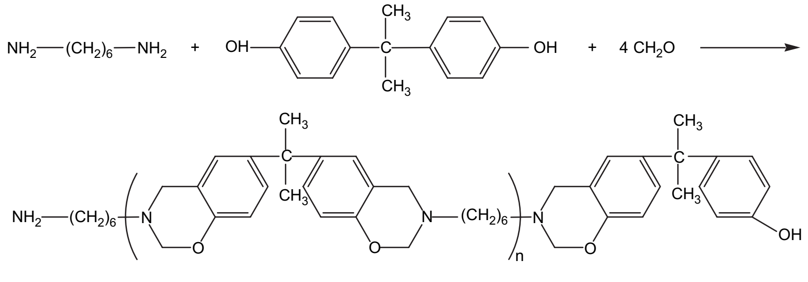
Fourier transform infrared spectra (FT-IR) were obtained using a Bomem Michelson MB100 FT-IR spectrometer which was equipped with a deuterated triglycine sulfate (DTGS) detector. Co-addition of 32 scans was recorded at a resolution of 4 cm^{-1} after purging with dry air. FT-IR spectrum of the polymer was taken by casting a film from polymer solution onto a KBr crystal.

Size exclusion chromatography (SEC) was performed on a Waters workstation equipped with a Waters 440 ultraviolet (UV) detector fixed at 254 nm and a Waters 410 refractive index (RI) detector. Three Styragel columns with pore sizes 1000 nm, 100 nm and 50 nm are connected in series. Tetrahydrofuran was used as the carrier solvent.

Curing behavior and thermal stability were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. A TA Instruments DSC model 2920 was used with heating rate of 10 °C/min and a nitrogen flow rate of 65 ml/min for all tests. All samples were crimped in hermetic aluminum pans with lids. A TA Instruments High Resolution 2950 thermogravimetric analyzer was used with nitrogen as a purge gas for all tests. A heating rate of 10 °C/min with a nitrogen flow rate of 90 ml/min was used for all tests.

3. Results and discussion

An ^{1}H NMR spectrum of the synthesized and washed polymer is shown in Fig. 1. It features well distinguished resonances of amine aliphatic chain protons at 1.38, 1.60 and 2.72 ppm, methyl groups of bisphenol-A at 1.60 ppm, polymer aromatic structure bands at 6.62−6.95 ppm region, and characteristic benzoxazine resonances at 3.92 and 4.81 ppm. Detailed analysis of the spectrum allows the determination of polymer end groups (Scheme 2). Chemical shift of the



Scheme 1. Synthesis of main chain benzoxazine polymer.

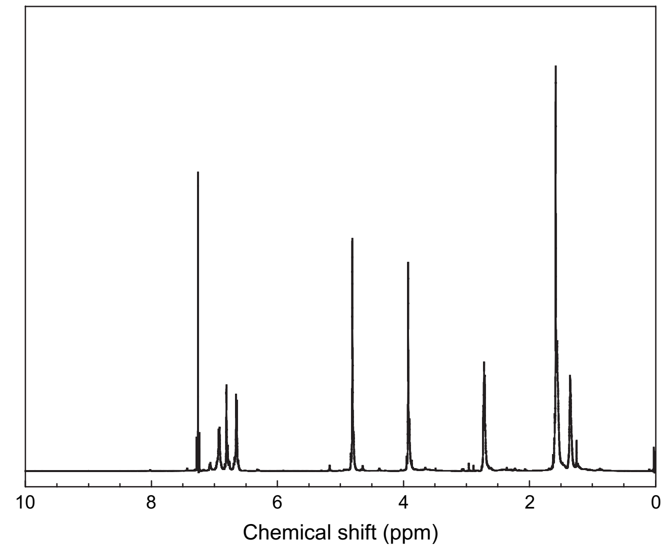
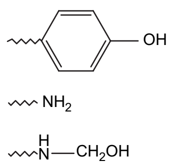


Fig. 1. ^{1}H NMR spectrum of main chain benzoxazine polymer.



Scheme 2. Possible end groups (phenol, primary amine, aminomethylol) of the polymer.

doublet at 7.07 ppm (Fig. 2) coincides with the resonance of the meta protons of bisphenol-A, indicating a free phenolic moiety at the chain end. The position of peak at 4.64 ppm (Fig. 3) is very close to the theoretically estimated resonance for a methylol group (4.60 ppm) and could be assigned to the amine related end species. The total relative intensity of these weak features is about 10% of the regular benzoxazine bands (3.92 and 4.81 ppm), which is in good agreement with the estimated number average chain length from SEC (assuming two end groups per molecule) of about 6 monomer units (although the most probable chain length occurs at 15–18 units). The ^{13}C NMR spectrum (Fig. 4) shows some weak resonances in the aromatic region at 115.01 and 128.18 ppm which are not related to the proposed major structure of the backbone and reflect the carbons of the end group bisphenol-A without an adjoining benzoxazine ring.

Analysis of proton NMR spectra taken at different times during the synthesis reveals structural features and end group changes during the reaction. Changes in concentration of phenol (7.07 ppm) and hydroxymethyl (4.64 ppm) end groups as well as active intermediate triazine [11] (4.39 ppm) are shown in Fig. 5. Concentrations of all three active structures decrease with the same rate after some initial step. By the end of the reaction triazine is completely consumed, although the ratio of phenolic and methylol species reaches a value of 1.3 after

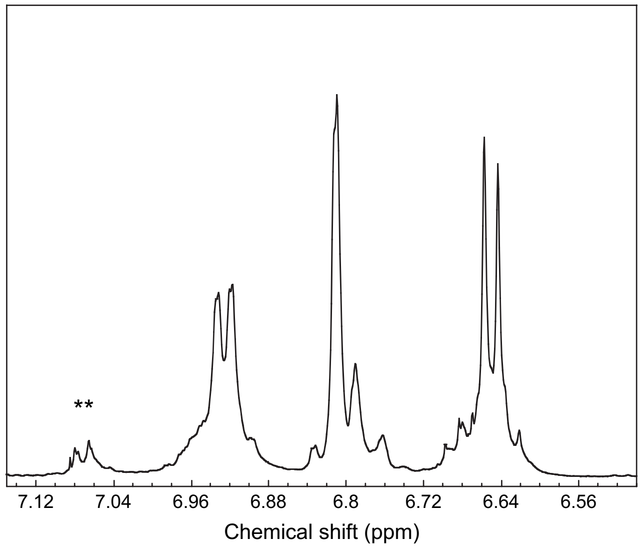


Fig. 2. ^{1}H peak (7.07 ppm) corresponding to phenol end group.

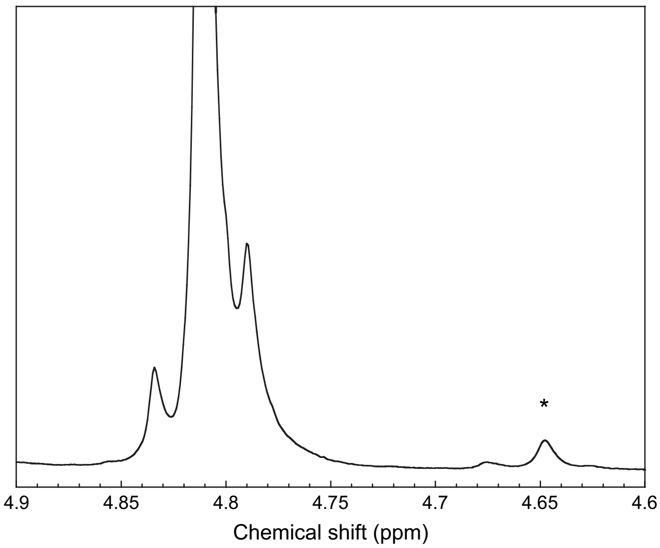


Fig. 3. ^{1}H peak (4.65 ppm) corresponding to aminomethylol end group.

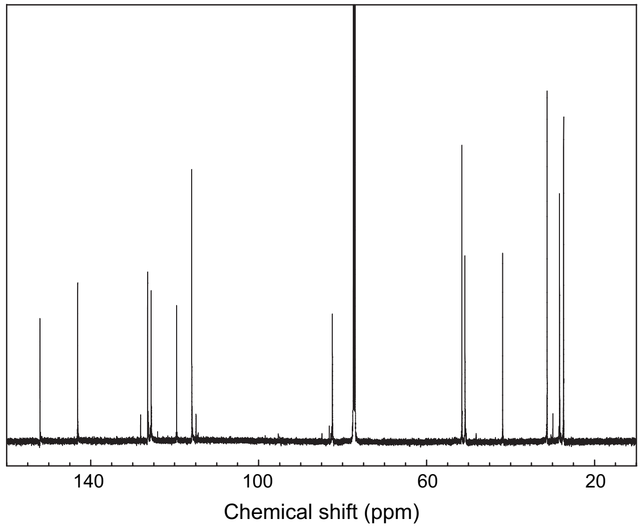


Fig. 4. ^{13}C NMR spectrum of main chain benzoxazine polymer.

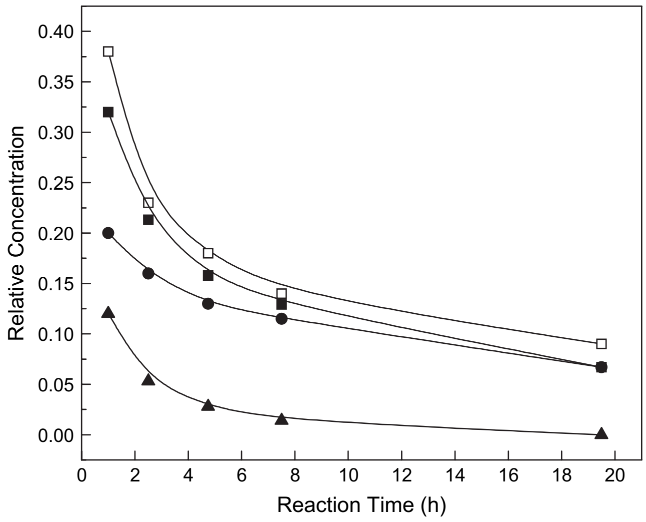


Fig. 5. Relative concentration profile of active groups during the synthesis: (▲) triazine, (●) methylol, (■) total amount of amine related active groups, (□) phenol.

20 h. It is expected that amine and phenol related end groups are equally probable; however, the existence of primary amine end groups is not detected in this analysis.

Fig. 6 represents the FT-IR spectrum of the polymer. If the proposed polymer is a linear structure with oxazine rings terminating the molecule, there should be no hydroxyl groups. However, there is a very weak, broad band around 3350 cm^{-1}. Also, there is a very broad and weak band centered around 2900 cm^{-1}. These features are consistent with the methylol and phenolic OH groups that are hydrogen bonded to the nitrogen atom of the aminomethylol [12,13]. The existence of the primary amine is not clearly visible in the 3400–3200 cm^{-1} region. Thus, even if such groups exist, the concentration must be very low. Strong sharp bands at 2933 and 2858 cm^{-1} are the antisymmetric and symmetric CH_2 bands of the hexane groups. The very strong and sharp band at 1498 cm^{-1} is the in-plane CH bending mode of the tri-substituted benzene ring. The strong band at 1230 cm^{-1} is the aromatic ether stretching. Of particular interest is the strong band at 931 cm^{-1} which is assigned to the benzene ring mode that is attached to the oxazine ring [14]. The medium intensity band at 822 cm^{-1} is from the CH out-of-plane bending mode of the tri-substituted benzene rings. All these assigned bands are consistent with the proposed structure of the substantially linear polymer chains with oxazine rings in the main chain.

The weight average molecular weight of the polymer obtained by SEC with THF as eluent appears to be around 10,000 Da based on polystyrene standards. After fractionation of the product, the achieved polydispersity index, PDI, is 3.0. The change in molecular weight and polydispersity of the product during the reaction is shown in Fig. 7. Both features change somewhat linearly with time. Interestingly, the polydispersity index of the as synthesized polymer, which is about 4.2 at high conversion, is significantly higher than the theoretical value of 2 for polymers derived from condensation polymerization showing "the most probable distribution". The broadening of distribution in this case may be caused by side reactions during synthesis of the linear polymer [15]. The proposed branches possibly could be created by the reaction of aminomethylol species with benzene rings in polymer main chain as well as a result of benzoxazine ring opening by free phenolic structures (Scheme 3). In both cases an open Mannich bridge is formed, which can be confirmed by the appearance of a weak resonance around 3.6 ppm (3.62 ppm according to estimation by ChemDraw software).

Thus, the PDI for such a branched system can be described by the equation [15]:

$$\frac{\overline{X}_{\mathrm{w}}}{\overline{X}_{\mathrm{n}}}=\frac{(1+\alpha)(1-\alpha f/2)}{1-(f-1)\alpha},$$

where α is the branching coefficient, and f is the average functionality of the polymerization system.

Knowing the degree of polymerization and PDI of the polymer, the equation above allows us to estimate α and f, which are equal to 0.74 and 2.25, correspondingly. The calculated average functionality suggests the existence of approximately

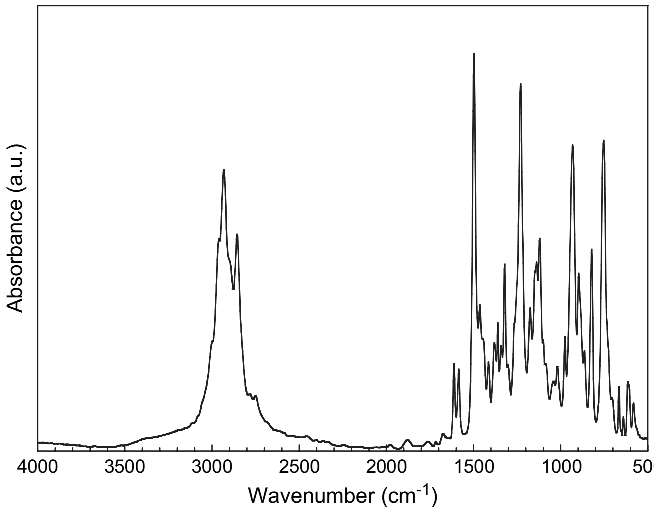


Fig. 6. FT-IR spectrum of the benzoxazine polymer.

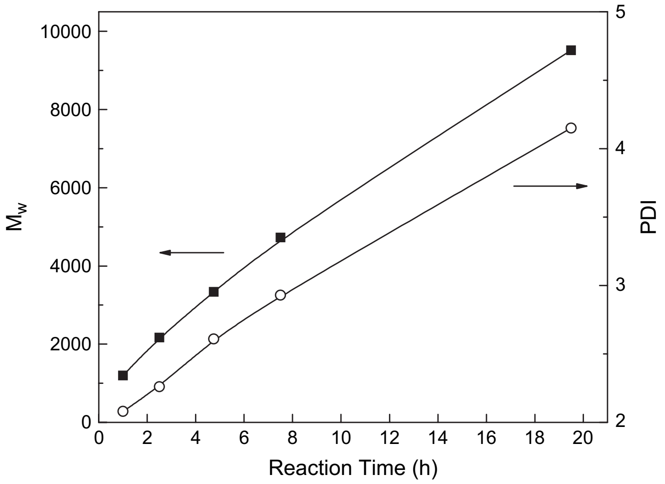
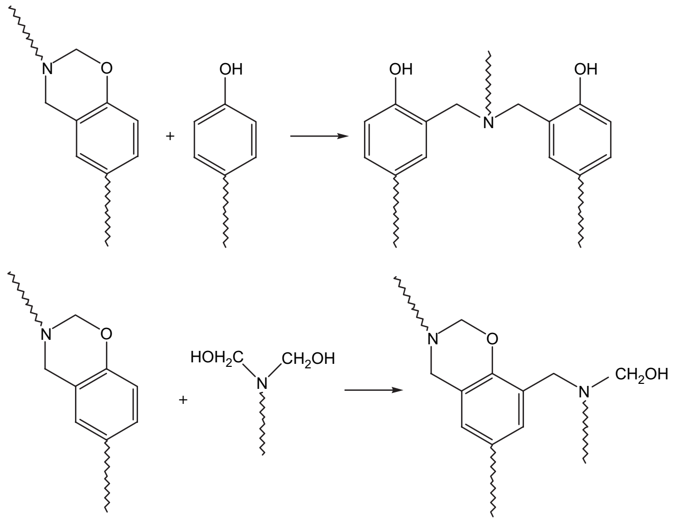


Fig. 7. Molecular weight and polydispersity changes during the reaction.



Scheme 3. Probable mechanism of branching formation during the main chain benzoxazine polymer synthesis.

one branching point per four monomer units. Further detailed spectroscopic analysis will be needed before a conclusive statement can be made. The limited molecular weight of the polymer can be explained by incomplete conversion of the reaction. Branch formation can lead to crosslinking, which means that there exists a critical degree of reaction according to the Carothers equation [15]:

$$p_c = \frac{2}{f_{avg}}.$$

Thus, assuming average functionality to be 2.25, the critical degree of reaction is about 0.9. Since, for condensation polymerization, molecular weight depends strongly on conversion, a high degree of polymerization can be achieved only at conversions close to 100%. For this reason the final molecular weight of the polymer does not reach higher values.

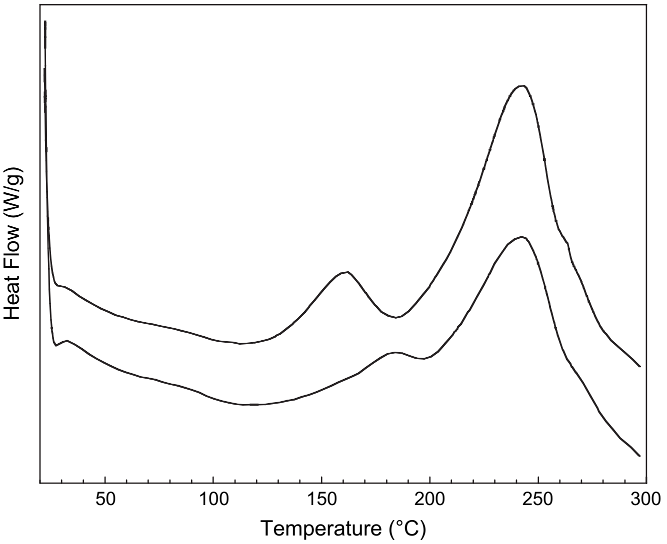


Fig. 8. DSC thermogram of polymer immediately after methanol wash (upper curve) and of material kept for 2 days at room temperature (lower curve).

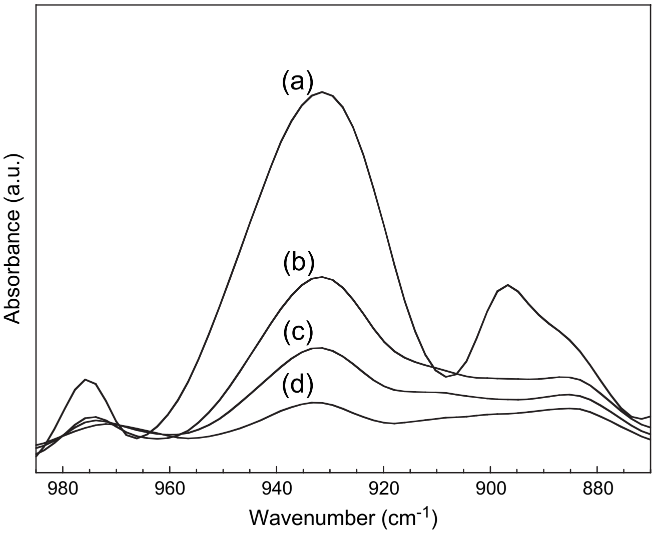


Fig. 9. The consumption of benzoxazine group: (a) initial polymer, (b) 40 min at 180 °C, (c) 20 min at 200 °C, (d) 60 min at 200 °C.

Fig. 8 represents the DSC thermogram of the polymer. No melting transition could be observed for this compound. However, two distinctive exothermic peaks (161 °C and 242 °C) appear. The first peak could be assigned to the crosslinking reaction due to the existence of the methylol end groups. Presence of these species can be detected by NMR as a peak at a chemical shift of 4.63 ppm with a calculated concentration of about 3%. The lower temperature exothermic peak shifts with time to higher temperatures. A possible explanation for this is that, after keeping the polymer for a prolonged time, some active groups react even at lower temperature. The higher temperature peak refers to conventional benzoxazine polymerization. This is confirmed by a decreasing intensity of the characteristic infrared band at 931 cm^{-1} (Fig. 9), which shows consumption of benzoxazine groups in the main chain.

The TGA thermogram of the polymer heated to 170 °C for 1 h is shown in Fig. 10. The derivative weight-loss curve

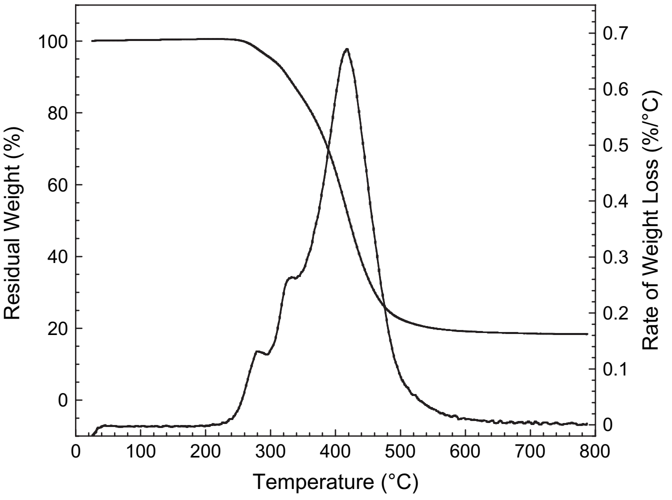
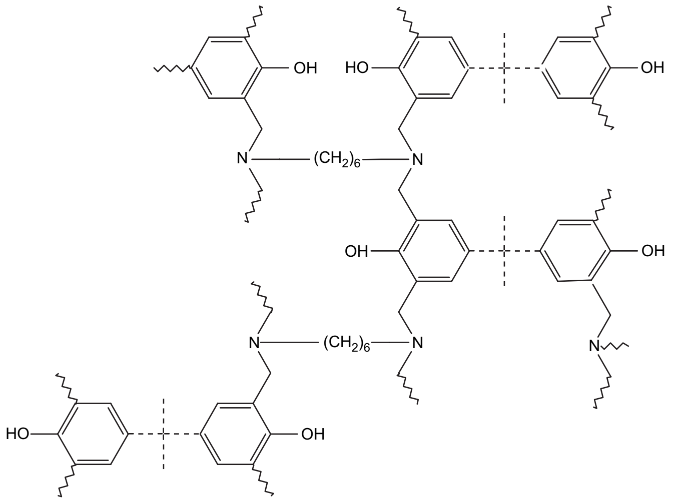


Fig. 10. TGA thermogram of crosslinked benzoxazine polymer.



Scheme 4. Additional connectivity (dashed) of the network structure in the crosslinked main chain benzoxazine polymer compared to the crosslinked aliphatic diamine-based benzoxazine.

shows that the polymer degrades in a three-stage weight-loss process. However, in comparison with the polymer derived from a similar diaminohexane based monomeric benzoxazine [6], the crosslinked polymer derived from the main chain oxazine rings seems to be thermally more stable (the temperature of 1% weight loss is 270 °C against 266 °C and 302 °C against 280 °C at 5% weight loss). This could be caused by better decomposition resistance due to the improved network connectivity in the crosslinked material derived from the reactive polymer (Scheme 4). The char yield is 18.4% that is identical to that for the cured diamine benzoxazine monomer which can be explained by both compounds containing the same amount of aliphatic segments in their chemical structures.

4. Conclusions

A novel polymer with benzoxazine units in the main chain has been synthesized. The chemical structure of the chain was characterized by NMR, FT-IR and SEC. The quantitative end-group analysis was made by proton NMR. The obtained compound is a thermoplastic polymer with an average molecular weight of about 10,000 Da and a polydispersity index of 3.0. This reactive thermoplastic can be further crosslinked using elevated temperatures, which could enhance the application of polybenzoxazines where increased viscosity, film forming, molecular connectivity and one-dimensional ordering are needed. The polymerization of the reactive polymer was studied using DSC and FT-IR.

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