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ORIGINAL PAPER

A novel benzoxazine monomer with methacrylate functionality and its thermally curable (co)polymers

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Abstract Benzoxazine monomer with methacrylate functionality, namely 2-(2-(2H-benzo[e][1,3]oxazin-3(4H)-yl)ethoxy) ethyl methacrylate (BEM) was synthesized by simple esterification reaction of hydroxyl containing benzoxazine (B–OH) with methacryloyl chloride, and characterized. BEM was then copolymerized with styrene in 1:4 mol ratio by free radical polymerization using 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. The structure, chemical composition, and molecular weight characteristics of the resulting copolymer were confirmed by FT-IR, ^{1}H-NMR spectroscopy, and GPC, respectively. The curing behavior and thermal properties of both monomer and copolymer were also studied by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

Keywords Benzoxazine · Polybenzoxazine · Methacrylate · Copolymer · Thermal curing · Thermoset

Introduction

Polybenzoxazines are class of phenolic thermosets formed by thermal ring opening of the corresponding benzoxazines without any catalyst (see Scheme 1). They can also be polymerized at room temperature by certain conventional cationic initiators [1, 2] and photo-initiators [3]. However, in these cases, mechanical and thermal properties are rather poor due to the formation of N–CH_2–O acetals and complex structures. Thus, thermally produced polymers have attracted more attention due to their typical characteristics including low water absorption, nearly zero shrinkage upon curing, thermal stability, and chemical resistance [4].

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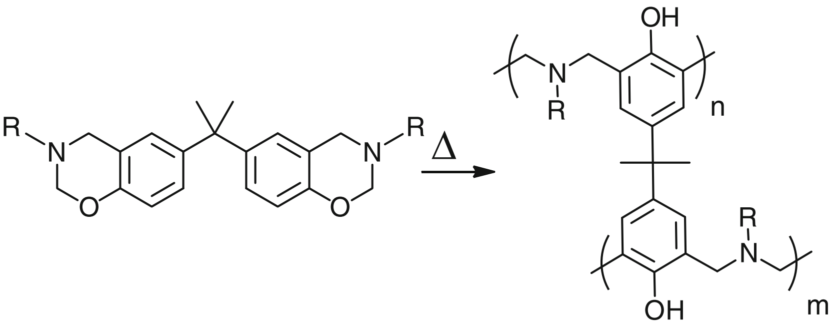


Scheme 1 Thermally activated ring opening reaction of bisbenzoxazines

Due to the straight forward synthesis of benzoxazines from any phenolic compounds and primary amines in conjunction with formaldehyde, these monomers offer molecular design flexibility [5, 6]. A wide range of functional benzoxazine monomers possessing hydroxyl [7, 8], carboxyl [9], nitrile [10], allyl [11], propargyl [12], and phenylazo [13] were readily prepared by taking advantage of such synthetic methodology using suitably selected functional amines or phenols. Benzoxazine monomers and their polymers exhibit rather poor film forming properties and processability, which limit their wider use in many industrial applications. These deterrents can be overcome by either incorporating benzoxazine moieties into polymers or forming linear polymeric precursors [14]. We have previously reported on several polymerization routes to combine benzoxazine structures with conventional polymers, namely polystyrene [15], poly(ε-caprolactone) [16], poly(methyl methacrylate) [17], and poly(propylene oxide) [18]. The polymers contained one or two benzoxazine functionalities per chain, and they showed that film forming properties as well as thermal curability. Several approaches, such as oxidative polymerization, monomer synthesis, condensation reactions, and Pt-catalyzed hydrosilylation reactions were recently reported as successful routes to prepare main chain benzoxazine polymers [19–21]. On the other hand, 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*-hydroxystyrene) by applying usual benzoxazine synthesis [22]. We reported an alternative route by copolymerizing maleimide benzoxazine with styrene [23]. A recent report from our laboratory suggested that side-chain benzoxazine polymers could also be obtained by a simple click reaction route. Typically, polystyrene (PSt) and poly(vinyl chloride) (PVC) were functionalized with benzoxazine groups using click reaction of propargyl benzoxazine with azido-containing PSt and PVC [24–26]. Propargyl ether group containing benzoxazine as click component can be polymerized with Rh catalyst alone. The polymerization conducted in the presence of triethylamine co-catalyst yields helical polymers with thermally curable side-chain benzoxazines [27].

As part of our continuous interest in developing benzoxazine-based thermosets with additional functionalities and enhanced properties, we describe here the synthesis and characterization of a new benzoxazine monomer with methacrylate functionality. The monomer was then copolymerized with styrene by free radical polymerization. The molecular structures of the monomer and resulting side-chain benzoxazine functional polymer were characterized with ^{1}H-NMR and Fourier transform infrared spectroscopy (FT-IR) spectroscopy. Furthermore, thermally activated curing behavior of the monomer and polymer by ring opening of benzoxazine ring was investigated by differential scanning calorimeter (DSC) analysis. Thermal properties of the cured structures were also investigated and compared with the polystyrene networks cross-linked by conventional method.

Experimental

Materials

Formaldehyde (Acros, 96 %), 2-(2-aminoethoxy) ethanol (Acros, 98 %), phenol (Acros, +99%), methacryloyl chloride (Fluka, $\geq$97) were purchased and used as received. Styrene (St; Merck, $\geq$99), triethylamine (Aldrich, $\geq$99.5%) were purchased and used after distillation. 2,2′-Azobis(2-isobutyronitrile) (AIBN) (Fluka, $\geq$98) was used after recrystallization from methanol.

Characterization

^{1}H-NMR spectra were recorded in deuterated chloroform with tetramethyl silane as an internal standard, using a Bruker AC250 instrument at a proton frequency of 250.133 MHz. FT-IR spectra were recorded on Perkin-Elmer FT-IR spectrum. DSC was performed on Perkin-Elmer Diamond DSC with a heating rate of a 10 °C/min under nitrogen flow (20 mL/min). Thermogravimetric analysis (TGA) was performed on Perkin-Elmer Diamond TA/TGA with a heating rate of 10 °C under nitrogen flow (200 mL/min). Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, three ViscoGEL GPC columns ($G2000_{HHR}$, $G3000_{HHR}$, and $G4000_{HHR}$), a Viscotek UV detector and Viscotek a differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30 °C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software.

Synthesis of hydroxyl containing benzoxazine (B-OH)

Synthesis of B-OH was performed as follows. 2-(2-Aminoethoxy) ethanol (42.5 mmol, 4.47 g), phenol (42.5 mmol, 4 g), and formaldehyde (85 mmol, 2.55 g) were dissolved in 150 mL of 1,4-dioxane and refluxed for 3 days. The reaction mixture was filtered and 1,4-dioxane was evaporated under vacuum. Resulting oily product was dissolved in chloroform and washed five times with 40 mL 0.1 N NaOH aqueous solution and distilled water, respectively. Then, the chloroform solution was dried with anhydrous sodium sulfate. Removal of solvent by evaporation afforded orange–yellow oil (Yield: % 46). ^{1}H-NMR ($CDCl_3$, δ): 7.17–6.75 (4H, m), 4.89 (2H, s), 4.04 (2H, s), 3.73 (2H, t), 3.70 (1H, s), 3.68 (2H, t), 3.0 (2H, t).

Synthesis of 2-(2-(2H-benzo[e][1,3] oxazin-3(4H)-yl)ethoxy)ethyl methacrylate (BEM)

2-(2-(2H-benzo[e][1,3] oxazin-3(4H)-yl)ethoxy)ethyl methacrylate (BEM) was synthesized by an esterification reaction. A stoichiometric amount of reactants (B-OH:methacryloyl chloride:triethylamine = 1:1:1) was reacted in dry chloroform at room temperature for 24 h. Reaction mixture was washed successively with cold 1% aqueous HCl, cold 1% aqueous NaOH solution, saturated calcium chloride solution, and finally distilled water. Then, the chloroform solution was dried with anhydrous calcium chloride. Removal of solvent by evaporation afforded orange-yellow oil. (Yield: % 44) ^{1}H-NMR ($CDCl_3$, δ): 6.12 (1H, t), 5.58 (1H, t), 4.88 (2H, s), 4.04 (2H, s), 4.29 (2H, t), 3.68 (4H, m), 2.7 (2H, t), 1.94 (1H, s).

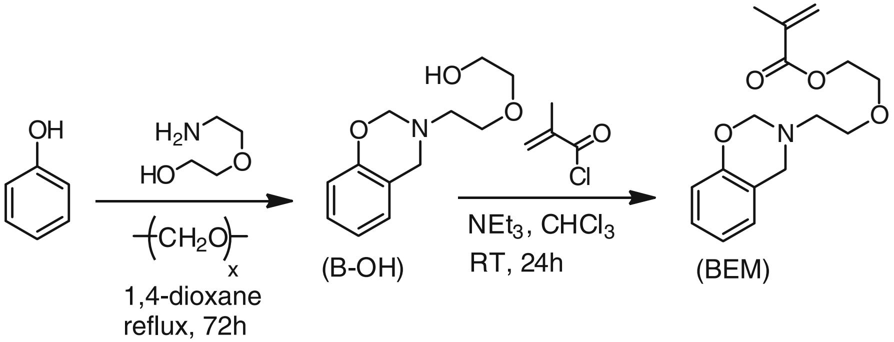
Free radical copolymerization of BEM and Styrene

2-(2-(2H-benzo[e][1,3] oxazin-3(4H)-yl)ethoxy)ethyl methacrylate (BEM) (3.7 mmol, 1.07 g), styrene (14.8 mmol, 1.54 g), and AIBN (0.1 mmol, 0.016 g) were added in a previously flamed and nitrogen-purged Schlenk tube equipped with magnetic stirrer under nitrogen. Polymerization was carried out at 80 °C. After 24 h, the polymerization was terminated by cooling the tube to the room temperature and pouring into 10-fold excess of cold methanol. Final product was filtered and dried at room temperature in a vacuum for 2 days.

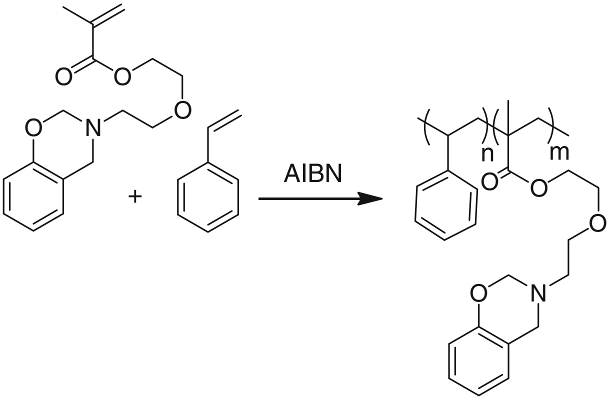
Results and discussions

The precursor compound, mono-hydroxyl functional benzoxazine (B-OH) was prepared from 2-(2-aminoethoxy)ethanol and phenol, and used for the synthesis of the desired bifunctional monomer, 2-(2-(2H-benzo[e][1,3]oxazin-3(4H)-yl)ethoxy) ethyl methacrylate (BEM). The synthesis involves simple esterification reaction of the hydroxyl compound with methacryloyl chloride and in the presence triethylamine under inert atmosphere (Scheme 2). The structures of the precursor hydroxyl compound and BEM were confirmed by FT-IR and ^{1}H-NMR, and the related data are given in the experimental section.

2-(2-(2H-benzo[e][1,3] oxazin-3(4H)-yl)ethoxy)ethyl methacrylate (BEM) possesses both methacrylate and thermally curable benzoxazine functionalities, which may be activated sequentially. For our ultimate purpose, it seemed appropriate to polymerize the methacrylate first, since the benzoxazine ring is thermally stable at the polymerization temperature. Thus, free radical copolymerization of BEM with styrene was performed at 80 °C in toluene using AIBN initiator to yield side-chain benzoxazine functional polymers (Scheme 3).



Scheme 2 Synthesis of B-OH and BEM



Scheme 3 Synthesis of poly(BEM-*co*-St)

The ^{1}H-NMR spectrum of the copolymer (Fig. 1) exhibits typical broad aromatic peaks of polystyrene as well as phenyl protons of benzoxazine ring in the range of 7.0–7.2 ppm. Moreover, the presence of signals at 4.8 and 4.0 ppm in the spectrum corresponding to N–CH_2–O and N–CH_2–Ar clearly indicates the retention of the oxazine ring during the free radical polymerization which is important for the subsequent thermal treatment. Notably, alkyl protons of the ethoxyethyl group appear between 3.5 and 3.8 ppm.

Copolymer compositions of polymers were determined using ^{1}H NMR spectroscopy. The mole fractions of BEM and St were calculated from the ratio of the peak areas of –CH_2 of oxazine rings to the total area of aromatic protons of styrene and benzoxazine. The molar compositions of copolymers and number average molecular weights of P(BEM-*co*-St) determined by GPC are presented in Table 1. As can be seen, polymers with lower molecular weight are obtained when the initiator concentration is increased. It is also noted that BEM is less incorporated into polymer chain in both experiments. This behavior may be due to the lower reactivity of the benzoxazine monomer in the polymerization arising from the

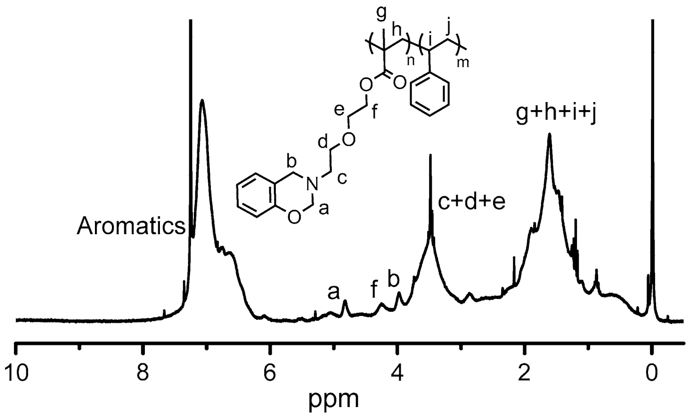


Fig. 1 ^{1}H-NMR spectrum of poly(BEM-*co*-St)

Table 1 Free radical co-polymerization of BEM and St

[BEM] (mmol)	[St] (mmol)	[AIBN] (mmol)	[BEM]/[St]	M_n^a	Composition^b (mole %) poly(BEM/St)
3.7	14.8	0.1	20/80	8900	8/92
3.7	14.8	0.3	20/80	4000	7/93

Polymerization was carried out at 80 °C for 24 h under nitrogen atmosphere

[a] M_n the number average molecular weight determined by GPC measurements based on polystyrene standard

[b] Calculated from ^{1}H-NMR spectrum, poly(BEM/St): poly(BEM-*co*-St)

sterically hindered bulky structure. The concentration of BEM in the feed was deliberately kept low so as to achieve sufficient solubility.

Fourier transform infrared spectroscopy (FT-IR) spectrum of mono hydroxyl functional benzoxazine is shown in Fig. 2a, the stretching vibration of O–H is at 3410 cm^{-1}, which disappears after esterification reaction (see Fig. 2b). Carbon–nitrogen stretching vibrations of oxazine at 1492 cm^{-1} and stretching vibrations of ester carbonyl of acrylate monomer at 1722 cm^{-1} in Fig. 2b are detectable after copolymerization reaction at Fig. 2c, which indicates the incorporation of benzoxazine into the copolymer.

It is known that 1,3-benzoxazines polymerizes exothermally around 200–250 °C, which can be monitored by DSC. The DSC thermogram of hydroxyl functional 1,3-benzoxazine is presented in Fig. 3a. An exotherm can clearly be detected having an onset of polymerization reaction at 173 °C with a maximum at 192 °C. The second exothermic process began after curing with maximum at 234 °C, which was attributed to degradation with probable water elimination.

The curing exotherm of the BEM starts at 171 °C and reaches its maximum at 204 °C, which are relatively low temperatures compared to many benzoxazine monomers (Fig. 3b). This curing exotherm includes both the curing of both double

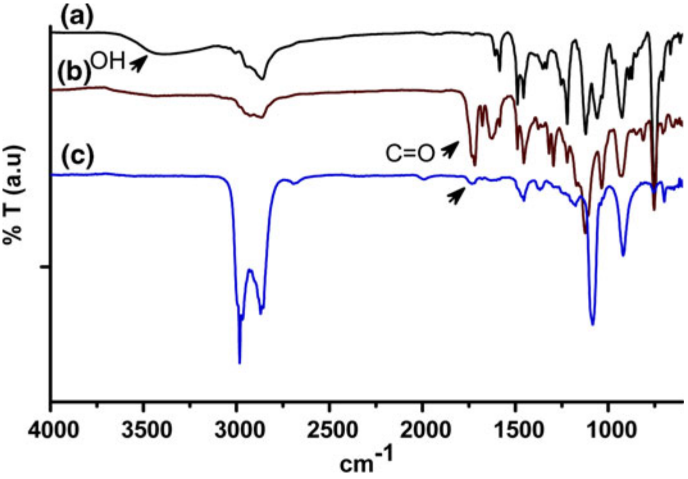


Fig. 2 FT-IR spectra of B-OH (**a**), BEM (**b**), poly(BEM-*co*-St) (**c**)

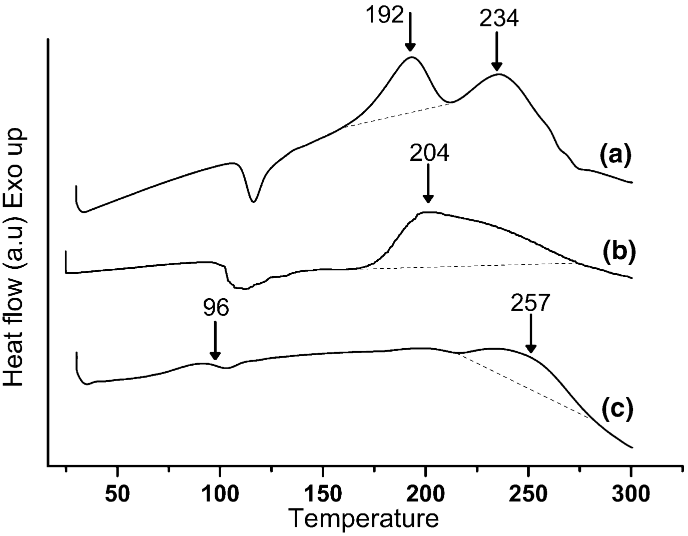


Fig. 3 DSC traces of B-OH (**a**), BEM (**b**), poly(BEM-*co*-St) (**c**)

bonds of methacrylate and oxazine ring. In Fig. 3c, the T*g* of the copolymer emerges at 96 °C and thermally activated curing of benzoxazine units in the copolymer are clearly detectable. The onset and the maximum temperatures for curing are 216 and 257 °C, respectively.

Thermogravimetric behavior of cured hydroxyl containing benzoxazine (b) is compared with cured copolymer (a) and polystyrene beads (c) in TGA thermogram and derivative weight (%) graph (Figs. 4 and 5). Hydroxyl containing poly(benzoxazine) underwent decomposition in two stages. The first degradation is Mannich base

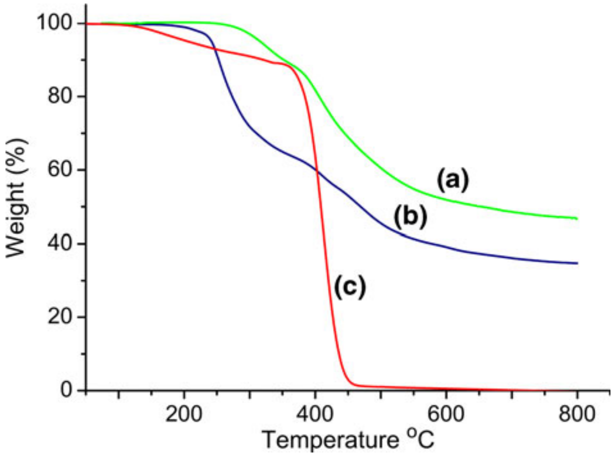


Fig. 4 TGA thermograms of cured poly(BEM-*co*-St) (**a**), cured B-OH (**b**), and polystyrene beads (**c**)

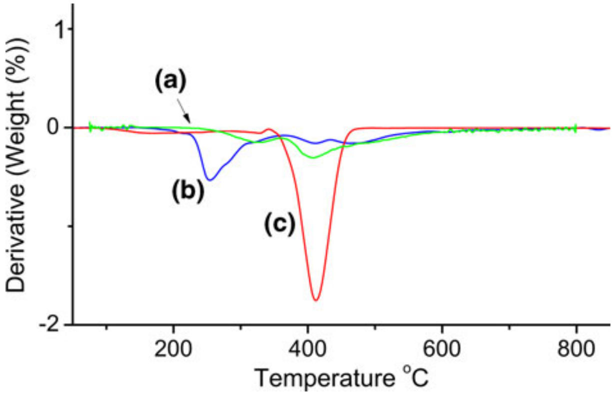


Fig. 5 Derivative of TGA thermograms of cured poly(BEM-*co*-St) (**a**), cured B-OH (**b**), and polystyrene beads (**c**)

cleavage; subsequent weight loss can be attributed to the phenolic decomposition. Thermal aromatization and cross-linking during degradation will finally lead to char formation [28, 29]. The temperature for 5% weight loss is 240 °C and 10% weight loss is 250 °C. Char yield at 800 °C is 34%. The cured copolymer was also degraded in two stages. The first degradation can be speculated as the delayed Mannich base cleavage and the second can be attributed to thermal aromatization according to Fig. 5. The temperature for 5% weight loss is 312 °C and 10% weight loss is 350 °C. Char yield at 800 °C is 46%. The TGA results indicate that, when polystyrene beads exposed to elevated temperatures, the polymer beads collapse at about 120 °C. The collapsed beads start to vaporize at temperatures greater than about 275 °C. Complete volatilization occurs in the temperature range 460–500 °C [30]. The cross-linked copolymer exhibited higher thermal stability due to the additional benzoxazine groups compared to polystyrene beads. Besides, the char yield and overall thermal stability of cured copolymer is even higher than the hydroxyl containing polybenzoxazine.

In conclusion, bifunctional monomer possessing both methacrylate and benzoxazine functionalities, polymerizable by free radical and thermally activated ring opening reactions, respectively, was synthesized and characterized. It was found that free radical copolymerization of this monomer is a convenient pathway that allows easy synthesis for polymers with side-chain benzoxazines which can be cured thermally. The polymerization behavior of the monomer and its styrene copolymer was studied by DSC. Thermally cured copolymer exhibited an excellent thermal stability.

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