Synthesis and Characterization of Boron Acrylate–Styrene Copolymers*

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Abstract

Boron acrylate monomer was synthesized by esterification reaction. Boric acid, neopentyl glycol and HEMA (2-hydroxyethyl methacrylate) were reacted to obtain boron containing acrylic monomer. Characterization was achieved by FT-IR, $^{13}$C-NMR, $^1$H-NMR ve $^{11}$B-NMR and results of synthesized monomer were compared with HEMA. Homopolymer and copolymers with styrene (St) and methyl methacrylate (MMA) were synthesized by free radical polymerization. Properties of copolymers synthesized with St were examined in detail. Monomer reactivity ratios for the studied monomer pair were calculated by using extended Kelen-Tudos (EKT) method. Copolymerization composition and reactive ratios showed that the copolymerization occurred randomly. Thermal behaviors of synthesized polymers were studied by TGA and DSC methods. Boron acrylate homopolymer showed one glass transition temperature at 74.2 °C. Depending on the copolymer composition, the glass transition temperatures of boron acrylate-styrene copolymers have between at 62.9 °C and 97.2 °C.

Keywords: Boron acrylate; polystyrene; reactivity ratio; free radical polymerization

1. Introduction

Boron compounds have specialized roles in high strength, low weight structural materials. For example, boron is used in glass and ceramic industry for making material resistant to heat. In increasing the flame retardancy of polymeric materials the use of borates was probed earlier in the 20th century. Borates are noticeable flame retardants because impenetrable glass coatings form when they thermally degrade. [1]. Boric acid and borate salts have been used as flame retardant additives since early 1800s, but they have been less studied than phosphorous, halogen and other compounds. The use of borates in enhancing the flame retardancy of polymeric materials was reported earlier in the 20th century [1-2]. Borates are effective flame retardants because impenetrable glass coatings form when they thermally degrade. The glass coatings form on the surface, and can contribute to the intumescent effect, because they exclude oxygen and prevent further propagation of combustion. The water of hydration is lost by endothermic decomposition and therefore both dilutes and cools, by absorbing the thermal energy from the flame. The flame retardant action of the boron-containing compounds on polymeric materials is chemical as well as physical. It was found that these inorganic boron compounds promote char formation in the burning [3] process. Acrylic polymers can be used in many industries, primarily in dye industry, and also it has many copolymer derivatives. Acrylates are a family of polymers, which are a type of vinyl polymer. Acrylate monomers are esters which contain vinyl groups, that is, two carbon atoms double-bonded to each other, directly attached to the carbonyl carbon. Some acrylates have an extra methyl group attached to the alpha carbon, and these are called methacrylates. In this study, boron containing acrylic monomer was synthesized and characterized. Synthesized monomer was polymerized via free radical polymerization and copolymerized with styrene monomer. Emerging monomer and polymers were characterized with FT-IR, $^{13}$C-NMR, $^1$H-NMR and $^{11}$B-NMR. The thermal behaviour of these compounds were examined by DSC and TGA analyses.

2. Experimental

2.1. Materials

Styrene (St, 99%, Aldrich), it was passed through a basic alumina column to remove the inhibitor before use and distilled in vacuo over CaH$_2$ just before use. Hexane ($\geq$ 99%, Sigma), Toluene ($\geq$ 99%, Sigma), Diethyl ether (Carlo Erba), Methanol (99.9%, Merck), Dimethylformamide (DMF) ($\geq$ 99.5%, Merck), 1,4-Dioxane (99.5%, Labkim), Dimethyl-1,3-propanediol (Neopentyl glycol) (99%, abcr), 2-Hydroxyethylmethacrylate (HE-
MA) (BDH Chemicals), Hypophosphorus acid, 50% w/w aqueous solution (acer), Hypophosphorous acid, 99.5-100.5%, Merck), 2-Methylhydroquinone (99%, abcr), 2,2'-Azobis(2-methyl-propionitrile) (AIBN) (98%, Acros Organics) were used as received. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over benzophenone-Na.

2.2. Equipments

FT-IR analyses were performed with Thermo Scientific Nicolet IS FT-IR Spectrometer. Resolution mode is 4 cm⁻¹. Sixteen scans were averaged for each sample in the range 4000-400 cm⁻¹. ¹H-NMR, ¹³C-NMR, ¹¹B-NMR analyses were performed with Agilent VNMRS spectrometer at 500 MHz. Deuterated dimethyl sulfoxide (DMSO-d6) and deuterated chloroform (CDCl₃) were used as solvent. Gel Permeation Chromatography (GPC) analyses were performed with a set up consist of Agilent pump and refractive index detector and three Agilent Zorbax PS 1000S, 300S, 60S columns (6.2 x 250 mm, 5 micron) measuring in the range of 10⁴-10⁶, 3x10³-3x10⁵,5x10²-10³ respectively. THF was used as the eluent at a flow rate of 0.5 ml/min at 30°C. Mws were calculated with the aid of pSt and pMM standards. Viscosities of polymer solutions were measured with DMF as a solvent at 25 °C by using Ubbelohde glass viscometer. The driving pressure in this viscometer was determined by measuring the distance from the level of the liquid in the bulb to the level, which is the bottom of the capillary. Differential Scanning Calorimetry (DSC) measurements were performed with TA DSC Q10 instrument in a flowing nitrogen atmosphere from 30°C at scanning rate of 10°C/min. Analyses were performed with TA Q50 instrument under the nitrogen atmosphere at a heating rate of 20°C/min rising rom room temperature to 800°C. The weights of samples are between 6-10 mg. Calibration was achieved with indium as reference material.

3. Synthesis

3.1. Synthesis of boron acrylate monomer (BAc)

The monomer was synthesized with two step by esterification reaction. In first step 17 mL toluene was added to a 100 mL two-necked round flask that equipped with a Dean-Stark apparatus and a Friedrich condenser. The flask equipped with a stopper and needle for air pump. Additionally the flask equipped with drying tube. The heater was opened and set to 60 °C. Than 5 g boric acid, 0.056 mL Hyphophosphorous acid, Neopentyl glycol was added to system and the heat was set to 125 °C for dissolving. The system was stirred and exp sured to air during all reaction. 2 eqv. water was re moved by azeotropic distillation with Dean-Stark a paratus. In second step 0.0556 g Methylhydroquinone, 9.8 mL HEMA was added to flask and 1 eq water re moved. At the end of reaction the solvent was removed to system with vacuum distillation. Product was sy thesized transparent and liquid. The yield was 78% and it was calculated by water content.

3.2. Synthesis of boron acrylate homopolymer (pBAc)

The polymerizations were performed in a dry Schlenk tube which was charged with determined amount of monomer BAc, 5 ml of methanol and AIBN ( 2.5 mol % of total monomer). Oxygen was removed by three freeze-pump-thaw cycles by applying vacuum and backfilling with nitrogen. The tube with the polymerization mixture was immersed into a silicon oil o bath, preheated to 70 °C. After the desired time, the tube was removed from the bath and cooled rapidly down to ambient temperature, and the reaction mixture was diluted with methanol. The polymers were precipitate into diethyl ether and dried under vacuum.

4. Results and Discussions

Boron Acrylate monomer is classified as a saturated cy clic borate ester which was synthesized from 2,2-dimethyl-1,3-propanediol(neopentyl glycol) and boric acid by esterification reaction (Figure 4.1). This reaction was performed in two-steps. 2 eqv. H₂O collected on first step with dean-stark apparatus, then 1 eqv. H₂O collected on second step. Toluene was to be a carrier phase in this reaction.

Insert Figure 4.1
The FT-IR spectra of HEMA and BAc given in Figure 4.3. Differences between these two spectra are the disappearance of characteristic peak of -OH group around 3420 cm\(^{-1}\) and new B-O band ensued at 1417 cm\(^{-1}\).

Figure 4.4 represented the \(^1\)H-NMR spectrum of BAc which were recorded in CDCl\(_3\). The peak observed between 5.5 ppm and 6.1 ppm corresponded to C=C-H protons. Spectrum indicated two different -OCH\(_2\) protons. One of them observed between 3.8 ppm and 4.2 ppm, the other peaks observed one signal around 3.5 ppm. -CH\(_3\) protons signal were recorded at 1.8 ppm and 0.8 ppm. We showed that the BAc monomer form by comparing \(^1\)H-NMR spectrum of HEMA and \(^1\)H-NMR spectrum of BAc in Figure 4.4 and Figure 4.5. While -OH peak of HEMA disappeared, new C=C-H peaks and -CH\(_3\) peak formed in these reaction.

Boron acrylate homopolymer were synthesized via free radical polymerization with AIBN in methanol at 70 °C for 1 hour (Figure 4.6). The polymer precipitated in diethyl ether. The polymer were characterized with \(^1\)H-NMR and \(^{11}\)B-NMR.

Insert Figure 4.6

The different between \(^1\)H-NMR spectra of BAc monomer and BAc homopolymer is disappearance of the peak between 5.5 ppm and 6.1 ppm corresponded to C=C-H protons in Figure 4.7 because of the polymerization. The spectrum of BAc homopolymer indicated two different -OCH\(_2\) protons like BAc monomer. One of them observed between 3.9 ppm and 4.8 ppm, the other peaks observed one signal between 3.6 ppm. -CH\(_3\) and -CH\(_2\) signals were observed between 1.9 ppm and 0.8 ppm.

Insert Figure 4.7

In \(^{11}\)B-NMR of BAc monomer, there is a sharp peak between -20 ppm and 20 ppm. After polymerization the peak remains the same range but it gets broader (Figure 4.8)

Insert Figure 4.8

p(BAc-co-St) synthesized via free radical copolymerization with AIBN in Toluene at 80 °C for 0.5 hour and precipitated in Hexane (Figure 4.9). The polymer were characterized with \(^1\)H-NMR.

Insert Figure 4.9
In the 1H-NMR spectrum of p(BAc-co-St) (Figure 4.10) peaks appearing at around 6.5-7.5 ppm were assigned to the aromatic protons and peaks appearing at around 3.4-3.6 ppm were assigned to –OCH₂ protons. The other –OCH₂ protons appeared between 3.8 ppm and 4.1 ppm. All other remaining peaks observed between 0.8 ppm and 2.0 ppm.

**Insert Figure 4.10**

Table 4.1 lists the polymer characteristics of the prepared samples. The following notation will be used for the different copolymers. p(BAc) and p(St) are the homopolymers of BAc and St. p(BAc-co-St)-50/50 represents a random copolymer of 50 mol % BAc and 50 mol % St in the monomer feed. Thus, p(BAc-co-St)-10/90 is a random copolymer of 10 mol % BAc and 90 mol % St in the monomer feed. The copolymer compositions of the p(Bac-co-St) copolymers were determined by 1H-NMR. The experimental fraction of BAc monomers was slightly lower than the corresponding fraction in monomer feed, as shown in Table 4.1.

**Table 4.1 : Free radical copolymerization of BAc(M₁) and St (M₂) at 80°C.**

**Insert Table 4.1**

In the 1H-NMR spectra of p(BAc-co-St) copolymers spectra peaks appearing at around 6.5-7.5 ppm were assigned to the aromatic protons from p(St) polymer fraction, at around 3.4-3.6 ppm were assigned to –OCH₂ protons from p(BAc) polymer fraction. The compositions of the copolymers in Table 4.1 were calculated on the basis of the 1H-NMR results, comparing the values of the integrals of the peaks appearing at around 3.4-3.6 ppm, which is characteristic for –OCH₂ protons in the BAc monomer and the peaks appear in the range of 6.5-7.5 ppm which are for aromatic protons of St monomer. Copolymerization of newly synthesized Boron acrylic monomer (BAc) with St was evaluated by free radical polymerization with different monomer feeds to calculate the reactivity ratio of the monomers. For this purpose, during the copolymerizations, total monomer composition and time were maintained constant as well as temperature within ±0.1 °C. All runs were carried out by employing the initiator 2.5 mol % of the total monomer amount. Monomer reactivity ratios are important quantitative values to predict the copolymer composition for any starting feed in the batch, semi-batch or continuous reactors and to understand the kinetic and mechanistic aspects of copolymerization. The change in the reaction medium with conversion affects the monomer reactivity ratio values. Among several procedures available to determine monomer reactivity ratio, the methods of Mayo - Lewis (ML) [33], Finemann - Ross (FR) [34], inverted Finemann - Ross (IFR), Kelen - Tüdos (KT) [35], extended Kelen - Tüdos (EKT) [35-36], Tidwell - Mortimer (TM) [37], Mao-Huglin (MH) [38], are appropriate for the determination of monomer reactivity ratios at low conversions. Extended Kelen-Tüdos and Mao-Huglin methods consider the drift of comonomer and copolymer composition with conversion. Therefore they are suitable for the manipulation of high conversion data. For our system the monomer reactivity ratios of BAc and St for their free radical copolymerization were calculated by the well known extended Kelen-Tüdos method from the composition of the monomer feed and that of the instantaneously formed copolymer (Table 4.2).

**Insert Table 4.2**
This method essentially uses the equation

\[ \eta = (r_1 + r_2) \eta' - r_2 \eta'' \]  

(4.1)

where \( \eta \) and \( \xi \) are functions of both feed and copolymer compositions defined as,

\[ \eta = G/(H + \alpha) \quad \text{and} \quad \xi = H/(H + \alpha) \]  

(4.2)

\( H \) and \( G \) are defined using a conversion-dependent constant \( Z \), which is expressed as,

\[ Z = \log(1 - \xi)/\log(1 - \eta) \]  

(4.3)

\( \xi_1 \) and \( \xi_2 \) are respectively, the partial molar conversions in monomers \( M1 \) and \( M2 \) and are given as,

\[ \xi_i = (Y/X) \quad \text{and} \quad \xi_j = (Y + X)/(Y + 1) \]  

(4.4)

where,

\[ Y = F_1/F_2 \quad \text{and} \quad X = F_1/F_2 \]  

(4.5)

\( \mu_1 \) and \( \mu_2 \) represent the molecular weights of monomer 1 and 2, respectively, and \( \omega \) is the total fractional conversion. Thus, the \( H \) and \( G \) values are defined,

\[ H = Y/2^2 \quad \text{and} \quad G = (Y - 1)/Z \]  

(4.6)

and \( \alpha \) is an arbitrary parameter, usually taken as,

\[ \alpha = (H_{\text{max}}/H_{\text{min}})^{1/2} \]  

(4.7)

Monomer reactivity ratios \( (r_1 \) and \( r_2) \) were calculated using experimental data, presented in Table 4.3, treated by EKT method [39].

Insert Table 4.3

The linear plot according to equation (4.1) gives \( r_1 + r_2/\alpha \) as slope and \(-r_2/\alpha \) as intercept (Figure 4.11).

Insert Figure 4.11

The reactivity ratios which were found to be \( r_1 = 0.08 \), \( r_2 = 0.95 \) and \( r_1 \cdot r_2 < 1 \) for the pair BAc-St show that this system undergoes random copolymerization. The value of \( r_1 \) is less than 1 which means that boron acrylic monomer (BAC) terminated propagating chain prefers to add St than another BAC monomer that is involved in the reaction. According to the obtained results it can be concluded that there occurs some composition drift that the produced copolymer contains more St than expected. The value of \( r_2 \) nearly than unity implies the copolymerization initially is dominated by this species which is the more reactive monomer.

Thermal behaviours of synthesized polymers were analysed with DSC and TGA methods. DSC measurements were conducted with a heating rate of 20 °C/min. The thermal stability measurements were evaluated by TGA under nitrogen at a heating rate of 20 °C/min. The results of thermal analysis are summarized in Table 4.4.

Insert Table 4.4

The Tg value of pBAc was 74.2 °C (Figure 4.13) and the Tg value of pSt was 72.3 °C (Figure 4.14). Normally, standart pSt Tg values is above 100 °C in many references. But the Tg of pSt change to the molecular weight which shown in Figure 4.12 [40]. Depending on the copolymer composition, St copolymers glass transition temperatures have between at 62.9 °C and 97.2 °C (Figure 4.15).

Insert Figure 4.13

Insert Figure 4.14

Insert Figure 4.15

Figure 4.16 shows us TGA diagrams of copolymers were determined to be in between TGA diagrams of pBAc and pSt. Based on these results, while St homopolymer and copolymers have one decomposition, BAc homopolymer has two decomposition. In these results, char yields were increased by pBAc content in pSt copolymers.

Insert Figure 4.16
Solubility of synthesized polymers were tested in different solvents. Results can be seen in Table 4.5.

Insert Table 4.5

As a result, BAc homopolymer was dissolved only in DMSO and DMF. On the other hand p(BAc-co-St) copolymer was dissolved in DMSO, THF, DMF, ethylacetate, diethyl ether, methanol. p(BAc-co-MMA) almost showed behaviour as p(BAc-co-St) except ethylacetate. While p(BAc-co-St) was dissolved in ethylacetate, p(BAc-co-MMA) was not dissolved in ethylacetate.

5. Conclusions

The aim of this study is to synthesize novel boron containing monomer and polymers. In this study, BAc monomer initiators was synthesized and used to perform free radical polymerization of its homopolymer and copolymer with St. The structures of the monomer and polymers were characterized and confirmed using NMR and FT-IR spectroscopy. Monomer reactivity ratios for the studied monomer pair were calculated by using extended Kelen-Tudos (EKT) method. Copolymerization composition and reactive ratios show that the copolymerization is occurred randomly. The Tg value of pBAc was 74.2 °C and the Tg value of pSt was 72.3 °C. Depending on the copolymer composition, St copolymers glass transition temperatures have between 62.9 °C and 97.2 °C. TGA diagrams of copolymers were determined to be in between TGA diagrams of pBAc and pSt. Based on these results, while St homopolymer and copolymers have one decomposition, BAc homopolymer has two decomposition. Char yields were increased by pBAc content in pSt copolymers. Also solubility of homopolymers and copolymers were examined with different solvents.

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