Homopolymerization and synthesis of a new methacrylate monomer bearing a boron side group: characterization and determination of monomer reactivity ratios with styrene

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Abstract: Boron methacrylate (BAc) monomer was synthesized via an esterification reaction. Boric acid, neopentyl glycol, and 2-hydroxyethyl methacrylate (HEMA) were reacted to obtain boron-containing acrylic monomer. Characterization was achieved by FT-IR, ^{13}C NMR, ^{1}H NMR, and ^{11}B NMR and the results for the synthesized monomer were compared to those for HEMA. Homopolymer and copolymers with styrene (St) were synthesized via free radical polymerization. The properties of the synthesized styrene copolymers were investigated using several techniques. Monomer reactivity ratios for the studied monomer pair were calculated using the extended Kelen–Tüdos method. Copolymerization compositions and reactive ratios showed that the obtained copolymers had random characters. Thermal behaviors of the synthesized polymers were studied by thermal gravimetric analysis and differential scanning calorimetry methods. Boron methacrylate homopolymer showed one glass transition temperature at 73.7 °C. Depending on copolymer composition, the glass transition temperatures of boron methacrylate-styrene copolymers were between 68.4 °C and 81.5 °C.

Key words: Boron acrylate, polystyrene, reactivity ratio, free radical polymerization

1. Introduction

Boron compounds have specialized roles in many materials due to their good mechanical and thermal properties. Boron is used in the glass and ceramic industries for making materials resistant to heat. Boric acid and borate salts have been used as flame retardant additives since the early 1800s but they have been studied less than have phosphorus, halogens, and other compounds. The use of borates in enhancing the flame retardant property of polymeric materials was reported in the early 20th century.[1,2] Borates are noticeable flame retardants because impenetrable glass coatings form when they are thermally degraded.[1] 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 flame retardant action of boron-containing compounds on polymeric materials is chemical as well as physical.[3] It was found that these inorganic boron compounds promote char formation in the burning process.[4]

Boron-containing polymers are an important class of materials in the field of inorganic and organometallic polymers. Of particular interest is the incorporation of organoboranes into the polymers because they can act as Lewis acids due to the empty p-orbital on the boron center. Boron-containing polymers can be classified as

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main chain and side-chain functionalized compounds.[5] The first main-chain organoboron-containing conjugated polymers were synthesized via hydroboration polymerization, but their characterization was hampered by their sensitivity to air and moisture.[6,7] Chujo and co-workers pioneered the hydroboration polymerization methodology and systematically studied the resulting polymers. They have been successful in synthesizing a number of polymers that bear a boron atom in the main chain.[8] Fabre and co-workers reported the synthesis of boronic acid and boronate ester functionalized polypyrrole and its use as a fluoride sensor was studied electrochemically using cyclic voltammetry.[9] A variety of polymerization methods can be used to prepare organoborane polymers from organoboron monomers.[10,11] Ring-opening metathesis polymerization is another methodology that has been employed for the synthesis of boron-containing polymers from boron-containing monomers.[12,13]

From a family of polymers, acrylates are a type of vinyl polymers. They can be used in many industries, primarily in the dye industry, and also they have many copolymer derivatives. Acrylate monomers, which are esters, 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.

Monomer reactivity ratios are important quantitative values to predict the copolymer composition for any starting feed in batch, semibatch, 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),[14] Finemann–Ross (FR),[15] inverted Finemann–Ross (IFR), Kelen–Tüdos (KT),[16] extended Kelen–Tüdos (EKT),[17] Tidwell–Mortimer (TM),[18] and Mao–Huglin (MH)[19] are appropriate for the determination of monomer reactivity ratios at low conversions. The EKT and MH methods consider the drift of comonomer and copolymer composition with conversion. Therefore, they are suitable for the manipulation of high conversion data.

In the present study, a boron-containing acrylic monomer was synthesized and characterized. Synthesized monomer was polymerized via free radical polymerization and copolymerized with styrene monomer. The reactivity ratio was evaluated by the KT method. Emerging monomer and polymers were characterized with FT-IR, ^{13}C NMR, ^{1}H NMR, and ^{11}B NMR. The thermal behavior of these compounds was examined by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

2. Results and discussion

Boron methacrylate monomer, which is classified as a saturated cyclic borate ester, was synthesized from 2,2-dimethyl-1,3-propanediol (neopentyl glycol) and boric acid via the esterification reaction in Figure 1.

The structure of BAc monomer was confirmed by spectroscopic investigations. The FT-IR spectrum of BAc monomer showed a –CH band at 2960 cm^{-1}, characteristic C=O ester band at 1717 cm^{-1}, C=C band at 1637 cm^{-1}, and B–O group at 1417 cm^{-1}.

Differences in the spectra of 2-hydroxyethyl methacrylate (HEMA) and BAc monomer are the disappearance of the characteristic peak of HEMA's –OH group around 3420 cm^{-1} and new B–O band at 1417 cm^{-1} in Figure 2.
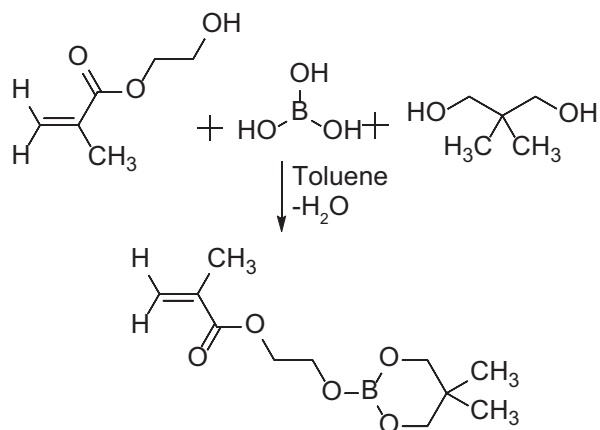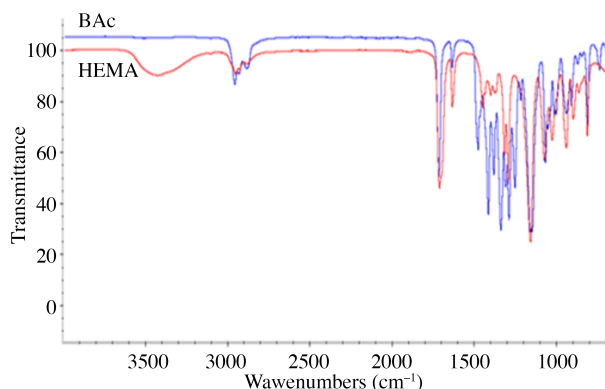
Figure 1. Synthesis of BAc.

Figure 2. FT-IR spectrum of BAc and HEMA.

Figure 3 represents the ^{1}H NMR spectrum of Bac, which was recorded in $CDCl_3$. The peak observed between 5.5 ppm and 6.1 ppm corresponded to C=C–H protons. The spectrum indicated two different –OCH_2 protons. One of them was observed between 3.8 ppm and 4.2 ppm, the other peaks were observed as one signal at around 3.5 ppm. The signals of –CH_3 protons were recorded at 1.8 ppm and 0.8 ppm. According to the ^{1}H NMR spectrum, while the –OH peak of HEMA disappeared, new C=C–H peaks and a –CH_3 peak were formed in these reactions.

Boron methacrylate homopolymer was synthesized via free radical polymerization by AIBN in methanol at 70 °C for 1 h (Figure 4). The polymer was precipitated in diethyl ether and characterized with ^{1}H NMR and ^{11}B NMR.
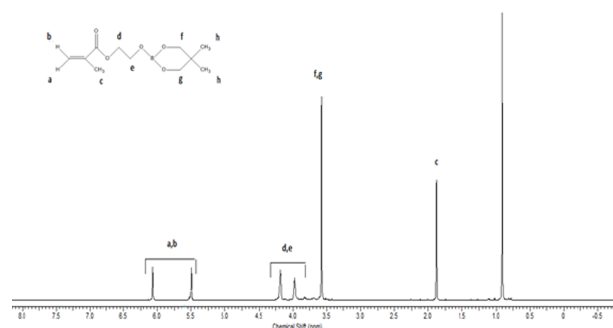

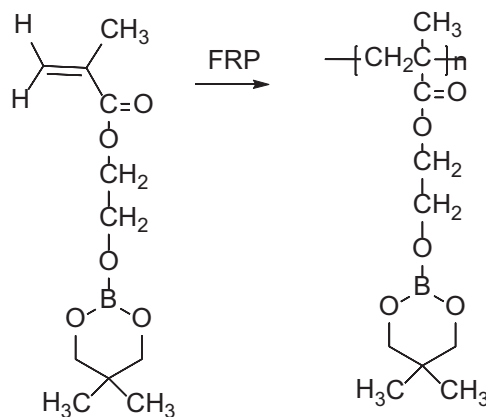
Figure 3. ^{1}H NMR spectrum of BAc.

Figure 4. Synthesis of BAc homopolymer.

We can observe the difference between BAc monomer and BAc homopolymer with disappearance of the peak between 5.5 ppm and 6.1 ppm that corresponded to C=C–H protons in Figure 5 because of polymerization. The spectrum of BAc homopolymer indicated two different –OCH_2 protons like BAc monomer. One of them was observed between 3.9 ppm and 4.8 ppm; other peaks were observed as one signal at 3.6 ppm. –CH_3 and –CH_2 signals were observed between 1.9 ppm and 0.8 ppm.

In the ^{11}B NMR of BAc monomer, there is a sharp peak between –20 ppm and 20 ppm. After polymerization, the peak remains within the same range, but it gets broader as seen in Figure 6.
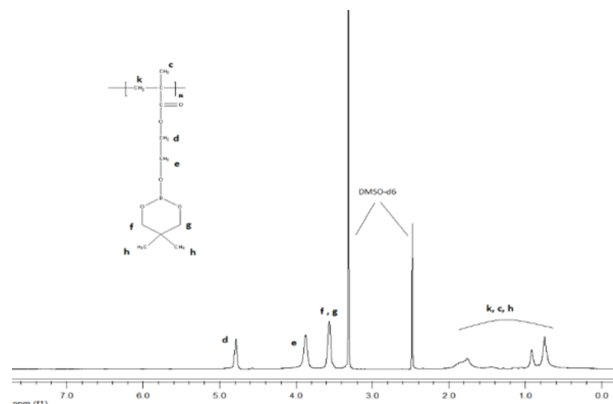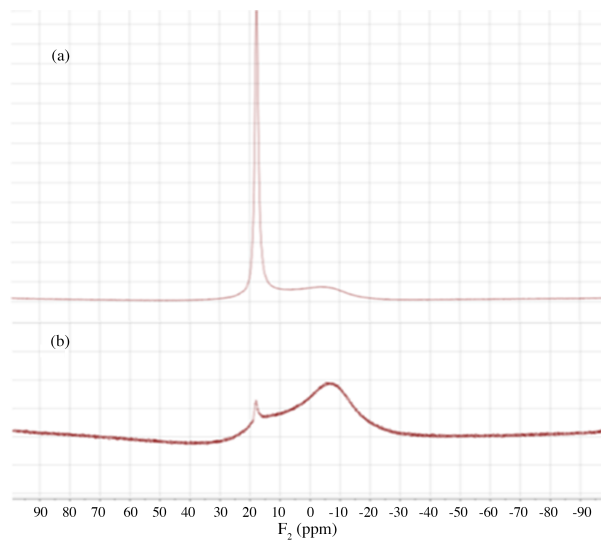
Figure 5. ^{1}H NMR spectrum of BAc homopolymer.

Figure 6. (a) ^{11}B NMR spectrum of BAc monomer, (b) ^{11}B NMR spectrum of BAc homopolymer.

p(BAc-*co*-St) was synthesized via free radical copolymerization with AIBN in toluene at 80 °C for 0.5 h and precipitated in hexane (Figure 7). The polymer was characterized with ^{1}H NMR.
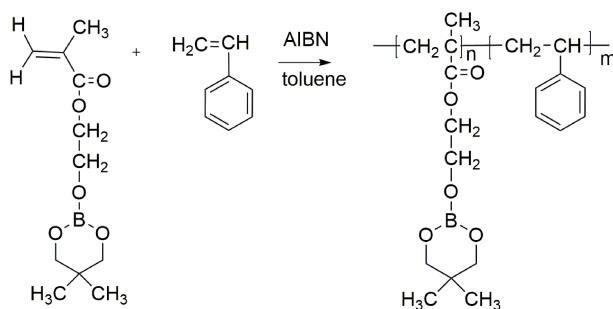

Figure 7. Synthesis of p(BAc-*co*-St) copolymer.

In the ^{1}H NMR spectrum of p(BAc-*co*-St) in Figure 8, the peaks appearing at around 6.5–7.5 ppm were assigned to the aromatic protons and peaks that appeared at around 3.4–3.6 ppm were assigned to –OCH$_2$ protons. Other –OCH$_2$ protons appeared between 3.8 ppm and 4.1 ppm. All other remaining peaks were observed between 0.8 ppm and 2.0 ppm.

In Table 1 free radical copolymerization feeding polymer ratios of the prepared samples are given. 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. As shown in Table 1, copolymers with increasing compositions of boron methacrylate were obtained with overall polymer conversions of 7%, 31%, 12%, 30%, 27%, and 46%. For the homopolymers of BAc and St, conversion of 44% and 29% was obtained, respectively.
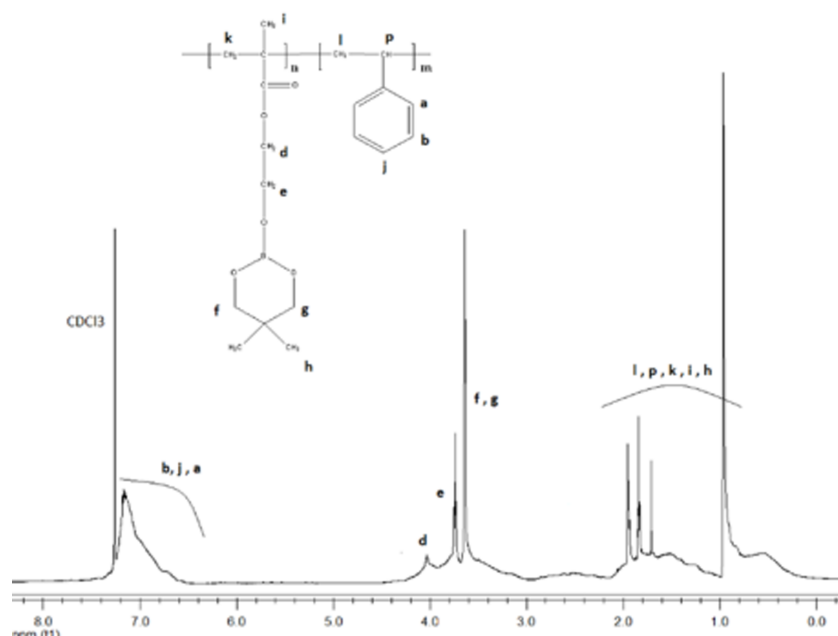
Figure 8. ^{1}H NMR spectrum of p(BAc-*co*-St) copolymer.

Table 1. Free radical copolymerization of BAc (M_1) and St (M_2) at 80 °C.[a]

Sample	F_1^e	F_2^e	f_1^d	f_2^d	Conv. (%)	Mn^b	Mw/Mn^b
p(BAc-co-St)-10/90	10	90	9	91	7	5830	1.81
p(BAc-co-St)-20/80	20	80	17	83	31	6358	1.81
p(BAc-co-St)-30/70	30	70	28	72	12	8563	1.90
p(BAc-co-St)-40/60	40	60	32	68	30	6692	1.76
p(BAc-co-St)-50/50	50	50	35	65	27	10,650	2.30
p(BAc-co-St)-60/40	60	40	41	59	46	6838	2.80
p(BAc)	100	-	100	-	44	14,669 [c]	-
p(St)	-	100			29	6624	1.40

[a] Initiator: AIBN (8.5×10^{-3} M), [BAc] + [St] = 0.034 M, time: 0.5 h. [b] Determined by GPC measurement.
[c] Determined by Ubbelohde viscometer. K = 8.9×10^{-3}, a = 0.73 in DMF at 25 °C.[32] [d] f_1 and f_2 are the copolymer composition (mol%) determined by ^{1}H NMR data. [e] F_1 and F_2 are the monomer feeds (mol%).

Copolymer compositions of p(Bac-*co*-St) copolymers were determined by ^{1}H NMR. The experimental fraction of BAc monomer was slightly lower than the corresponding fraction in monomer feed, as shown in Table 1.

In the ^{1}H NMR spectral peaks of p(BAc-*co*-St) copolymers appearing at around 6.5–7.5 ppm were assigned to the aromatic protons from p(St) polymer fraction and at around 3.4–3.6 ppm were assigned to –OCH$_2$ protons from p(BAc) polymer fraction. Compositions of copolymers in Table 1 were calculated on the basis of ^{1}H NMR results, comparing the values of integrals of peaks that appeared at around 3.4–3.6 ppm, which is characteristic for –OCH$_2$ protons in the BAc monomer and peaks that appeared in the range of 6.5–7.5 ppm, which are for aromatic protons of St monomer. Copolymerization of the newly synthesized BAc with St was evaluated via free radical polymerization with different monomer feeds to calculate the reactivity ratio of the monomers. For this purpose, during the copolymerizations, total monomeric composition and time were

maintained constant, as was the temperature, which was kept within ± 0.1 °C. All runs were carried out by employing the initiator 2.5 mol % of the total momomer amount. Monomer reactivity ratios of BAc and St for their free radical copolymerization were calculated by the well-known EKT method from the composition of the monomer feed and that of the instantaneously formed copolymer (Table 2).

Table 2. EKT parameters for monomer BAc and St using ^{1}H NMR.

Run	H	G	ξ	η
p(BAc-co-St)-10/90	0.13	−1.02	0.11	−0.88
p(BAc-co-St)-20/80	0.33	−1.01	0.24	−0.74
p(BAc-co-St)-30/70	0.48	−0.68	0.32	−0.45
p(BAc-co-St)-40/60	1.09	−0.81	0.51	−0.38
p(BAc-co-St)-50/50	2.39	−0.97	0.70	−0.28
p(BAc-co-St)-60/40	8.13	−1.04	0.89	−0.11

This method essentially uses the equation

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - r_2/\alpha, \tag{1}$$

where η and ξ are functions of both feed and copolymer compositions defined as

$$\eta = G/(H + \alpha)\,\text{and}\,\xi = H/(H + \alpha) \tag{2}$$

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

$$Z = \log\,(1{-}\xi_1)\,/\log\,(1{-}\xi_2) \tag{3}$$

ξ_1 and ξ_2 are, respectively, the partial molar conversions in monomers M_1 and M_2 and are given as

$$\xi_1 = \xi_2\,(Y/X)\,\text{and}\,\xi_2 = (\omega\,(\mu + X))/(\mu + Y), \tag{4}$$

where

$$Y = f_1/f_2, \quad X = F_1/F_2, \quad \mu = \mu_2/\mu_1 \tag{5}$$

μ_1 and μ_2 represent the molecular weights of monomer 1 and 2, respectively, and ω is the total fractional conversion. Thus, the H and G values are defined as follows:

$$H = Y/Z^2\,\text{and}\,G = (Y - 1)/Z \tag{6}$$

and α is an arbitrary parameter, usually taken as

$$\alpha = (H_{max}\,.\,H_{min}\,)^{1/2} \tag{7}$$

Monomer reactivity ratios (r_1 and r_2) were calculated using experimental data, presented in Table 3, treated by EKT method.[17,20]

Table 3. Monomer reactivity ratios (r_1, r_2).

M_1	M_2	$r_1 = k_{11}/k_{12}$	$r_2 = k_{22}/k_{21}$	$r_1.r_2$	$1/r_1 = k_{12}/k_{11}$	$1/r_2 = k_{21}/k_{22}$
BAc	St	0.08	0.95	0.07	12.50	1.05

The linear plot according to Eq. (1) gives $r_1 + r_2/\alpha$ as slope and $-r_2/\alpha$ as intercept in Figure 9.
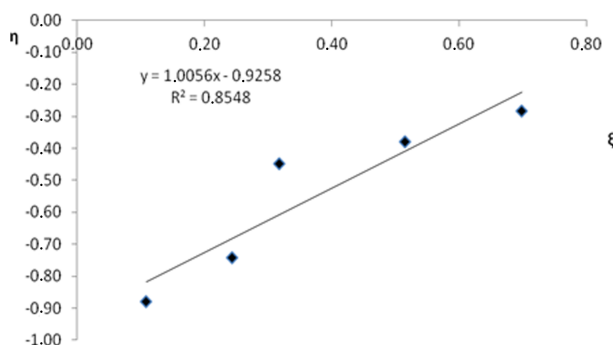

Figure 9. EKT plots of ξ versus η for the free radical copolymerization of BAc (M1) with St (M2) ($\alpha = 1.03$).

The reactivity ratios, which were found to be $r_1 = 0.08$, $r_2 = 0.95$, and $r_1 . r_2 < 1$ for the pair BAc-St show that this system undergoes random copolymerization. The value of r_1 is less than unity, 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 near to unity implies the copolymerization initially is dominated by this species, which is the more reactive monomer.

Thermal behaviors of the synthesized polymers were investigated with DSC and TGA. 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 thes thermal analysis are summarized in Table 4.

Table 4. DSC and TGA results for synthesized polymers.

	Tg (°C)	Mn	Residue at 500 °C	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)
p(BAc)	73.7	14669	2.1	215.5	356.3
p(St)	85.4	6624	1.3	341.7	419.1
p(BAc-co-St)-10/90	68.4	5830	1.2	307.9	417.9
p(BAc-co-St)-20/80	74.5	6358	1.2	312.1	409.7
p(BAc-co-St)-30/70	77.4	8563	1.4	278.5	410.7
p(BAc-co-St)-40/60	75.5	6692	1.7	291.7	406.4
p(BAc-co-St)-50/50	81.5	10650	1.5	285.7	404.1

Normally, Tg values of standard polystyrenes are above 100 °C in many references, but the Tg of polystyrene can change according to the molecular weight.[21] One structure factor that greatly influences the physical properties of polystyrene is molecular weight. The glass transition of polymers corresponds with the start of the translational motion of chain segments and the Tg is essentially independent of molecular weight. However, it is known that in the molecular weight range where the degree of polymerization is low, the effects of chain ends lower Tg.[22] The research regarding the relationship between polystyrene molecular weight and glass transition has been widely reported in the past.[23,24] Figure 10 shows the dependence of glass transition temperature on molecular weight, which has been investigated in the literature. Claudy et al. used DSC to investigate the relationship of the degree of polymerization of polystyrene and glass transition.

In our study we also found 85.4 °C for the Tg of polystyrene with a molecular weight of 6624. As seen in Figure 11 and Table 4, depending on the copolymer composition and the molecular weight and also for

being random copolymers, glass transition values of BAc-St copolymers were in between the glass transition temperature values of homopolymers pSt and pBAc. Although pBAc homopolymer had a Tg value of 73.7 °C, the Tg value of copolymer p(BAc-co-St)-50/50 was 81.5 °C due to the high molecular weight and high polystyrene percentage. In the case of p(BAc-co-St)-10/90, it was 68.4 °C. Since the molecular weight was 5830 no effect of 10% BAc could be observed.
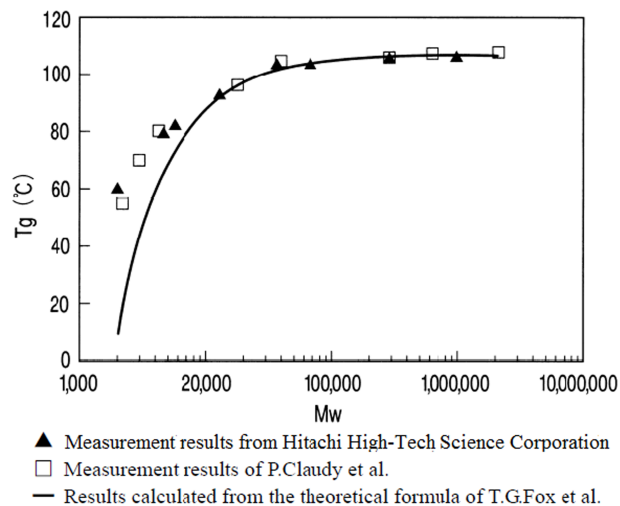

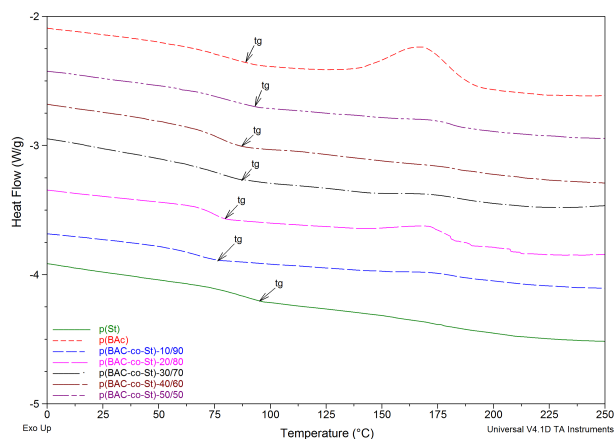**Figure 10.** Dependence of glass transition temperature on molecular weight.

Figure 11. DSC thermogram of synthesized polymers.

Figure 12 shows TGA diagrams of the obtained copolymers. St homopolymer and copolymers have one decomposition step, while BAc homopolymer has two decomposition steps. Char yields were increased by pBAc content in pSt copolymers. pBAc homopolymer had the highest char yield because of the boron group but first decomposition started just after 160 °C as can be seen in the DSC plot as well.
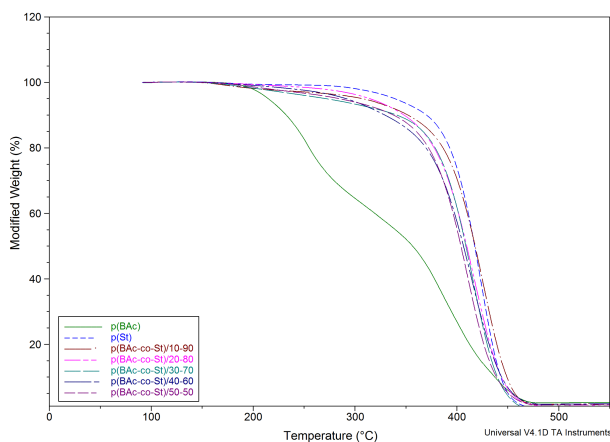
Figure 12. TGA thermograms of synthesized polymers.

Solubility of the synthesized polymers was tested in different solvents at room temperature; 100 mg of monomer or copolymer was used to dissolve in 1 mL of different solvents and the results can be seen in Table 5.

BAc homopolymer was dissolved only in DMSO and DMF. On the other hand, p(BAc-co-St) copolymer was dissolved in DMSO, THF, DMF, ethyl acetate, diethyl ether, and methanol.

Table 5. Solubility of synthesized monomer and polymers (100 mg) in different solvents of 1 mL.

	BAc	p(BAc-*co*-St)
DMSO	+	+
THF	–	+
DMF	+	+
Acetonitrile	–	–
Ethyl acetate	–	+
Diethyl ether	–	–
Chloroform	–	+
DCM	–	+
Methanol	+	+

In conclusion, BAc monomer, its homopolymer, and styrene copolymers were synthesized. 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 using the EKT method. Copolymerization composition and reactive ratios showed that the copolymerization occurred randomly. The Tg value of pBAc and pSt was 73.7 °C and 85.4 °C, respectively. Depending on the copolymer composition, St copolymers' glass transition temperatures were between 68.4 °C and 81.5 °C. TGA analysis showed that while St homopolymer and copolymers have one decomposition step, BAc homopolymer has two decomposition steps. Char yields were increased by pBAc content in pSt copolymers. Furthermore, solubility of the homopolymers and copolymers was examined with different solvents.

3. Experimental

3.1. Materials

Styrene (St, 99%, Aldrich) was passed through a basic alumina column to remove the inhibitor and distilled in vacuo (30 mmHg, 23 °C) 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 (HEMA) (BDH Chemicals), hypophosphorus acid, 50% w/w aqueous solution (Abcr), boric acid (99%, Merck), 2-methylhydroquinone (99%, Abcr), and 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.

3.2. Equipment

FT-IR analyses were performed with a Thermo Scientific Nicolet IS FT-IR Spectrometer. Resolution mode was 4 cm^{-1}. Sixteen scans were averaged for each sample in the range 4000–400 cm^{-1}. ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR analyses were performed with an Agilent VNMRS spectrometer at 500 MHz. Deuterated dimethyl sulfoxide (DMSO-d_6) and deuterated chloroform ($CDCl_3$) were used as solvent. Gel permeation chromatography (GPC) analyses were performed with a set-up consisting of an Agilent pump and refractive index detector and three Agilent Zorba$\times$ PSM 1000S, 300S, 60S columns (6.2 $\times$ 250 mm, 5 μm) measuring in the range of 10^4–10^6, 3×10^3–10^5, and 5×10^2–10^4, respectively. THF was used as the eluent at a flow rate of 0.5 mL/min at 30 °C. Molecular weights were calculated with the aid of polystyrene (pSt) standards. Viscosities of polymer solutions were measured with DMF as a solvent at 25 °C by using an Ubbelohde glass viscometer.[20] The driving pressure in this viscometer was determined by measuring the distance from the level

of the liquid in the bulb to the level at the bottom of the capillary. DSC measurements were performed with a TA DSC Q10 instrument in a flowing nitrogen atmosphere from 30 °C at a scanning rate of 10 °C/min. Analyses were performed with a TA Q50 instrument under nitrogen atmosphere at a heating rate of 20 °C/min rising from room temperature to 800 °C. The weights of samples were between 6 and 10 mg. Calibration was achieved with indium as reference material.

3.3. Synthesis of boron methacrylate monomer (BAc)

Boron methacrylate monomer was synthesized according to our previously mentioned method with two steps by esterification reaction.[25] In the first step, 17 mL of toluene was added to a 100-mL two-necked round flask equipped with a Dean-Stark apparatus and a Friedrich condenser. The flask was also equipped with a stopper, drying tube, and needle for air pump. The heater was set to 60 °C. Then 5 g of boric acid, 0.056 mL of hypophosphorous acid, and neopentyl glycol were added to the system and the temperature was increased and set to 125 °C for dissolving. Two equivalents of water were removed by azeotropic distillation with a Dean-Stark apparatus. In the second step, 0.0556 g of methylhydroquinone and 9.8 mL of HEMA were added to the flask and one equivalent of water was removed. At the end of the reaction, the solvent was removed from the product by vacuum distillation at 30 mmHg, 40 °C, and the product was obtained as a transparent liquid. The yield of the reaction was 78%.

3.4. Synthesis of boron methacrylate homopolymer (pBAc)

The polymerizations were performed in a dry Schlenk tube charged with a determined amount of BAc monomer, 5 mL of methanol, and AIBN (2.5 mol % of total monomer). Oxygen was removed by nitrogen via applying a vacuum using three freeze pumps. The reaction tube was immersed into a silicon oil 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 precipitated into diethyl ether and dried under vacuum of 20 mmHg at room temperature.

3.5. Synthesis of boron methacrylate-styrene copolymers (p(BAc-co-styrene))

The polymerizations were performed by general copolymerization method as mentioned in our previous work in a dry Schlenk tube charged with determined amounts of monomers (BAc and styrene), 2 mL of toluene, and AIBN (2.5 mol % of total monomer).[26] Oxygen was removed by nitrogen via applying a vacuum using three freeze pumps. The reaction tube was immersed into a silicon oil bath, preheated to 80 °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 THF. The polymers were precipitated into hexane, filtered, and dried under vacuum of 20 mmHg at room temperature.

Acknowledgment

References

1. Martín, C.; Ronda, J. C.; Cádiz, V. Boron-containing novolac resins as flame retardant materials. *Polym. Degrad. Stab.* **2006**, *91*, 747-754.

2. Shen, K. K.; Griffin, T. S.: Zinc Borate as a Flame Retardant, Smoke Suppressant, and Afterglow Suppressant in Polymers. In *Fire and Polymers*; ACS Symposium Series 425; American Chemical Society, 1990; Vol. 425; pp 157-177.

3. Wilkie, C. A.; Morgan, A. B.; Editors. *Fire Retardancy of Polymeric Materials, Second Edition*; CRC Press: Boca Raton, FL, USA, 2010.

4. Köster, R. The Organic Chemistry of Boron, von W. Gerrard. Academic Press, London-New York 1961. 1. Aufl., X, 308 S., 28 Tab., geb. $ 2.15.0. *Angew. Chem.* **1963**, *75*, 696-696.

5. Kolel-Veetil, M. K.; Keller, T. M. In *Macromolecules Containing Metal and Metal-Like Elements*; Wiley: New York, NY, USA, 2006; pp 1-76.

6. Jäkle, F. Lewis acidic organoboron polymers. *Coord. Chem. Rev.* **2006**, *250*, 1107-1121.

7. Carré, F. H.; Corriu, R. J. P.; Deforth, T.; Douglas, W. E.; Siebert, W. S.; Weinmann, W. A boron-bridged tetrathiaporphyrinogen. *Angew. Chem. Int. Ed.* **1998**, *37*, 652-654.

8. Matsumi, N.; Chujo, Y. π-Conjugated organoboron polymers via the vacant p-orbital of the boron atom. *Polym. J. (Tokyo, Jpn.)* **2008**, *40*, 77-89.

9. Nicolas, M.; Fabre, B.; Simonet, J. Electrochemical sensing of fluoride and sugars with a boronic acid-substituted bipyridine Fe(II) complex in solution and attached onto an electrode surface. *Electrochim. Acta* **2001**, *46*, 1179-1190.

10. Jaekle, F. Borylated polyolefins and their applications. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 293-307.

11. Cheng, F.; Jakle, F. Boron-containing polymers as versatile building blocks for functional nanostructured materials. *Polym. Chem.* **2011**, *2*, 2122-2132.

12. Ramakrishnan, S.; Chung, T. C. Poly(exo-5-hydroxynorbornene): a functional polymer using metathesis polymerization of an organoborane derivative. *Macromol.* **1989**, *22*, 3181-3183.

13. Branger, C.; Lequan, M.; Lequan, R. M.; Large, M.; Kajzar, F. Polyurethanes containing boron chromophores as sidechains for nonlinear optics. *Chem. Phys. Lett.* **1997**, *272*, 265-270.

14. Mayo, F. R.; Lewis, F. M. Copolymerization. I. A basis for comparing the behavior of monomers in copolymerization; the copolymerization of styrene and methyl methacrylate. *J. Am. Chem. Soc.* **1944**, *66*, 1594-1601.

15. Fineman, M.; Ross, S. D. Linear method for determining monomer reactivity ratios in copolymerization. *J. Polym. Sci.* **1950**, *5*, 259-262.

16. Tüdos, F.; Kelen, T.; Földes-berezsnich, T.; Turcsányi, B. Analysis of linear methods for determining copolymerization reactivity ratios. III. Linear graphic method for evaluating data obtained at high conversion levels. *J. Macromol. Sci. Part A Chem.* **1976**, *10*, 1513-1540.

17. Tüdös, F.; Kelenm, T. Analysis of the linear methods for determining copolymerization reactivity ratios. V. Planning of experiments. *J. Macromol. Sci. Part A Chem.* **1981**, *16*, 1283-1297.

18. Tidwell, P. W.; Mortimer, G. A. An improved method of calculating copolymerization reactivity ratios. *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 369-387.

19. Mao, R.; Huglin, M. B. A new linear method to calculate monomer reactivity ratios by using high conversion copolymerization data: terminal model. *Polymer* **1993**, *34*, 1709-1715.

20. Nair, C. P. R.; Mathew, D.; Ninan, K. N. Free radical copolymerisation of N-(4-hydroxy phenyl) maleimide with vinyl monomers: solvent and penultimate-unit effects. *Eur. Polym. J.* **1999**, *35*, 1829-1840.

21. Claudy, P.; Letoffe, J. M.; Camberlain, Y.; Pascault, J. P. Glass transition of polystyrene versus molecular weight. *Polym. Bull. (Berlin)* **1983**, *9*, 208-215.

22. Fox, T. G.; Flory, P. J. The glass temperature and related properties of polystyrene. Influence of molecular weight. *J. Polym. Sci.* **1954**, *14*, 315-319.

23. Fox, T. G., Jr.; Flory, P. J. Second-order transition temperatures and related properties of polystyrene. I. Influence of molecular weight. *J. Appl. Phys.* **1950**, *21*, 581-591.

24. Couchman, P. R. The effect of degree of polymerization on glass-transition temperatures. *Polym. Eng. Sci.* **1981**, *21*, 377-380.

25. Canak, T. C.; Kaya, K.; Serhatli, I. E. Boron containing UV-curable epoxy acrylate coatings. *Prog. Org. Coat.* **2014**, *77*, 1911-1918.

26. Canak, T. C.; Hamuryudan, E.; Serhatli, I. E. Synthesis and characterization of perfluorinated acrylate-methyl methacrylate copolymers. *J. Appl. Polym. Sci.* **2013**, *128*, 1450-1461.