

A Simple Method for Synthesizing Ultra-high-molecular-weight Polystyrene through Emulsion Polymerization Using Alkyl-9-BBN as an Initiator

Chao Zhao, Ryuichi Sugimoto*, and Yusuke Naruoka

School of Environmental Science and Engineering, Kochi University of Technology, Kochi 782-8502, Japan

Abstract Styrene emulsion polymerization using an alkyl-9-BBN, synthesized by reacting 9-BBN (9-borabicyclo-[3.3.1]-nonane) and styrene, in an aqueous sodium dodecyl sulfate (SDS) solution was studied. Ultra-high-molecular-weight ($> 1.0 \times 10^7$) polystyrene was synthesized using a radical initiator formed through the aerobic oxidation of this alkyl-9-BBN in a high yield ($> 80\%$). The kinetics of this emulsion polymerization of styrene with the alkyl-9-BBN was investigated. We confirmed that in the initial stage of the polymerization, the initial reaction rate followed first-order kinetics. The activation energy for this emulsion polymerization of styrene was approximately 56.2 kJ/mol.

Keywords Emulsion polymerization; 9-BBN; Ultra-high molecular weight polystyrene

Citation: Zhao, C.; Sugimoto, R.; Naruoka, Y. A Simple Method for Synthesizing Ultra-high-molecular-weight Polystyrene through Emulsion Polymerization Using Alkyl-9-BBN as an Initiator. Chinese J. Polym. Sci. 2018, 36(5), 592–597.

INTRODUCTION

Organoboranes and their derivatives are becoming increasingly important as key reagents in radical chemistry^[1]. One widely used organoborane is tributylborane (TBB), which has been used as a polymerization initiator. Welch^[2] has reported the polymerization of vinyl monomers initiated by alkylboranes in the presence of oxygen or electron donors; polymerization proceeded *via* a free-radical mechanism.

Alkyl-9-borabicyclo-[3.3.1]-nonanes (BBNs) have been used as radical polymerization initiators since the report by Masuda *et al.*^[3] in 1991. Chung *et al.*^[4] successfully used 1-octyl-9-BBN to initiate the polymerization of methyl methacrylate, which exhibited characteristics of living polymerization. In the presence of oxygen, alkyl-9-BBNs will form complexes that rearrange to alkylperoxyboron compounds (C—O—O—B), which are easily homolytically cleaved at ambient temperature to generate an alkoxy radical and a stable borinate radical^[4]. Chung's group has also conducted a lot of research on graft polymerization^[5, 6] and block copolymerization using this stable borinate radical as an initiator^[7, 8]. However, since these alkyl boron compounds are hydrolytically unstable, there are very few reports on polymerization in aqueous systems.

Recently, a number of publications have appeared that describe the syntheses of ultra-high-molecular-weight polymers through living radical polymerization processes, including atom transfer radical polymerization (ATRP)^[9]

(24 h, 50 °C, poly(2-dimethylamino)-ethyl methacrylate, M_w (weight average molecular weight) = $\sim 1.1 \times 10^6$), reversible addition fragmentation chain transfer (RAFT)^[10, 11], and organotellurium-mediated living radical emulsion polymerization (emulsion TERP)^[12] (24 h, 60 °C, polystyrene, M_n = $\sim 1.2 \times 10^6$). Although living polymerization provides a means to synthesize ultra-high-molecular-weight polymers, it has a major drawback, which is that long reaction time is required.

High-speed processes for polymerization that are less energy intensive are thus highly desired for industry. Emulsion polymerization has a unique advantage in the production of ultra-high-molecular-weight polymers^[12, 13] due to the segregation effect^[14–16], and provides a facile route for the syntheses of high-molecular-weight polymers with high reaction rates.

Emulsion polymerization of vinyl monomers in aqueous media has been carried out using various initiator systems^[17–19]; however, the use of a conventional thermal initiator, *e.g.*, persulfate, has been reported for most polymerizations. No information appears to be available for emulsion polymerization induced by alkyl-9-BBNs. This is because trialkylboranes are hydrolytically and oxidatively unstable, decomposing in water very rapidly to trialkylboroxines, borate esters, and boric acid.

The oxidized adduct that forms upon mixing an alkyl-9-BBN with oxygen homolytically decomposes to produce alkoxy radicals and stable borate radicals. Using this stable borate radical to initiate polymerization is advantageous in terms of energy conservation owing to its rapid decomposition at lower temperatures. Hence, the

* Corresponding author: E-mail sugimoto.ryuichi@kochi-tech.ac.jp
Received August 23, 2017; Accepted October 17, 2017; Published online January 18, 2018

polymerization can be conducted at a lower reaction temperature than those used when conventional thermal initiators are employed, which are usually in the 70–90 °C range.

Recently, we attempted the emulsion polymerization of styrene using an alkyl-9-BBN in an aqueous sodium dodecyl sulfate (SDS) solution. A stable borinate radical generated from the oxidation adduct of the alkyl-9-BBN was found to be able to initiate the emulsion polymerization of styrene within a short time and produce polystyrene with a high yield and ultra-high molecular weight. We also report the kinetics of this emulsion polymerization of styrene initiated by an alkyl-9-BBN in this paper.

EXPERIMENTAL

Materials

9-BBN (0.5 mol/L in tetrahydrofuran) was purchased from Sigma-Aldrich. Styrene was purchased from Wako Pure Chemical Industry, Ltd., and purified by washing with a 10% aqueous solution of sodium hydroxide and treated with anhydrous sodium sulfate. SDS, tetrahydrofuran, NaOH, and MgSO₄ were purchased from Wako Pure Chemical Industry, Ltd. and used as received. All aqueous solutions were prepared with deionized (DI) water that was generated using a Millipore MilliQ Academic Water Purification System and deoxygenated by sparging with argon for 30 min.

Characterization and Measurements

Size-exclusion chromatography (SEC) was carried out using a system equipped with a Jasco PU-2080 Plus pump and a Jasco RI-2031 Plus Intelligent RI detector. The molecular weights and molecular weight distributions (PDI) of the polymers relative to a polystyrene standard were determined using Chrom NAV software. Chloroform served as the polymer solvent and eluent in an equilibrated system at 40 °C. A Malvern Zetasizer Nano series instrument was used to measure the diameters of the polymer particles, and average particle diameter distributions were determined in cumulant mode using Zetasizer v7.11 software.

Polymerization Procedure

All experiments were conducted under an argon atmosphere. The emulsion polymerizations were carried out in 50 mL double-neck round bottom flasks connected with an argon gas inlet and with a magnetic stirrer. SDS was first dissolved in degassed water, and then styrene monomer was added to the solution while it was stirred at 400 r/min. The initiator was prepared by mixing 9-BBN and styrene (molar ratio = 1:1) in another 50 mL flask and stirring at 23 °C for 1 h just before use. The two solutions were mixed together, and the resulting solution was stirred at 400 r/min for 48 h under an argon atmosphere.

A fixed amount of latex was removed from the reaction mixture at regular time intervals and the size of the polymer particles was measured. Then, the polystyrene was precipitated in methanol and collected, and the conversion, molecular weight, and molecular weight distribution of the polymer were determined. Polymerization was repeated three times for each set of reaction conditions.

RESULTS AND DISCUSSION

Effect of Amount of Emulsifier on Reaction

The effect of SDS surfactant concentration on polymerization yield in the emulsion polymerization of styrene was investigated.

The emulsion polymerization reactions were carried out at 23 °C with a constant styrene/alkyl-9-BBN ratio of 1000:1. Figure 1 shows the plots of yield versus polymerization time with different amounts of SDS. The yield increased monotonically with the polymerization time in the initial stage of the reaction. When the SDS concentration was 0.12 and 0.18 g/mL, the yields reached a certain value after approximately 24 h. However, the yields of the other two groups kept increasing as the reaction time increased.

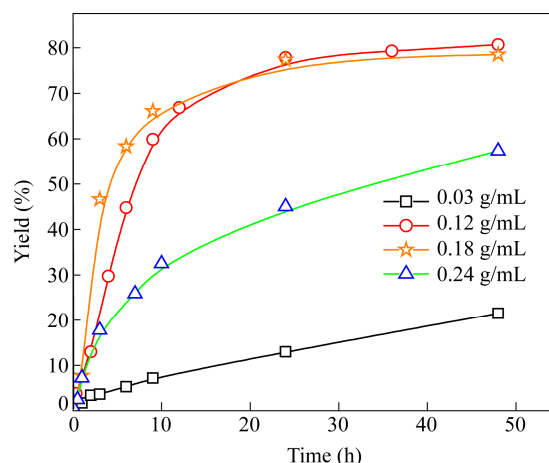


Fig. 1 Effect of SDS surfactant concentration on polymerization yield in emulsion polymerizations of styrene (SDS g/monomer mL)

The yield after polymerization for 48 h with an SDS concentration of 0.03 g/mL was 22%. In addition, the yield after polymerization for 48 h increased from 22% to 81% when the SDS concentration was increased by four times from 0.03 g/mL to 0.12 g/mL. When the amount of emulsifier increases within a specific range, the micelle becomes more stable and the number of micelle increases. As a result, the initiator content in each micelle decreases. Since the rate of chain initiation and propagation is not affected, the reaction time of each macromolecule becomes shorter. Similar results could be obtained when the SDS amount was 0.18 g/mL. However, when the SDS concentration further increased to 0.24 g/mL, the yield decreased to 57%.

Figure 2 shows the plots of molecular weight (M_w) versus polymerization time with different amounts of SDS under similar conditions. Very-high-molecular-weight polystyrene ($M_w > 5 \times 10^6$) was obtained with all SDS concentrations. In particular, ultra-high-molecular-weight ($M_w = 1.2 \times 10^7$) polystyrene was obtained with a high yield of 81% when 0.12 g/mL of SDS was used. It is known that as the surfactant concentration increases and the initiator concentration decreases, the molecular weight increases with conventional surfactants. So the molecular weights obtained by using 0.12 and 0.18 g/mL SDS were higher than that of using 0.03 g/mL SDS. Under the protection of enough emulsifier,

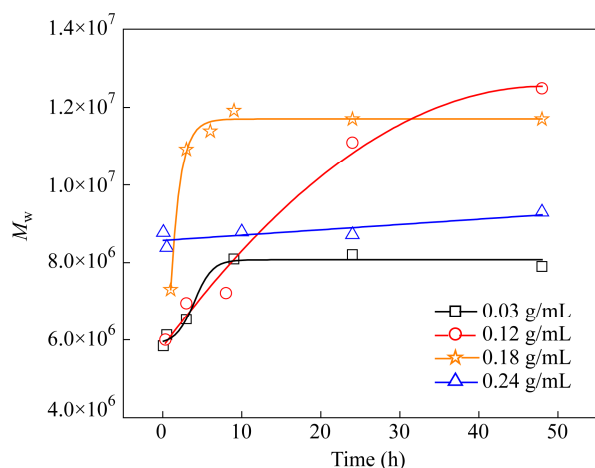


Fig. 2 Time dependence of molecular weight in the emulsion polymerization of styrene with 9-BBN using different amounts of SDS (M_w : weight-average molecular weight)

the initiator can keep long reaction time and free monomer can enter the emulsion particle to participate in the reaction. However, when the amount of SDS was doubled to 0.24 g/mL, the molecular weight of polystyrene decreased slightly to 9.3×10^6 . By analyzing the particle size data, an increase in particle size caused the micelle to become unstable and inhibited monomer transport into micelles. Therefore, the yield of polymer prepared with 0.24 g/mL SDS was lower and increased more slowly with time than the polymer synthesized with 0.12 g/mL SDS.

Figure 3 shows the plots of particle size versus polymerization time with different amounts of SDS under similar conditions. With an SDS concentration of 0.03 g/mL, the particle size increased from 110 nm to 220 nm as the polymerization progressed. On the other hand, when the amount of SDS was very high (0.24 g/mL), the particle size increased continuously from 190 nm to 320 nm as polymerization proceeded. However, when the amount of SDS was 0.12 and 0.18 g/mL, the particle size was quite stable throughout the polymerization. The particle size values of SDS concentration of 0.18 g/mL were slightly larger than that of 0.12 g/mL group. There are two possible reasons for

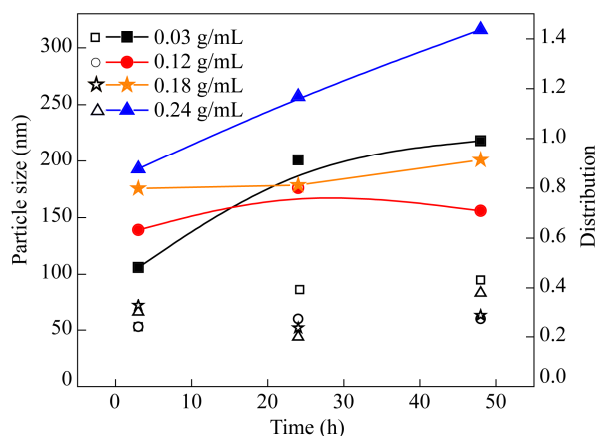


Fig. 3 Particle size (filled) and distribution (hollow) of polystyrene particles prepared via emulsion polymerization

the phenomenon of increased particle size at SDS concentrations above 0.12 g/mL. The first reason is that the excess emulsifier in water phase leads to fusion of several particles or deformation of micelle particles. Another reason is that the water content of the surrounding hydration layer increases because of many emulsifiers located at the oil-water interface. As a result, transport of monomer into micelles was hindered and the yield using 0.24 g/mL SDS decreased to 57%. That is, when the amount of SDS is too low or too large, particle formation becomes unstable, and it was found that there exists an optimum amount of SDS for the stabilization of the particle diameter. Since the appropriate SDS concentration for polymerization was 0.12 g/mL based on these results, it was used in subsequent experiments.

Particle size distribution (relative amount of particles according to the size) was affected by emulsifier concentration. When SDS concentration was 0.03 g/mL, the emulsifier amount was not enough to form stable emulsion particles. Therefore, particle size distribution in the emulsion system was relatively large. When the SDS concentration was greater than 0.03 g/mL, the particle size was quite stable and the distribution remained at a relatively stable range throughout the reaction. However, when increased the SDS concentration to 0.24 g/mL, overmuch emulsifier led to fusion of some particles and the particle size distribution tended to increase with the extension of reaction time.

Influence of the Ratio between Initiator and Monomer

Figure 4 shows the effect of the monomer/initiator molar ratio on the polymerization. In the early stages of the polymerization of styrene using an alkyl-9-BBN as the initiator, the reaction rates were slower when higher amounts of initiator were used. However, in polymerization using conventional radical initiators, it is known that the reaction rate becomes higher as the amount of initiator increases because more radicals are generated^[20]. In the polymerization of styrene using this alkyl-9-BBN, radicals are generated through the decomposition of the oxidized adduct formed via the reaction between the alkyl-9-BBN and oxygen. Therefore, the presence of an excess amount of the alkyl-9-BBN leads to

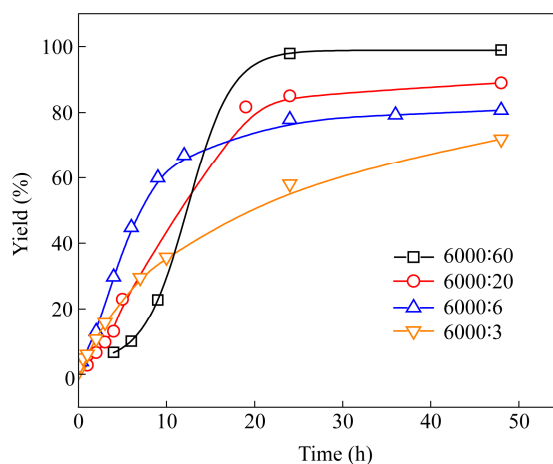


Fig. 4 Plots of yield versus time for the emulsion polymerization of styrene with 9-BBN using different monomer-to-initiator ratios of 6000:60 ($\square$), 6000:20 ($\circ$), 6000:6 ($\triangle$), and 6000:3 (∇)

the formation of more radical species, increasing the probability of the coupling of the generated radicals. As a result, the coupling of excess radicals occurs preferentially, decreasing the amount of effective active species and, consequently, the polymerization rate. At the same time, the lifetime of free radicals was shortened and the molecular weight decreased. When the polymerization time exceeded 20 h, the relationship between the yield and the amount of initiator was the opposite of that in the initial stage of polymerization. Since the alkyl borane compound reacts with water easily, when the polymerization time exceeds 20 h, the apparent reaction rate is considered to become slow because the amount of radicals generated in proportion to the amount of the alkyl-9-BBN decreases.

Figure 5 shows the M_w of polystyrene prepared using different monomer/initiator molar ratios. The molecular weight of polystyrene changed markedly as a result of changing the monomer-to-initiator molar ratio; the molecular weight of polystyrene can be increased significantly by decreasing the monomer-to-initiator molar ratio. Because of the segregation effect, when the initiator concentration decreases, the radical termination rate decreases, which increases the lifetime of the radical species; as a result, the M_w of polystyrene will increase^[12, 14, 15]. When the monomer-to-initiator molar ratio was 6000:60 or 6000:20, the M_w of polystyrene was between 1×10^6 and 3×10^6 regardless of the polymerization time. These molecular weights are relatively high, but one order of magnitude lower than those of polystyrene obtained with the other two ratios. When an excess amount of the alkyl-9-BBN is used, the yield of polystyrene increases, but the chain termination reaction between the radical and the growing polymer chain occurs more frequently, so the molecular weight decreases^[13]. Another possible reason that excess alkyl-9-BBN may reduce the M_w of the polymer is that it acts as a chain transfer agent. When the monomer-to-initiator molar ratio was 6000:3, the M_w exceeded 1×10^7 within 10 h, and radical termination such as through chain termination reactions hardly occurred,

so ultra-high-molecular-weight polystyrene was obtained. When the monomer-to-initiator molar ratio was 6000:6, the increase in the molecular weight was slower, and ultra-high-molecular-weight polystyrene with a M_w exceeding 1×10^7 was obtained after 24 h. When the monomer-to-initiator molar ratio was 6000:20 or lower, the M_w of polystyrene was constant irrespective of the polymerization time. However, when the molar ratio was 6000:6 or higher, the molecular weight was 6–7 times higher after 48 h, and ultra-high-molecular-weight polystyrene with a M_w exceeding 1.2×10^7 was obtained. In all cases, the polystyrene emulsion particles were stable and did not coagulate.

Kinetic Studies

In order to gain a better understanding of the characteristics of styrene polymerization initiated by 9-BBN, a kinetic study was performed at four different polymerization temperatures: 23, 40, 60, and 80 °C. The effects of variations in the reaction temperature on the yield and M_w of polystyrene were investigated.

Table 1 summarizes the results of the emulsion polymerization of styrene for 48 h at different reaction temperatures. The M_w was higher than 1×10^7 when the polymerization temperature was 40 °C or lower, but decreased when the reaction temperature was increased to higher than 60 °C, which may be caused by the promotion of the generation of free radicals at higher temperatures. As has already been discussed, increasing the concentration of radicals will lead to lower molecular weights.

Table 1 Results of emulsion polymerization of styrene at different temperatures

Temperature (°C)	Yield (%)	$M_w \times 10^{-6}$	PDI
23	81	12	2.45
40	92	10	2.69
60	89	6.6	2.54
80	96	3.3	1.93

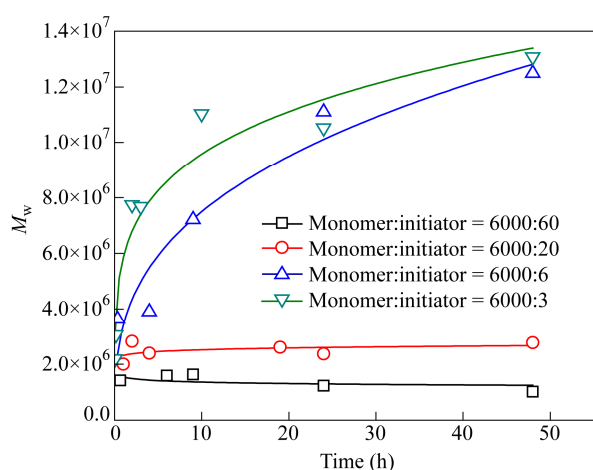


Fig. 5 Plots of M_w versus polymerization time for the emulsion polymerization of styrene with 9-BBN using different monomer-to-initiator ratios

The profile of the emulsion polymerization of styrene was obtained by monitoring the progress of the reaction. The polymerization rate (R_p) was calculated using the following equation: $R_p = (dC/dt) \times [M_0]$, where C is the conversion, t is the reaction time, and $[M_0]$ is the initial monomer concentration.

As can be seen from Fig. 6, it is clear that the R_p increased and reached a maximum in a very short time. Thereafter, the reaction rate decreased sharply, and the polymerization was complete within 30 min, giving a 96% yield at 80 °C. This indicates that there was no induction period before polymerization started. Higher monomer conversions could be achieved at higher temperatures perhaps because of the lower solution viscosity at higher temperatures, which facilitates monomer consumption^[9]. Even with a polymerization temperature of 60 °C, the R_p increased rapidly to the maximum in the same way and was followed by rapid retardation, and the polymerization was complete in 6 h. When the reaction temperature was decreased to 40 and 23 °C,

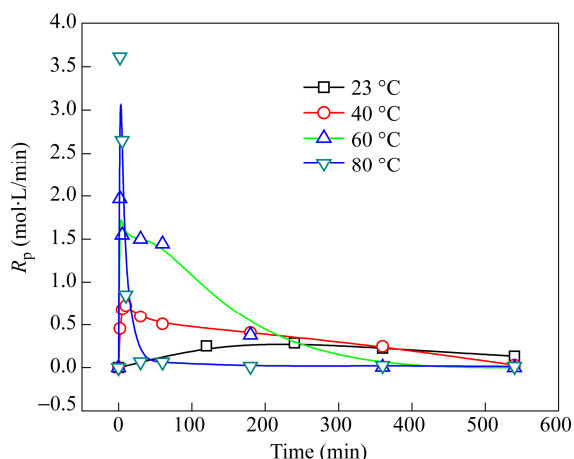


Fig. 6 Time dependence of R_p

the R_p decreased further, and the time required for the reaction to reach completion increased. The results showed that a long polymerization time is required, since the polymerization activity is relatively low under mild reaction conditions.

The study of the dynamics was conducted at the early stages of the polymerization of styrene using the alkyl-9-BBN. The plots of polymerization time versus $-\ln(1 - X)$, where X is the fraction conversion, showed linear relationships, as shown in Fig. 7. For this polymerization of styrene using an alkyl-9-BBN, we confirmed that the initial reaction rate followed first-order kinetics in the initial stage.

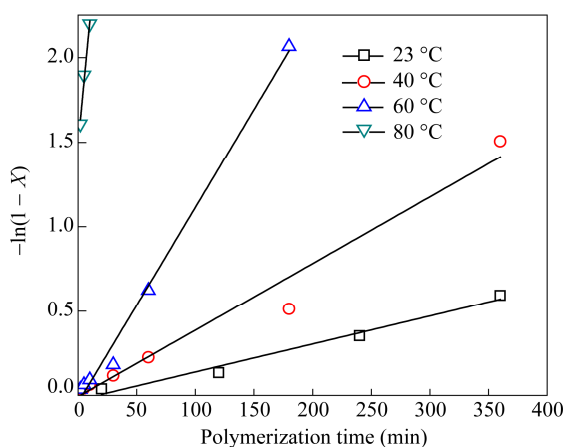


Fig. 7 Polymerization time versus $-\ln(1 - X)$ for the emulsion polymerization at 23 (□), 40 (○), 60 (△), and 80 °C (▽)

Then, the polymerization rate constants at different temperatures were determined from the slopes of these lines. The Arrhenius equation is used to calculate the overall activation energy as follows:

$$\ln K = -\frac{E_a}{RT} + \ln A$$

The Arrhenius plot of $\ln K$ versus $1/T$ showed a good linear relationship and the activation energy for the emulsion polymerization of styrene was estimated to be approximately 56.2 kJ/mol (Fig. 8).

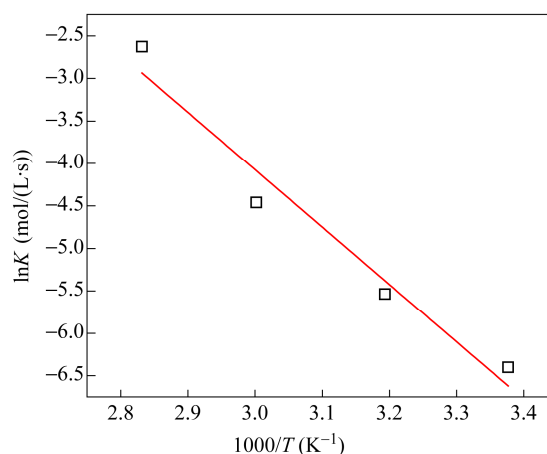


Fig. 8 Arrhenius plot for the emulsion polymerization of styrene with an alkyl-9-BBN at 23–80 °C

CONCLUSIONS

We have demonstrated that a hydrolytically unstable alkyl-9-BBN can be used as an emulsion polymerization initiator for the efficient polymerization of styrene at room temperature. Furthermore, we have developed a new and convenient method to synthesize ultra-high-molecular-weight ($> 1 \times 10^7$) polystyrene at room temperature, under low pressure and with a short reaction time *via* emulsion polymerization using alkyl-9-BBN as an initiator in an aqueous SDS solution. The optimum amount of SDS was 0.12 g/mL, and if the amount of SDS was too large or too small, particle formation became unstable. The activation energy for this emulsion polymerization of styrene was estimated to be approximately 56.2 kJ/mol based on a kinetic study. This novel polymerization process is not limited to the preparation of polystyrene but can be extended to the polymerizations of many other vinyl monomers, such as methyl methacrylate. This research is currently underway and the results will be reported in the near future.

REFERENCES

- 1 Renaud, P.; Beauseigneur, A.; Brecht-Forster, A.; Becattini, B.; Darmency, V.; Kandhasamy, S.; Montermini, F.; Ollivier, C.; Panchaud, P.; Pozzi, D.; Scanlan, E. M.; Schaffner, A.; Weber, V. Boron: a key element in radical reactions. *Pure Appl. Chem.* 2007, 79(2), 223–233.
- 2 Welch, F. J. Polymerization of methyl methacrylate by triethylboron-oxygen mixtures. *J. Polym. Sci.* 1962, 61, 243–252.
- 3 Yuzuru, M.; Masayuki, H.; Yutaka, N.; Akira, A. A remarkably efficient initiation by 9-BBN in the radical addition reactions of alkanethiols to alk-1-enes. *J. Chem. Soc., Chem. Commun.* 1991, (20), 1444–1445.
- 4 Chung, T. C.; Janvikul, W.; Lu, H. L. A novel “stable” radical initiator based on the oxidation adducts of alkyl-9-BBN. *J. Am. Chem. Soc.* 1996, 118(3), 705–706.
- 5 Chung, T. C.; Rhubright, D.; Jiang, G. J. Synthesis of polypropylene-graft-poly(methyl methacrylate) copolymers by the borane approach. *Macromolecules* 1993, 26(14), 3467–3471.
- 6 Dong, J. Y.; Manias, E.; Chung, T. C. Functionalized

- syndiotactic polystyrene polymers prepared by the combination of metallocene catalyst and borane comonomer. *Macromolecules* 2002, 35(9), 3439–3447.
- 7 Chung, T. C.; Lu, H. L.; Janvikul, W. A novel synthesis of PP-*b*-PMMA copolymers *via* metallocene catalysis and borane chemistry. *Polymer* 1997, 38(6), 1495–1502.
 - 8 Chung, T. C.; Xu, G. Metallocene-mediated olefin polymerization with B-H chain transfer agents: synthesis of chain-end functionalized polyolefins and diblock copolymers. *Macromolecules* 2001, 34(23), 8040–8050.
 - 9 Mao, B. W.; Gan, L. H.; Gan, Y. Y. Ultra high molar mass poly[2-(dimethylamino) ethyl methacrylate] *via* atom transfer radical polymerization. *Polymer* 2006, 47(9), 3017–3020.
 - 10 Truong, N. P.; Dussert, M. V.; Whittaker, M. R.; Quinn, J. F.; Davis, T. P. Rapid synthesis of ultrahigh molecular weight and low polydispersity polystyrene diblock copolymers by RAFT-mediated emulsion polymerization. *Polym. Chem.* 2015, 6(20), 3865–3874.
 - 11 Read, E.; Guinaudeau, A.; Wilson, D. J.; Cadix, A.; Violleau, F.; Destarac, M. Low temperature RAFT/MADIX gel polymerization: access to controlled ultra-high molar mass polyacrylamides. *Polym. Chem.* 2014, 5(7), 2202–2207.
 - 12 Kitayama, Y.; Okubo, M. A synthetic route to ultra-high molecular weight polystyrene ($> 10^6$) with narrow molecular weight distribution by emulsifier-free, emulsion organotellurium-mediated living radical polymerization (emulsion TERP). *Polym. Chem.* 2016, 7(14), 2573–2580.
 - 13 Jang, Y. C.; Choi, D. S.; Kim, J. G. First emulsion polymerization of styrene with sodium borohydride: evidence of the generation of radical intermediates by sodium borohydride in H₂O. *Langmuir* 2004, 20(16), 6570–6574.
 - 14 Zetterlund, P. B. Controlled/living radical polymerization in nanoreactors: compartmentalization effects. *Polym. Chem.* 2011, 2(3), 534–549.
 - 15 Zetterlund, P. B.; Okubo, M. Compartmentalization in nitroxide-mediated radical polymerization in dispersed system. *Macromolecules* 2006, 39(26), 8959–8967.
 - 16 Szkurhan, A. R.; Georges, M. K. Aqueous stable free radical polymerization processes. *Chinese J. Polym. Sci.* 2004, 22(4), 309–312.
 - 17 Jiang, Q. M.; Huang, W. Y.; Yang, H. J.; Xue, X. Q.; Jiang, B. B.; Zhang, D. L.; Fang, J. B.; Chen, J. H.; Yang, Y.; Zhai, G. Q.; Kong, L. Z.; Guo, J. Radical emulsion polymerization with chain transfer monomer: an approach to branched vinyl polymers with high molecular weight and relatively narrow polydispersity. *Polym. Chem.* 2014, 5(6), 1863–1873.
 - 18 Gao, J.; Jang, F. C.; Zhai, G. G. Ultra-high molecular weight alpha-amino poly(methyl methacrylate) with high T_g through emulsion polymerization by using transition metal cation-tertiary amine pairs as a mono-centered initiator. *Macromol. React. Eng.* 2016, 10(3), 269–279.
 - 19 Fan, X.; Jia, X.; Liu, Y.; Zhang, H.; Zhang, B.; Zhang, H.; Zhang, Q. Morphology evolution of poly(glycidyl methacrylate) colloids in the 1,1-diphenylethene controlled soap-free emulsion polymerization. *Eur. Polym. J.* 2017, 92, 220–232.
 - 20 Zhan, M. G.; Li, S. Y.; Zhong, Y.; Shen, C. H.; Gao, S. J. Preparation and characterization of a foam regulator with ultra-high molecular weight. *J. Appl. Polym. Sci.* 2017, 134(7), DOI: 10.1002/app.44479