



Kinetic Studies on Bulk Atom Transfer Radical Polymerization of Styrene

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To cite this article:

Samiul Islam Chowdhury, Lamya Zahir, Tariqul Hasan. Kinetic Studies on Bulk Atom Transfer Radical Polymerization of Styrene. *American Journal of Polymer Science and Technology*. Vol. 3, No. 6, 2017, pp. 103-107. doi: 10.11648/j.ajpst.20170306.12

Received: November 9, 2017; **Accepted:** December 1, 2017; **Published:** December 21, 2017

Abstract: The long chain vinyl end-functional polystyrene has been synthesized in bulk polymerization method using atom transfer radical polymerization (ATRP) with Undecenyl-2-Bromopropionate (UnBP) and CuCl/bipyridine catalytic system. The polymerizations demonstrate an increase in molecular weight and conversion in direct proportion to the polymerization time by consumed monomer which exhibited first-order kinetics. This study concludes the simple kinetics of polystyrene synthesized by ATRP using initiator and ligand-to-copper(I) halide was found to be 1:2:1, which tentatively indicates that the coordination sphere of the active copper(I) center contains two bipyridine ligands. The propagation rate has been investigated for long range of time for ensuring that the rate of radical combination or disproportionation is sufficiently less.

Keywords: Polystyrene, Initiator, ATRP, Bulk Polymerization, Kinetics

1. Introduction

In polymer chemistry, the development of Living Radical Polymerization (LRP) via ATRP technique constitutes one of the key developments in the field of synthetic polymer chemistry, allowing for the synthesis of a variety of polymers with molecular weight distributions and well defined architectures, with precise control over the compositions and structures [1-3]. In general, a combination of an alkyl halide [R-X, X= Cl or Br] and a transition metal catalyst in lower oxidation state (Cu(I)X/2,2'-bipyridine) is used to initiate the ATRP system [4-6]. The resulting polymers have degrees of polymerization predetermined by $\Delta[M]/[I]_0$ up to $M_n \cdot 10^5$ and low polydispersities in range $1.05 < M_w/M_n < 1.5$ [7]. For example, styrene is polymerized by atom transfer radical additions using 1-phenylethyl chloride [8] or arenesulfonyl chloride [9] as an initiator and CuCl/4,4'-diheptyl-2,2'-bipyridine or 4,4'- di(5-nonyl)-2,2'-bipyridine (dNbipy) complex as the catalyst to yield a well-defined polymer with a narrow molecular weight distribution ($M_w/M_n = 1.05$). The kinetics of syndiospecific slurry polymerization of styrene in

heptane has been investigated with pentamethylcyclopentadienyl titanium trimethoxide [Cp*Ti(OMe)₃] catalyst with methylaluminoxane [10]. Confinement effect of graphene nanoplatelets on the kinetics of styrene atom transfer radical polymerization was studied by a grafting from reaction [11]. The kinetic studies of atom transfer radical polymerizations of styrene and chloromethylstyrene has been studied with poly(3-hexyl thiophene) macroinitiator for synthesis of Poly(3-hexyl thiophene)-*b*-poly(styrene-*co*-chloromethylstyrene) copolymers [12]. The structure of the alkyl halide initiator should be adjusted for each class of monomers to generate a rate of initiation at least equal to the rate of propagation [13]. Considering this point, most authors prefer to use activated alkyl initiating systems with a chemical surrounding as similar to the growing polymer chain end as possible. The rate constant of initiation for styrene is higher than the rate constants of propagation [14, 15]. The kinetic study is investigated of bulk free radical polymerization of styrene initiated with the commercial bifunctional initiator 2,5-dimethyl-2,5-bis(2-ethyl hexanoyl peroxy)hexane [16] and

with α , α -dichlorotoluene (DCT) as initiator [17]. According to the kinetic study of styrene ATRP, the polymerization proceeds by monomer addition to free radicals which are reversibly generated by an atom transfer process from dormant polymer chains with halide end groups [18]. In these reactions, a small amount of Cu (II) species are considered to serve as a deactivator which moderates reaction rates and are responsible for maintaining low polydispersities [19, 20]. The Cu (II) species can be separately added to the system or can be formed spontaneously by the so-called persistent radical effect [21]. A rough estimate of the amount of CuBr₂/dNbipy species formed from kinetic studies was ~5%, based on the CuBr/ dNbipy catalyst [4]. Kinetic modeling is used to better understand and optimize initiators for continuous activator regeneration atom-transfer radical polymerization (ICAR ATRP) [22-24]. Here, the report presents a kinetic investigation by the time dependence bulk ATRP of styrene. It is the first long alkyl chain initiator which is investigated for the kinetic data of styrene polymerization.

2. Materials and Methods

2.1. Materials

Styrene was purchased from Aldrich and it was purified by passing through an alumina column to remove stabilizer and then stirred with CaH₂ for 8 h and filtered. Finally it was stored at 0°C under nitrogen prior to use. Copper (I) Chloride was purified by recrystallization in methanol and washed with ether. Bipyridine from Fluka, 2-bromopropionyl bromide and 10-undecene-1-ol were purchased from Aldrich and used without further purification. Triethylamine was distilled over CaH₂. All solvents were purified by distillation followed by refluxed with sodium and benzophenone.

2.2. Analytical Methods

Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymer were measured by gel permeation chromatography (Toyo soda HLC-802; Column, GMH6 \times 2 + G4000H8) and eluent, THF as solvent and calibrated by polystyrene standards. ¹H and ¹³C NMR spectra of polymers were recorded at room temperature on a JEOL GX 500 spectrometer operated at 125.65 MHz in pulse Fourier Transform mode with chloroform-*d* as solvent. The peak of chloroform in chloroform-*d* (7.26 ppm for ¹H and 74.47 ppm for ¹³C) was used as internal reference.

2.3. Synthesis of Initiator UnBP

The Initiator UnBP was synthesized according to the literature procedure [25]. A 5 g (29.5 mmol) sample of 10-undecene-1-ol (1) and 5 mL (36 mmol) of triethylamine were dissolved in 80 mL of THF. The solution was cooled in an ice-water bath. To this solution was added drop-wise 3.20 mL (30 mmol) of 2-bromopropionyl bromide (2) in 20 mL of THF. The mixture was stirred for another 2 h at room temperature (1 reacted with 2 to yield UnBP and HBr; HBr was absorbed by triethylamine).

Triethylamine hydrogen bromide salt was filtered out. THF in the filtrate was removed under vacuum at room temperature. The residual was dissolved in CHCl₃ and washed with 50 mL of water three times. The aqueous parts were combined and shaken with 50 mL of fresh CHCl₃. The total CHCl₃ solution was then dried over anhydrous CaCl₂ for overnight. After filtering off the drying agent, CHCl₃ was distilled out under vacuum. A brown liquid was obtained. A further distillation under high vacuum gave a colorless liquid; yield 7.60 g (82%).

¹H NMR (CDCl₃): 5.72 ppm (m, 1H, CH₂=CH-); 4.85 ppm (dd, 2H, =CH₂); 4.41 ppm (q, 1H, CH₃CH(Br)-OC(O)-); 4.1 ppm (t, 2H, -O-CH₂CH₂-); 2.00 ppm (q, 2H, CH₂=CH-CH₂-); 1.80 ppm (d, 3H -CH(Br)-CH₃), 1.55 ppm (t, 2H, -O-CH₂CH₂-); 1.2 – 1.4 ppm (m, 14H, -O-CH₂CH₂-(CH₂)₇-

¹³C NMR (CDCl₃): δ = 167.46, 136.34, 111.47, 63.30, 37.48, 31.10, 25.71 - 26.73, 23.05, 18.97.

2.4. Polymerization Procedure

Polymerization was carried out in a 50 mL Schlenk type reactor equipped with magnetic stirrer in nitrogen atmosphere. The reactor was charged with prescribed amount of CuCl and bipyridine. Three freeze-pump-thaw cycles were performed, and the tubes were sealed under vacuum with rubber septum. A required amount of degassed styrene and initiator were added with syringe. The reactor was placed in an oil bath held by a thermostat at the desired temperature and the reaction mixture was stirred for certain time. At certain interval, the polymerization was stopped by added methanol followed by cooling the reactor into ice water and the polymer was precipitated in methanol by stirring over night. The polymers obtained were filtered, adequately washed with methanol and dried under vacuum at 60°C for 6h.

3. Results and Discussions

Styrene polymerization by ATRP at 110°C initiated with three different concentration of UnBP with copper (I) chloride and bipyridine as a catalyst under nitrogen atmosphere has been reported [25]. The polymerization rate with respect to monomer concentration and the number averaged molecular weight (M_n) of the polymer evolved linearly with conversion. The effect of temperature on polymerization of styrene with UnBP/CuCl/BiPy (1:1:2) was investigated at various temperatures (75, 110 and 130°C). The results obtained are listed in Table 1. The yield of polymers was increased with raising the polymerization temperature. The molecular weight of the polymers was increased and the molecular weight distribution became narrower with raising temperature. The narrow polydispersity ($M_w/M_n = 1.50$) of the polymers obtained at 110 and 130°C suggests that the living polymerization of styrene should proceed with these conditions. To confirm the living nature at 110°C, the dependence of M_n on polymerization time was investigated by sampling method. 1 mL of reaction mixture was sampled with a syringe at every 30 minutes during polymerization. The molecular weight and molecular weight distribution of the polystyrene obtained by sampling method were measured by GPC.

Table 1. Effect of Temperature on bulk Polymerization of styrene^a.

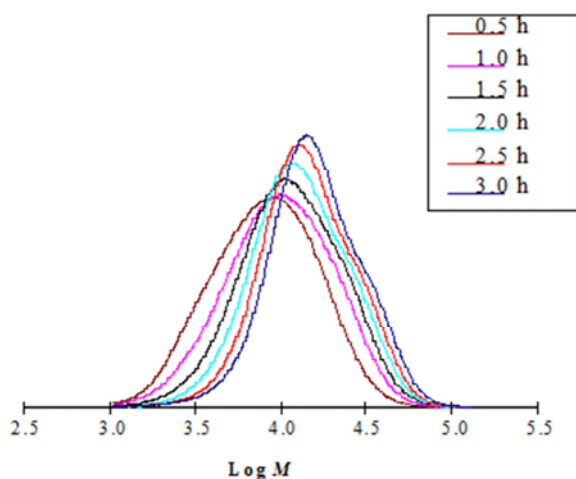
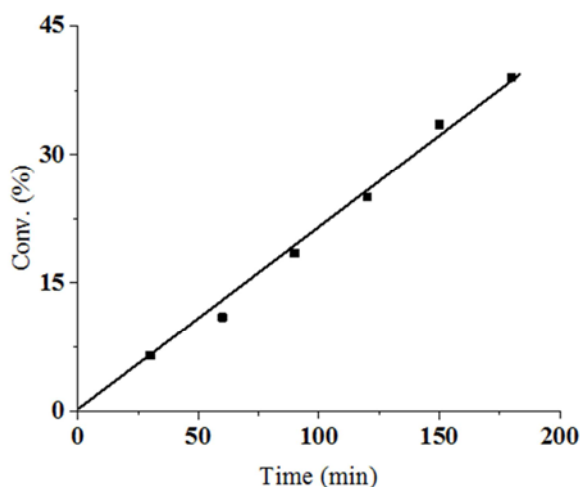
Entry	Temp. (°C)	Conv. (%)	M_n^b	M_w^c	M_w/M_n^d
1	75	1.0	8537	15499	1.81
2	110	24.0	13956	20934	1.50
3	130	39.5	14820	21236	1.45

^aPolymerization conditions; CuCl = UnBP = 0.08 mmol, BiPy = 0.16 mmol, Styrene = 5 mL, time = 2h. ^bNumber average molecular weight, ^cWeight average molecular weight and ^dMolecular weight distribution were measured by GPC analysis using polystyrene standard.

Table 2. Time dependence polymerization of styrene at 110°C by sampling method^a.

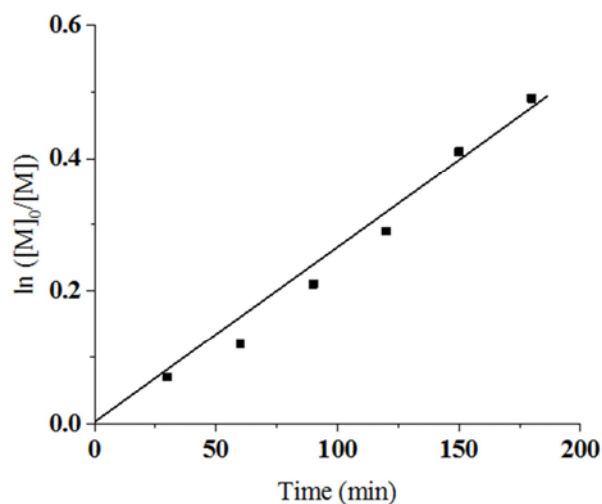
Entry	Time (min.)	Conv. (%)	$\ln([M]_0/[M])$	$M_{n,th}^b$	$M_{n,exp}^c$	M_w/M_n^d
4	30	6.5	0.07	3755	4305	1.62
5	60	11.0	0.12	6151	6563	1.62
6	90	18.5	0.21	10144	10168	1.56
7	120	25.0	0.29	13605	13956	1.49
8	150	33.5	0.41	18132	18516	1.45
9	180	39.0	0.49	21061	21147	1.45

^aPolymerization conditions; CuCl = UnBP = 0.08 mmol, BiPy = 0.16 mmol, Styrene = 5 mL, temperature = 110 °C, ^bTheoretical number average molecular weight. ^c Number average molecular weight and ^dMolecular weight distribution were measured by GPC analysis using polystyrene standard.

**Figure 1.** GPC curves of polystyrene obtained from sampling method.**Figure 2.** Plot of time vs conversion for the bulk polymerization of styrene at 110°C with UnBP as initiator.

The GPC curves obtained are displayed in Figure 1 and the

results are summarized in Table 2. The GPC curves of polymers obtained by sampling method were compared and the curves were shifted to the higher molecular weight region with increasing polymerization time keeping narrow M_w/M_n . The dependence of conversion and of $\ln([M]_0/[M])$ on time for the polymerization of styrene initiated with UnBP, catalyzed by CuCl/bipy in bulk system is shown in Figure 2 and 3. The linearity of the plot time vs $\ln([M]_0/[M])$ shows that the polymerization follows first order kinetics with respect to the monomer concentration and that the concentration of growing radicals remains constant.

**Figure 3.** Plot of time vs. $\ln([M]_0/[M])$ for the bulk polymerization of styrene at 110°C with UnBP as initiator.

The values of $M_{n,th}$ and $M_{n,exp}$ for polystyrene sample has been obtained with UnBP as a initiator. All experimental values are slightly higher than the calculated values but increase linearly with conversion (Table 2, Figure 4) demonstrating the living nature of polymerization system.

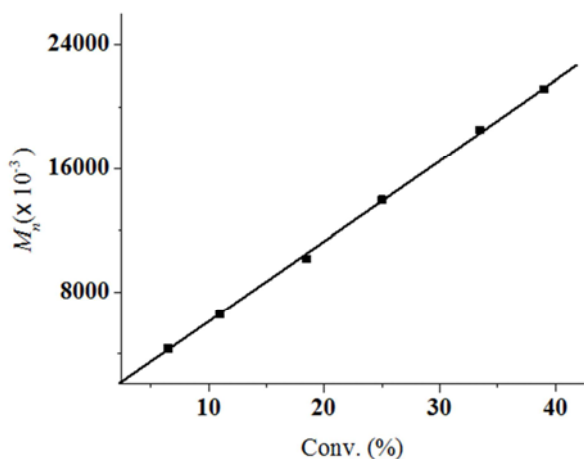


Figure 4. Plot of conversion vs M_n for the bulk polymerization of styrene at 110°C with UnBP as initiator.

The M_n value of the polystyrene linearly increased against conversion. The yield of the sampled polymer also increased linearly with polymerization time. The polydispersity index of all polystyrene samples is typical for polystyrene prepared via ATRP in bulk system.

The structure of polystyrene obtained using UnBP initiator was investigated by ^1H and ^{13}C NMR analysis of the polymer. The ^1H NMR spectrum of polystyrene the signals at 5.6 and 6.3 ppm assignable to vinyl protons and a signal at 4.7 ppm assignable to $-\text{CH}$ proton of α -Br indicates that the polymerization was initiated with UnBP. A broad signal at 7.26 ppm assignable to aromatic protons (meta- and para-position) of styrene unit and at 6.75 ppm for ortho-proton in Figure 5. The signals observed at 1.50 and 2.00 ppm assignable to $-\text{CH}_2$ and $-\text{CH}$ protons of main chain of polystyrene.

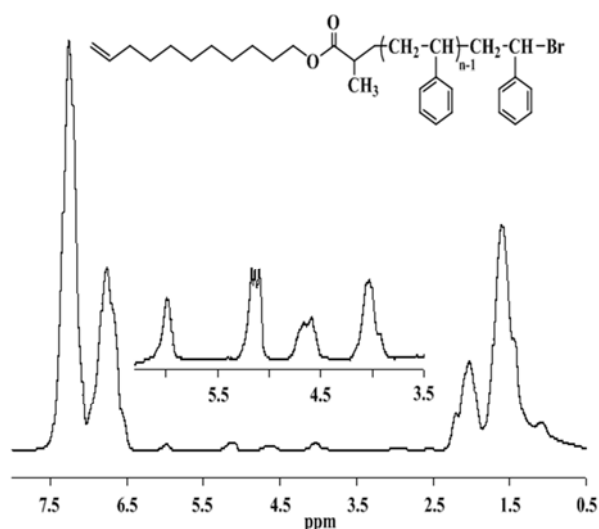


Figure 5. ^1H NMR spectra of polystyrene obtained by using UnBP as initiator.

The ^{13}C NMR spectrum of polystyrene was showed in the Figure 6. The signals for UnBP unit were clearly observed in the spectrum of the polystyrene. The signals at 136.34 and

111.47 ppm assignable to vinyl carbons indicate the presence of vinyl chain end in the polystyrene. The signals assignable to styrene unit were also observed in the ^{13}C NMR spectrum of the polymer as follows: $\delta = 143, 127, 126$ ppm for aromatic carbons, 50 ppm for $-\text{CH}_2\beta$ -carbon to Br, 43 ppm $-\text{CH}$ α -carbon to Br and 38 – 42 ppm for $-\text{CH}_2$ and $-\text{CH}$ carbons of main chain of polystyrene. These results clearly indicate the presence of vinyl group in the ω -end of polystyrene obtained with UnBP initiator.

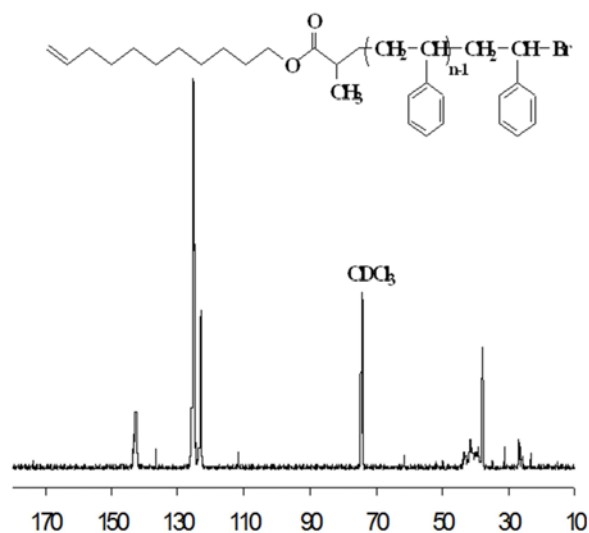


Figure 6. ^{13}C NMR spectra of polystyrene obtained by using UnBP as initiator.

These data can clear that the long chain vinyl end functional polystyrene has been synthesized by ATRP and the polymerization rate was first order with respect to conversion and the number averaged molecular weight (M_n) of the polymer.

4. Conclusion

The polymerization of styrene with $\text{Cu(I)}/\text{Bipy}/\text{UnBP}$ catalyst by ATRP method conducted on different temperatures but it follows the livingness at 110°C or more. The kinetic study was successfully confirmed by sampling method at 110°C. The initiator (UnBP) acts as an efficient initiator for the ATRP of styrene. The yield and the molecular weight of the polymers were increased, and the molecular weight distribution became narrower with raising polymerization temperature and time. Furthermore, for styrene polymerization it is the first initiator with long chains investigated the kinetic data. The feasibility of UnBP as an initiator for the facile preparation of block copolymers via ATRP is currently under investigation.

Acknowledgements

I am especially grateful to Dr. Jun-ichi Mamiya, Assistant Professor, Chemical Resources Laboratory, Tokyo Institute of technology, Japan for GPC analysis of polymer samples. I am

also grateful to Dr. Suman Chandra Mohanta, Research Fellow, the Institute of Scientific and Industrial Research (ISIR), Osaka University, Japan for NMR analysis of our samples.

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