



Synthesis of Well-defined Dihydroxyl End-Functional Polystyrene using Trifunctional Initiator via Atom Transfer Radical Polymerization

Samiul Islam Chowdhury¹, Tariqul Hasan²

¹Department of Chemistry, Bangladesh University of Textiles, Dhaka-1208, BANGLADESH

²Department of Chemistry, University of Rajshahi, Rajshahi-6205, BANGLADESH

Abstract: 2-bromopropionic [2,2-dimethyl-1,3-dioxolane-4-ylmethyl] ester (BPDME) was synthesized by two step reaction which involved on blocking of two hydroxyl group and esterification of the starting material. ¹H NMR of both the intermediate and final products has confirmed the structure of the BPDME. The well-defined dioxolane end-functional polystyrene was synthesized by using BPDME as initiator in ATRP method. The dioxolane end-functional polystyrene obtained was characterized by Gel Permeation Chromatography (GPC) and NMR analysis. Finally the dioxolane end group of polymer was deblocked to free hydroxyl groups by hydrolysis to produce dihydroxy end-functional polystyrene.

Key Words: Atom transfer radical polymerization (ATRP), polystyrene, trifunctional initiator

I. Introduction

Controlled radical polymerization, atom transfer radical polymerization (ATRP) [1] is a technique whereby a catalytic amount of a Cu(I) coordination complex reversibly abstracts a halogen atom (Cl or Br) from the polymer chain ends, switching them from a dormant to an active propagating state.

The ATRP process exhibits all of the experimental characteristics of a living polymerization, can be used for a large variety of monomers [1–9], allows facile control of chain topology, composition and functionality [10,11] and can employ a wide range of halogenated initiators and macroinitiators [12]. Since it is a catalytic process, the proportion of radicals and consequently the polymerization rate can be easily controlled, based on the amount and activity of the transition metal compounds used as redox catalyst. Moreover, experimental conditions are rather simple and Matyjaszewski and coworkers have showed that polymerization can be carried out in water [13], in a particular case in the presence of oxygen [14] and even at room temperature [15].

A further feature of polymers obtained by ATRP is that they possess an ω -halogen end-group that can be converted to other functional groups. Formation of azides, amines, double bonds and even sulfide have been shown to be feasible [16], however, Among the various functional group dioxolane end group in the polymer chain is a very interesting one because dioxolane end-functional group containing polymer can be converted to dihydroxy end-functional polymer. Which could be used as “microinitiator” for synthesis of various graft, block, two or three armed copolymer [17 -20]. Therefore a dioxolane group containing initiator 2-bromopropionic [2,2-dimethyl-1,3-dioxolane-4-ylmethyl] ester (BPDME) was synthesized and the ATRP of styrene was investigated using BPDME as initiator[20-22]. The initiator efficiency and polymer properties will also be studied. Finally the dioxolane ring was opened by the chemical reaction [20, 23-24].

II. Experimental

Materials: Glycerol (99 % Puriss Riedel-de Haen), Acetone (Normapur analytical reagent), Tetrahydrofuran (99 %, extra pure, stabilized with BHT, Acros Organics), molecular sieves 5A (Sigma-Aldrich). Dichloromethane (GPR Rectapur stabilized with 0.1 % of ethanol VWR Prolabo), Triethylamine (Reagent Plus 99.5 % Aldrich), Pyridine (ACS For Analysis CARLO ERBA), Methanol (Chromasolv Sigma Aldrich), 2,2'-bipyridyl (bipy, 98 %, Fluka), 2-bromopropionylbromide (98 %, Aldrich), p-toluenesulfonic acid (98 %, Aldrich) and styrene (99.5 %, Fluka) were dried over CaH₂ and distilled under vacuum just before use. Copper (I) bromide (98 %, Aldrich) was purified according to a published procedure [25].

Analytical Methods: Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymer were measured by Toyo soda HLC-802; Column, GMH6 2 + G4000H8; eluent, CDCl₃ as solvent and calibrated by polystyrene standards. ¹H and ¹³C NMR spectra were recorded at room temperature on a JEOL GX 500 spectrometer operated at

400 MHz in pulse Fourier transform mode with chloroform-*d* as solvent. The peak of chloroform in chloroform-*d* (7.26 ppm for ^1H) was used as internal reference.

Synthesis: (A) Synthesis of 2,2-dimethyl-1,3-dioxolane-4-methanol. The starting material was synthesized by the following reference procedure [21].

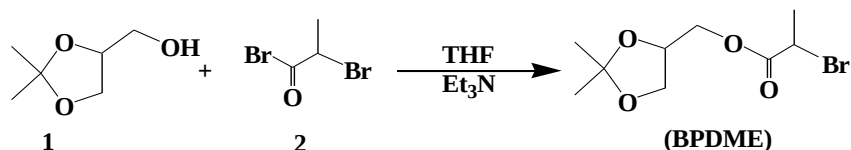
(B) Synthesis of Initiator 2-bromopropionyl[2,2-dimethyl-1,3-dioxolane-4-ylmethyl]ester (BPDME): To a 100 mL R.B. flask, 5.3 mL (40 mmol) of 2,2-dimethyl-1, 3-dioxolane-4-methanol (**1**), 11.1 mL (40 mmol) of triethylamine and 40 mL of THF were taken. The reaction mixture was cooled in an ice-water bath. To this solution, 4.65 mL (40 mmol) of 2-bromopropionyl bromide (**2**) in 20 mL of THF was added drop-wise. The mixture was stirred for another 2 hrs at room temperature (**1** reacted with **2** to yield BPDME and HBr was absorbed by triethylamine). Triethylamine hydrogenbromide salt was filtered out. THF in the filtrate was removed under vacuum at room temperature. The residual was dissolve in diethyl ether and washed with 50 mL of cold water. The organic layer was separated, washed with a saturated solution of sodium carbonate, acidified with HCl (pH = 4.5) and a second aliquot was washed with sodium carbonate. The organic layer was dried over anhydrous sodium sulphate, filtered and solvent was removed under vacuum. The product was finally isolated by vacuum distillation as slightly yellowish oil. The product yield was 79 %.

^1H NMR (CDCl_3) of (BPDME): 4.5 ppm (p, 1H, $-\text{CH}_2-\text{CH}-\text{O}-$); 4.4 ppm (q, 1H, $\text{Br}-\text{CH}(\text{CH}_3)-$); 4.2 ppm (d, 2H, $-\text{O}-\text{CH}_2-\text{CH}-$); 4.0 and 3.8 ppm (dd, 2H, $-\text{CH}_2-\text{O}-$); 1.8 ppm (d, 3H, $\text{Br}-\text{CH}(\text{CH}_3)-$); 1.35 and 1.40 ppm (s, 6H, $-\text{C}(\text{CH}_3)_2$);

Polymerization method: Polymerization was carried out in a 25 mL Schlenk tube with magnetic stirrer in nitrogen atmosphere. The reactor was charged with prescribed amount of CuBr, bipyridine and a tiny magnetic capsule. Three cycles of vacuum-evacuation of reactor and fill-up with nitrogen gas were performed, and the reactor then sealed with rubber septum. A required amount of degassed styrene and initiator BPDME were added with syringe. The reactor was placed in an oil bath to keep desired temperature by tuning thermostat and the reaction mixture was stirred for certain time using magnetic stirrer. At certain interval, the polymerization was stopped by added methanol followed by cooling the tube into ice-water and the polymer was precipitated in methanol by stirring for overnight. The polymers obtained were filtered, adequately washed with methanol and dried under vacuum at 60 $^\circ\text{C}$ for 6 hrs.

III. Results and Discussion

The initiator **(BPDME)** 2-bromopropionyl[2,2-dimethyl-1,3-dioxolane-4-ylmethyl] ester was synthesized from the reaction between 2,2-dimethyl-1,3-dioxolane-4-methanol and 2-bromopropionyl bromide in presence of triethylamine. The trifunctional hydroxyl compounds in this work are shown in Scheme 1.



Scheme 1. Preparation of functional initiator BPDME.

The structure of the initiator BPDME obtained was characterized by ^1H NMR analysis. In the ^1H NMR spectrum of the BPDME, several signals including the signals of 2-bromopropionyl bromide were observed. All signals correspond to the different protons of BPDME were assigned clearly and labeled in **Figure 1**.

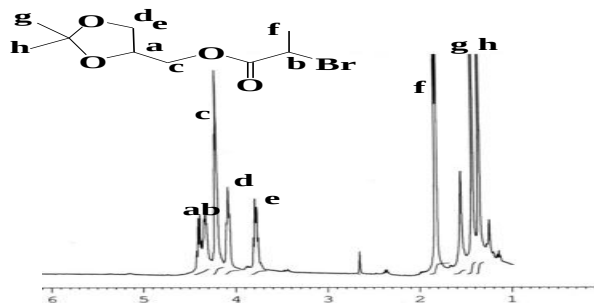


Figure 1. ^1H NMR spectrum of BPDME

Styrene was then polymerized by ATRP at 115 °C initiated with **BDPME** at different styrene/initiator ratio in conjunction with copper (I) bromide and bipyridine as a catalyst under nitrogen atmosphere. The ratio of styrene and **BDPME** (St/BDPME) significantly affect on the polymerization. The results obtained were listed in **Table 1**. The yield of polymers was increased with increasing the ratio of styrene and **BDPME**. The molecular weight and molecular weight distribution of the polymers obtained were measured with gel permeation chromatography (GPC). The polymers obtained with high molecular weight (M_n). The M_n value of the polymers was increased with the increasing St/BDPME ratio. The molecular weight distribution of polymer was narrow ($M_w/M_n \sim 1.2$). The GPC curves of the polymers obtained from the feed ration St/BDPME = 1000, St/BDPME = 500 and St/BDPME = 250 are displayed in **Figure 2**.

Table 1. Effect of the ratio of styrene/initiator on polymerization of styrene with CuBr/BiPy.

Entry	St/BDPME (mmol)	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n
1	250	0.51	3.667	4.389	1.19
2	500	0.75	15.42	20.20	1.31
3	1000	1.36	38.20	52.81	1.38

Polymerization conditions [CuBr : Bipy = 1:2, Styrene = 3.1 mL (27mmol), temperature = 115 °C, time = 5 hrs]

The GPC curve of the polymer obtained from higher monomer concentration (St/BDPME = 1000) shifted to the higher molecular weight region than that of the polymer obtained from lower monomer concentration (St/BDPME = 500). The M_n value (38.2×10^3) of the polymer obtained from the higher feed ration (St/BDPME = 1000) was more than double than the M_n value (15.4×10^3) of the polymer obtained from the lower feed ration (St/BDPME = 500). These results suggest that the higher propagation rate occurred at higher monomer concentration. The linear relationship of molecular weight of the polymers with ratio (**Figure 3a**) also supports the above results.

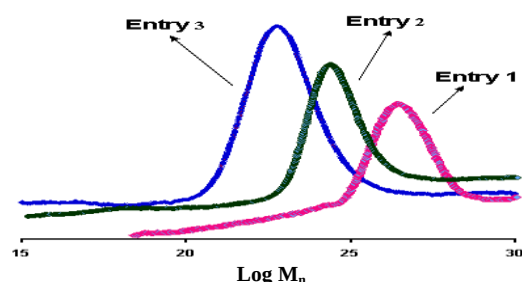


Figure 2. GPC curves of entry 1, entry 2 and entry 3

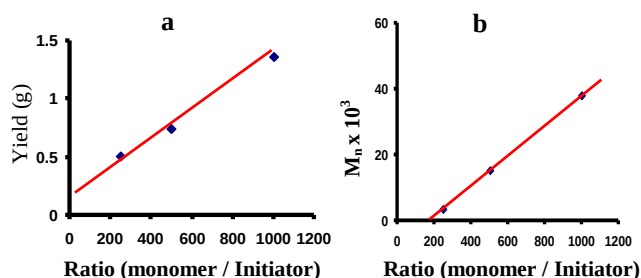


Figure 3. (a) The plot of Yield Vs Ratio, (b) The plot of M_n Vs Ratio

To produce polymer with narrow polydispersity is one of the main criteria for a living polymerization system. The initiator BDPME combined with CuBr/bipyridene catalyst system gave the polymers with narrow polydispersity ($M_w/M_n = 1.14$) at 115 °C (entry 6). This result therefore promotes us to make sure the living nature of BDPME/CuBr/bipyridene catalyst system at 115 °C. The dependence of polymer yield and M_n on polymerization time was investigated by batch method to check the living nature of this catalyst system. The molecular weight and molecular weight distribution of the polymers obtained by different polymerization time were measured by GPC and the results are summarized in **Table 2**.

Table 2. Time dependence polymerization of styrene with CuBr/BiPy/BDPME using batch method.

Entry	Time (hours)	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n
4	5	0.51	3.66	4.38	1.19
5	6.5	0.62	5.56	6.46	1.16
6	8.5	0.92	10.58	12.06	1.14

Polymerization conditions [CuBr = 0.108 mmol, Bipy = 0.216 mmol, Styrene = 3.1 mL, temperature = 115 °C]

The GPC curves of polymers obtained from different period of time (5, 6.5 and 8.5 hours) were compared in **Figure 4**. The GPC curves were shifted to the higher molecular weight region with increasing polymerization time with keeping narrow M_w/M_n . The plot of M_n vs time showed linear relationship with a slope at initial period in **Figure 5(b)**. The plot of yield vs time displayed in **Figure 5(a)** also showed linear relationship. These results suggest that the living polymerization of styrene proceeded at 115 °C by **BPDME**/CuBr/BiPy catalyst system with slow initiation.

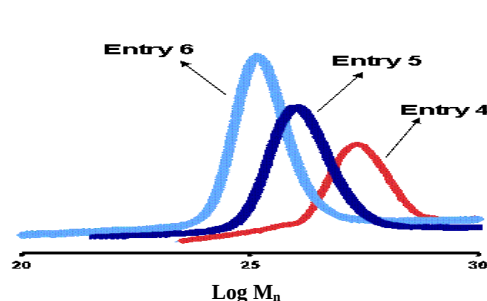


Figure 4. GPC curves of entry 4, entry 5 and entry 6.

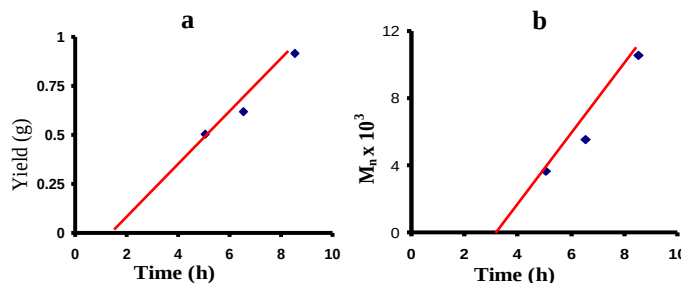


Figure 5. (a) The plot of Yield Vs Time, (b) The plot of M_n Vs Time

The dependence of polymer yield and M_n on polymerization temperature was investigated by batch method to check the living nature of this catalyst system. The yield of the polymers was increased with the increasing temperature. The GPC curves of the polymers obtained from different temperature are displayed in **Figure 6**.

Table 3. Effect of the temperature on polymerization of styrene with CuBr/BiPy.

Entry	St/ BDPME (mmol)	Temp (° C)	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n^d
7	250	75	trace	-	-	-
8	250	100	0.277	6.043	9.078	1.50
9	250	115	0.511	3.667	4.389	1.19

polymerization conditions; CuBr = 0.108 mmol, BiPy = 0.216 mmol, Styrene = 3.1 mL, time = 5 hrs

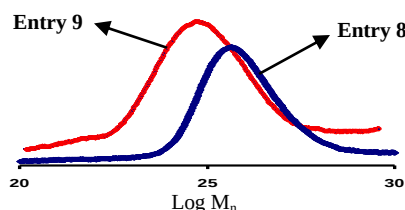
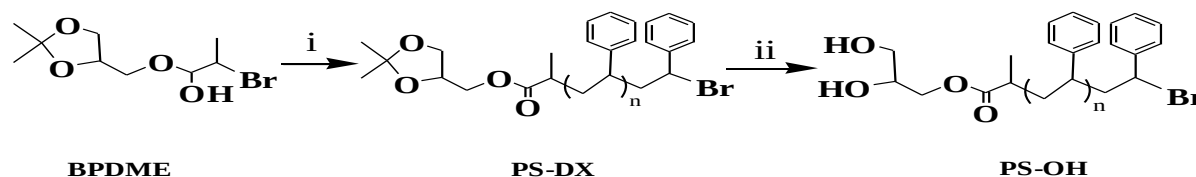


Figure 6. GPC curves of entry 8 and entry 9.

Styrene was then polymerized by ATRP with **BPDME** at different condition in conjunction with copper (I) bromide and bipyridine as a catalyst under nitrogen atmosphere. The hydroxylation of the dioxolane group of polystyrene (**PS**) was carried out using glacial acetic acid, water and anisole at 80 °C in THF for 1hour (Scheme 2).The quantitative conversion of dioxolane group to dihydroxyl group was confirmed by the ^1H NMR analysis.



i = CuBr, Bipyridine, 115 °C; ii = glacial acetic acid, water, anisole, 80 °C

Scheme 2. The hydroxylation of the dioxolane group of PS-DX

The structure of polystyrene obtained using **BPDME** initiator was investigated by ^1H NMR analysis of the polymer and comparison with the spectrum of **BPDME** initiator. The ^1H NMR spectrum of poly styrene obtained with **BPDME** was displayed in **Figure 7**. In the ^1H NMR spectrum of polystyrene, the signals at 4.6 ppm and 3.7 ppm assignable to $(-\text{O}-\text{CH}-\text{CH}_2-)$ and $(-\text{CH}-\text{CH}_2-\text{O}-)$ dioxolane protons and a signal at 4.4 ppm assignable to CH proton α to Br indicates that the polymerization was initiated with **BPDME**. A broad signal at 7.2 ppm assignable to aromatic protons (meta- and para-position) of styrene unit and at 6.5 ppm for ortho-proton. The signals observed at 1.35 and 1.77 ppm assignable to CH_2 and CH protons of main chain of polystyrene, respectively. These results clearly indicate the presence of dioxolane group in the ω -end of polystyrene obtained with **BPDME** initiator.

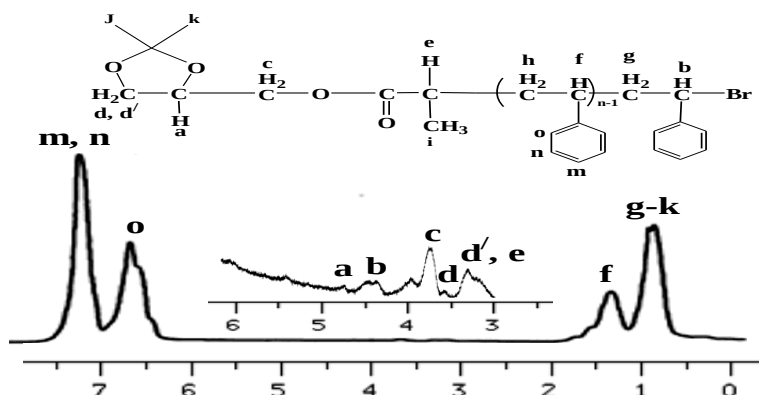


Figure 7. ^1H NMR spectrum of dioxolane end-functional PS

^1H NMR spectrum of **PS-OH** was displayed in **Figure 8**. The peaks at 5.66 and 5.19 ppm assigned for two $-\text{OH}$ groups and the signals assignable for main polystyrene chain were also appeared. This observation indicated the dihydroxy end-functional structure of **PS-OH**.

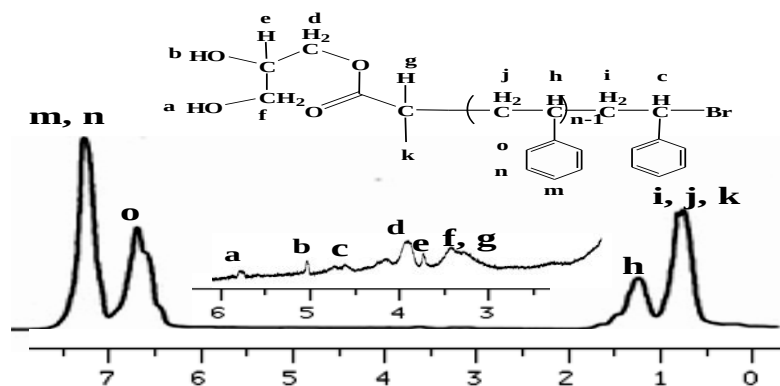


Figure 8. ^1H NMR spectrum of dihydroxy end-functional PS

IV. Conclusion

The initiator 2-bromopropionyl[2,2-dimethyl-1,3-dioxolane-4-ylmethyl]ester (**BPDME**) was synthesized in a good yield. The structure of **BPDME** was characterized by ^1H NMR analysis. The **BPDME** as initiator was successfully applied for Cu(I)-bipyridine mediated ATRP polymerization of styrene. The polymerization of styrene was investigated at various reaction conditions. The polymerization of styrene with **BPDME**/CuBr/BiPy (1:1:2) was investigated at various monomer feed ratio at 115 $^{\circ}\text{C}$. The yield and molecular weight of polymers were increased linearly with increasing the ratio of styrene and **BPDME**. These results suggest that the propagation rate was increased with increasing of monomer concentration. In time dependence polymerization, yield vs time plot showed linear relationship whereas the M_n values of the polymer linearly increased against time after a certain period. The molecular weight distribution was very narrow ($M_w/M_n = 1.14$). These results suggest that the living polymerization of styrene proceeded at 115 $^{\circ}\text{C}$ by **BPDME**/CuBr/BiPy catalyst system with slow initiation. The presence of dioxolane group in PS-DX was confirmed by ^1H NMR spectrum which indicated the dioxolane chain-end structure of the polystyrene. Finally, the dioxolane end group of the polystyrene was converted to dihydroxy

group by treatment of acetic acid, water and anisole at 80⁰ C. The structure of dihydroxy end-group was confirmed by ¹H NMR spectrum of the PD-OH. Dihydroxy group containing polystyrene can be use as functional macroinitiator or as coating material for the preparation of nanopartical which are under investigation.

V. References

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VI. Acknowledgements

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