Original Research Paper

Synthesis of Well-Defined Vinyl End-Functional Polystyrene Using Multifunctional Initiator by Atom Transfer Radical Polymerization

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Abstract: Atom Transfer Radical Polymerization (ATRP) has proven to be a powerful technique to obtain polymers with narrow polydispersities and controlled molecular weight. It also offers control over chain-ends. N-allyl-2-bromopropinamide (ABPN) was synthesized by one step reaction which involved on amidification of 2-bromo-propionyl bromide with allyl amine. ^{1}H NMR has confirmed the structure of the ABPN. The well-defined polystyrene was synthesized by using ABPN as initiator in ATRP method. The results of the polymerization were significantly affected by reaction conditions. The vinyl end-functional polystyrene obtained was characterized by Gel Permeation Chromatography (GPC) and NMR analysis.

Keywords: Functional Initiator, Atom Transfer, Radical Polymerization, Polystyrene, Acetamide

Introduction

The development of Living Radical Polymerization (LRP) techniques 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 (Wang and Matyjaszewski, 1995a; 1995b; Kato *et al*., 1995; Kotani *et al*., 1996; Matyjaszewski *et al*., 1997a). Synthesis of well defined reactive end-functional polymers has great importance for their use as macromonomer, macroinitiator, precursor for block copolymers etc. Recently a living radical polymerization method "Atom Transfer Radical Polymerization" (ATRP) has emerged as a versatile technique that has been applied broadly because of the robustness of the chemistry and the commercial availability of many initiators, catalysts and ligands (Tsarevsky *et al*., 2008; Kamigaito, 2011). As with other LRP techniques, control of the α-chain terminus is accessed from the initiator design, which for ATRP most often involves an alkyl halide with an activating substituent on the α-carbon that undergoes homolytic cleavage in the presence of catalyst to initiate polymerization. Since ester groups are good activating groups, α-haloester-based compounds are commonly used as ATRP initiators, whereby the ester unit can also carry functionality. The functionality incorporated into the polymer *via* an ester linkage is prone to hydrolysis; however, this lability has been overcome by their replacement with amide linkages through the use of α-halo amide-based initiators (Patten *et al*., 1996; Matyjaszewski *et al*., 1997b). The presence of amides are often considered to present unique challenges for ATRP in the production of polymers with narrow molecular weight distribution and having molecular weights in agreement with theoretical values. A recent report from Haddleton's laboratory thoroughly examined the conditions under which amide containing ATRP initiators gave well-controlled polymerization of various methacrylates and styrene (Matyjaszewski *et al*., 1997b). Prior work in Sawamoto's laboratory demonstrated the preparation of poly (methyl methacrylate) with narrow Polydispersity Index (PDI) using *N,N*-dimethyl-2-bromopropanamide as the initiator (Patten, *et al*., 1996). Matyjaszewski's laboratory has studied the polymerization of methacrylamides using a model α-haloamide-based initiators, obtaining well defined block copolymers (Coca *et al*., 1998). Recently, scientists (Xia *et al.*, 2005) have employed various chloro-propionamides as initiators to polymerize N-isopropylacrylamide with narrow molecular weight distribution to study the influence of the end group composition resulting from the initiators on the thermal properties (Percec *et al*., 1997). Well-defined end functional polymers are useful as building blocks for design and synthesis of various complex macromolecular architectures such as block (Guillerm *et al*., 2012;

Wang *et al.*, 2013; Glaied *et al.*, 2014), graft (Zhang *et al.*, 2012; Lav *et al.*, 2013), star (Cai *et al.*, 2012; Ratkanthwar *et al.*, 2013) copolymers etc. which find applications in biomedical (Bauer *et al.*, 2013), tissue engineering (Martina and Hutmacher, 2007), materials (Singh *et al.*, 2012) and surface sciences (Lee *et al.*, 2007). Although various end-functional polymers are reported so far, the synthesis of amide group containing reactive end-functional polymers still have an interest due to it's protein coupling ability to polymer and biomedical applications (Boyer *et al.*, 2011). Therefore, in this study amide group containing vinyl end-functional ABPN was synthesized and the ATRP of styrene was investigated using ABPN as initiator. The initiator efficiency and polymer properties also studied.

Materials and Methods

Materials

2-bromo-propionylbromide was purchased from Sigma Aldrich and used without further purification. Triethyl amine was purified by distillation followed by stirring with CaH_2 for 24 h. Allyl amine and bipyridine (BiPy) were purchased from Fluka. Styrene (St) was purchased from Aldrich and it was purified by passing through an alumina column to remove stabilizer and then stirred with CaH_2 for 8 h and filtered. Copper (I) bromide (98%, Aldrich) was purified according to a published procedure (Miller and Matyjaszewski, 1999). Tetrahydrofurane (THF), methanol and other common solvents were from Sigma Aldrich and purified by distillation.

Analytical Procedures

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, $CHCl_3$ as solvent and calibrated by polystyrene standards. ^{1}H NMR spectra of ABPN and polymers 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 ^{1}H) was used as internal reference.

Methods

Synthesis of ABPN

Allyl amine (1) (2.26 mL, 30 mmol) and triethylamine (6.0 mL, 43 mmol) were dissolved in 40 mL of THF. The

solution was cooled in an ice-water bath. To this solution, 3.2 mL (30 mmol) of 2-bromopropinyl bromide (2) in 20 mL of THF was added drop-wise. The mixture was stirred for 2 h at room temperature (1 reacted with 2 to yield ABPN 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 diethyl ether and washed with 50 mL of water three times. The aqueous part were combined and shaken with 50 mL of fresh diethyl ether. The total ether solution was then dried over anhydrous sodium sulphate for overnight. After filtering off the drying agent, ether was distilled out under vacuum. A yellowish liquid was obtained. A further distillation under high vacuum gave a light yellowish liquid; yield 1.8 mL, (69%). The structure of the product was characterized by NMR analysis.

^{1}H NMR ($CDCl_3$): 6.9 ppm (s, 1H, -NH); 5.6 ppm (m, 1H, CH_2=CH-); 5.1 ppm (dd, 2H, CH_2=CH-); 4.4 ppm (q,1H, -BrCH-CH_3); 3.8 ppm (d, 2H, CH-CH_2-NH-); 1.7 ppm (d, 3H, -CH-CH_3).

Polymerization

Polymerization was carried out in a 50 mL Schelnk type reactor equipped 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 was then sealed with rubber septum. A required amount of degassed styrene and ABPN were added with a syringe. The reactor was placed in an oil bath at the desired temperature controlled by a thermostat and the reaction mixture was stirred for certain time. At timed intervals, the polymerizations were stopped by addition of 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 6 h.

Results

The initiator N-allyl-2-bromopropinamide (ABPN) was synthesized from the reaction between allyl amine and 2-bromopropionyl bromide in the presence of triethylamine (Scheme 1) according to the procedure described in experimental section.
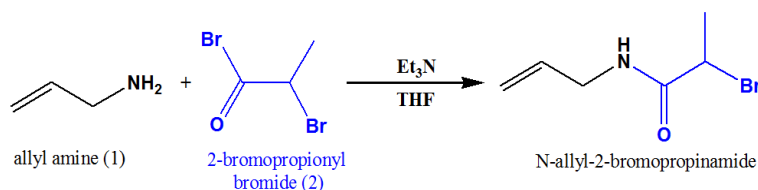
Scheme 1. Synthesis of N-allyl-2-bromopropinamide (ABPN)

Table 1. Effect of the temperature on polymerization of styrene with CuBr/BiPy/ABPN

Entry	St/ABPN (mmol)	Temperature (°C)	Yield (g)	M_n x 10^3	M_w x 10^3	M_w/M_n
1	500	75	trace	-	-	-
2	500	100	0.2274	10.565	14.451	1.36
3	500	115	1.4286	28.494	33.820	1.20

Polymerization conditions: [CuBr = 0.054 mmol, Bipy = 0.108 mmol, Styrene = 3.1 mL (27mmol), Time = 8 h]

Table 2. Effect of the ratio of styrene(St)/ABPN on polymerization of styrene

Entry	St/ABPN (mmol)	Temperature (°C)	Yield (g)	M_n x 10^3	M_w x 10^3	M_w/M
4	250	115	0.9926	11.735	14.167	1.18
5	500	115	1.4286	28.494	33.820	1.20
6	1000	115	1.8066	41.903	55.414	1.32

Polymerization conditions: [CuBr = 0.054 mmol, Bipy = 0.108 mmol, Styrene = 3.1 mL (27 mmol), Time = 8 h]

Table 3. Effect of time on polymerization of styrene with CuBr/Bipyridine/ABPN

Entry	Initiator	Time (hours)	Yield (g)	M_n x 10^3	M_w x 10^3	M_w/M_n
7	ABPN	6	0.725	14.878	18.908	1.27
8	"	8	1.429	28.494	33.820	1.20
9	"	9	2.068	41.382	49.938	1.20

Polymerization conditions: CuBr = 0.054 mmol, Bipy = 0.108, mmol, Styrene = 3.1 mL, Temperature = 115°C

The polymerization of styrene was carried out by ATRP using ABPN in conjunction with cupper (I) bromide and bipyridine as a catalyst under nitrogen atmosphere at different temperature (70, 100 and 115°C) to investigate the catalytic efficiency at a suitable conditions. The polymerization results obtained at various temperatures were displayed at Table 1.

Styrene was then polymerized by ATRP at 115°C initiated with ABPN at different styrene/initiator ratio using same catalyst system under nitrogen atmosphere. The effect of styrene/initiator ratio in the polymerization was summarized in Table 2.

The dependence of polymer yield and molecular weight (M_n) on polymerization time was investigated by batch method to check the living nature of this catalyst system at 115°C. The yield of the polymer, molecular weight and molecular weight distribution of the polymers obtained by different polymerization time were summarized in Table 3.

Discussion

The initiator ABPN was characterized by ^{1}H NMR. In the ^{1}H NMR spectrum of the ABPN (Fig. 1), several additional signals were appeared including the signals of 2-bromopropionyl bromide and the additional signals were clearly assigned as follows. A singlet at 6.9 ppm was appeared for assumable to –NH– proton. A mutiplate at 5.6 ppm and a double doublet at 5.1 ppm assignable to -CH=CH_2 and -CH=CH$_2$ protons, respectively, indicates the presence of vinyl group. The splitting (double doublet) of the vinyl (CH$_2$=) protons indicates the presence of *cis-trans* isomers of

ABPN. A doublet appeared at 3.8 ppm was assigned to =CH-CH_2-NH- proton.

The results of the polymerization styrene using ABPN as initiator in conjunction with cupper (I) bromide and bipyridine at different temperature (Table 1) showed that a trace amount of the polymer was obtained at 75°C whereas the yield of polymer was increased with raising the polymerization temperature at 100 and 115°C. The highest yield and M_n of the polymer were obtained at 115°C. The GPC curves of the polymer obtained at 115°C was shifted to the higher molecular weight region compared to the GPC curve of the polymer obtained at 100°C (Fig. 2). The molecular weight distribution (M_w/M_n) of the polymer became narrow with increasing polymerization temperature. These results suggest that both the initiation and propagation rate of the styrene polymerization in the presence of ABPN initiator were increased at high temperature.

The polymerization of styrene was then carried out by ATRP initiated with ABPN in the presence of cupper (I) bromide and bipyridine at different styrene/initiator ratio at 115°C under nitrogen atmosphere. The ratio of styrene and ABPN (St/ABPN) significantly affect on the polymerization of styrene (Table 2). The yield of polymers was increased with increasing the ratio of styrene and ABPN. The polymers obtained with high molecular weight (M_n) and narrow molecular weight distribution (M_w/M_n ~1.18). The M_n value of the polymers was increased with the increasing St/ABPN ratio. The GPC curves of the polymers obtained from the feed ration St/ABPN = 1000, St/ABPN = 500 and St/ABPN = 250 are displayed in Fig. 3.
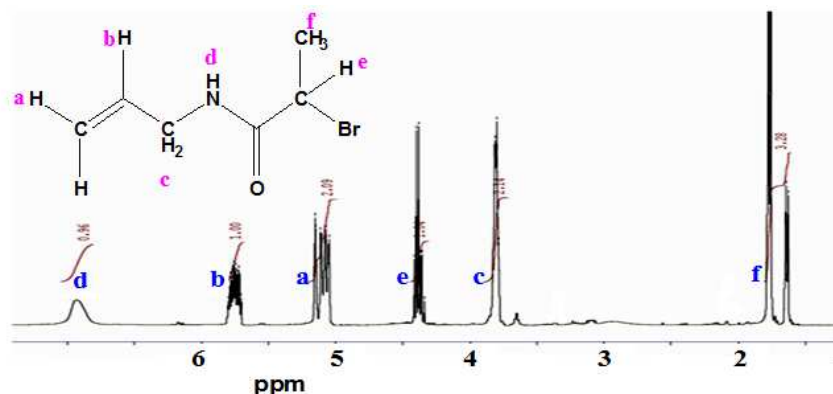
Fig. 1. ^{1}H NMR spectrum of initiator ABPN

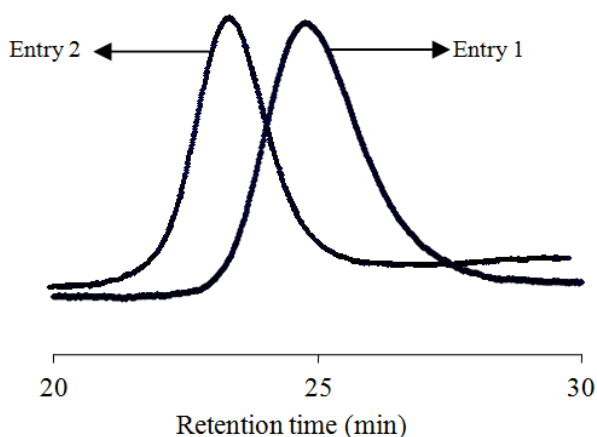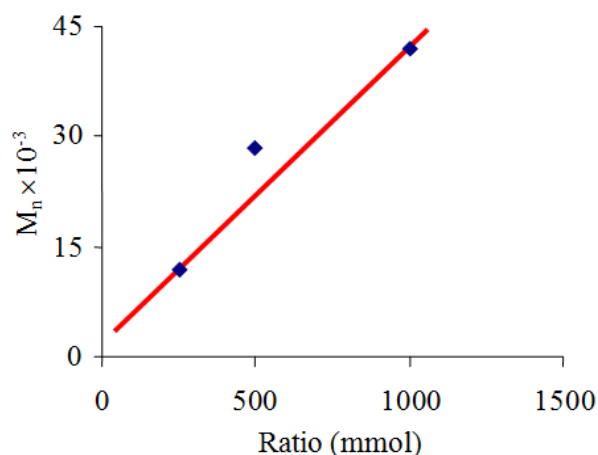Fig. 2. GPC curves polymer obtained using ABPN

Fig. 3. GPC curves polymer obtained using ABPN
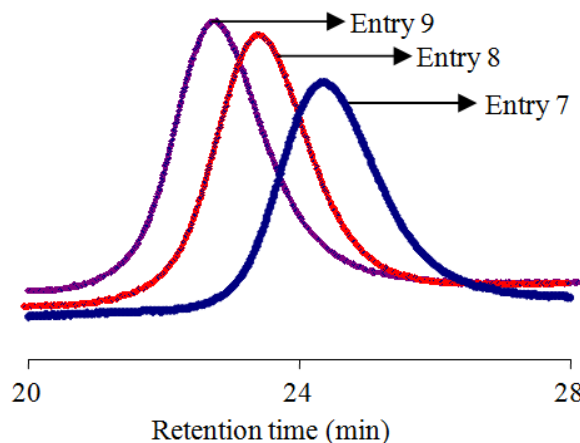

Fig. 4. Ratio (monomer/initiator) versus M_n
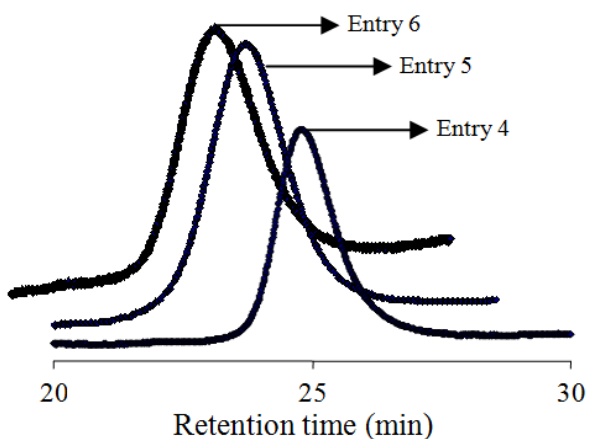
Fig. 5. GPC curves polymer obtained using ABPN

The GPC curve of the polymer obtained from the higher monomer concentration (St/ABPN = 1000) was shifted to the higher molecular weight region than that of the polymer obtained from lower monomer concentration (St/ABPN = 500). The M_n value (41.9×10^3) of the polymer obtained from the feed ratio of St/ABPN = 1000 was higher than the M_n value (28.5×10^3) of the polymer obtained from the feed ratio of St/ABPN = 500.

These results suggest that the higher propagation rate occurred at higher monomer concentration in feed. The linear relationship of molecular weight of the polymers with St/ABPN ratio (Fig. 4) also supported the above results.
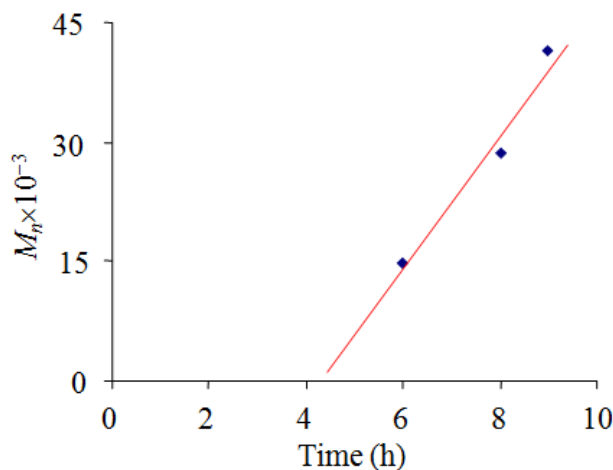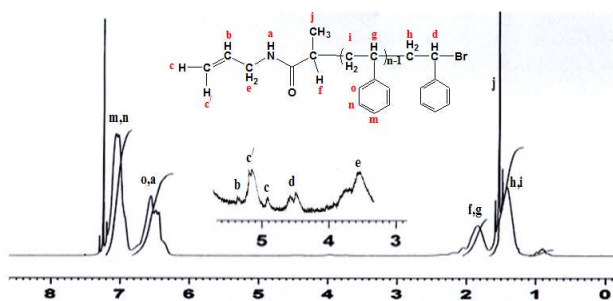
Fig. 6. Plot of Mn versus polymerization time

Fig. 7. ^{1}H NMR spectrum of vinyl end-functional polystyrene

To produce polymer with narrow polydispersity is one of the main criteria for a living polymerization system. The initiator ABPN combined with CuBr/bipyridene catalyst system gave the polymers with narrow polydispersity (M_w/M_n = 1.20 at 115°C (Table 2, entry 5). This result therefore promoted us to make sure the living nature of ABPN/CuBr/bipyridene catalyst system at 115°C. Thus, 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 summarized in Table 3.

The GPC curves of polymers obtained from different period of time (6, 8 and 9 h) were compared in Fig. 5.

The GPC curves were shifted to the higher molecular weight region with increasing polymerization time and keeping narrow M_w/M_n. The plot of time Vs M_n showed linear relationship with a slop at initial period in Fig. 6. The yield also increased with time and showed linear relationship. These results suggest that the living polymerization of styrene proceeded at 115°C by ABPN/CuBr/BiPy catalyst system with slow initiation.

The structure of polystyrene obtained with ABPN/CuBr/Bipyridine catalyst system was investigated by the ^{1}H NMR analysis. The ^{1}H NMR spectrum of polystyrene obtained was displayed in Fig. 7 and the signals appeared were assigned by compare with the ^{1}H NMR spectrum of ABPN.

In the ^{1}H NMR spectrum of polystyrene, the presence of a double doublet at 5.4 and 4.9 ppm assignable to vinyl protons and a signal at 4.5 ppm assignable to CH proton α- to Br indicated that the polymerization was initiated with ABPN. A broad signal at 7.1 ppm was assigned to aromatic protons (*meta-* and *para-*position) of styrene unit and at 6.5 ppm for *ortho-*proton. The signals observed at 1.37 and 1.79 ppm were assigned for the CH_2 and CH protons of main chain of polystyrene, respectively.

Conclusion

The initiator ABPN was synthesized in a good yield. The structure of initiator ABPN was characterized by ^{1}H NMR analysis. The initiator was successfully applied for Cu(I)-bipyridine mediated ATRP polymerization of styrene. The polymerization of styrene with ABPN/CuBr/BiPy (1:1:2) was investigated at various conditions. The yield and molecular weight of polymers were increased linearly with increasing styrene-ABPN ratio, time and temperature. In time dependence polymerization, the M_n values of the polymer linearly increased against time after a certain period keeping narrow molecular weight distribution (M_w/M_n = 1.14). These results suggest that the living polymerization of styrene proceeded at 115°C by ABPN/CuBr/BiPy catalyst system with slow initiation. The presence of amido-functional vinyl end group in the polymer chain was confirmed by ^{1}H NMR analysis.

Acknowledgement

Funding Information

Author's Contributions

Samiul Islam Chowdhury: All experimental works of this research were done by Mr. Chowdhury.

Roushown Ali: Interpretation of NMR spectra and GPC data were done Dr. Ali.

Tariqul Hasan: This research was carried out in Hasan's laboratory. Over all supervision of experimental works, data analyses were done by Professor Hasan.

Ethics

The amide group containing vinyl end-functional polystyrene obtained from the work is a reactive macromonomer, which could be used as a precursor for tailored copolymers and also in biomedical applications.

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