



Effect of Spacer Length from Vinyl Group of Vinyl-bromoester Initiator on Atom Transfer Radical Polymerization of Styrene

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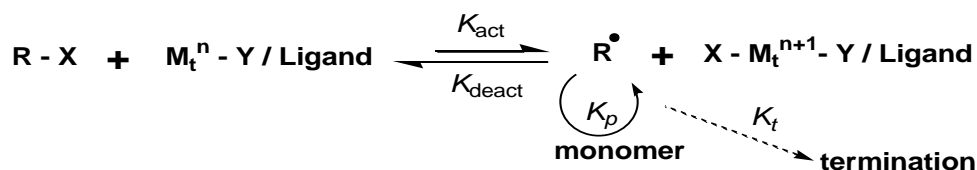
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Abstract: Two vinyl α -bromesters with shorter methylene spacer allyl bromopropionate (**ABP**) and longer methylene spacer undecenyl bromopropionate (**UBP**) were used as initiator for styrene polymerization by Cu-bipyridine mediated atom transfer radical polymerization. In both cases, the yield and the molecular weight of polymers were increased with increasing the ratio of styrene and initiator (St/In). The molecular weight of the polymer obtained by **UBP** system was higher than the polymer obtained by **ABP** system. It was assumed that the free radical formed from longer spacer containing **UBP** system is more stable than the free radical formed from the shorter spacer containing **ABP** system. The structure of the polystyrene obtained from both catalysts system was characterized by 1H -NMR analysis.

I. Introduction

Atom Transfer Radical Polymerization (ATRP), a controlled system reported by Matyjaszewski et. al. [1, 2] has been widely used for synthesis of end-functional, telechelic, block, graft and various polymers/copolymers with precisely controlled architecture [3,4]. The ATRP process, in which a free radical generates by the transfer of a halogen (typically bromine) from a dormant initiator or polymeric chain to a transition metal. This free radical then adds of monomer to yield polymer.



Scheme 1: Mechanism of metal complex-mediated ATRP

Although various type of initiators have been reported for ATRP, α -haloesters have been successfully employed for well-controlled ATRP to synthesis of various functional polymer or copolymers.[2,5-9] Structural adjustment of the α -haloesters initiator provides a handle to fine-tune the rate of initiation in the ATRP system. For instance, α -haloisobutyrate produce initiating radicals faster than the corresponding α -halopropionates due to better stabilization of the generated radicals after the halogen abstraction step. The polymerization of methacrylates with slow initiation was found to report using α -halopropionates.[10,11] Matyjaszewski *et. al.* reported the ATRP of styrene with vinyl chloroacetate and allyl chloroacetate as initiator using CuBr-bipyridine catalyst system.[5] The former was found as better initiator for styrene polymerization. The initiation and propagation rate of the polymerization depend on the structure of initiator as well as the generation and stability of the free radical. Although several papers have been reported to clarify the effect of the structure of the initiator on ATRP, [12, 13] it is an importance topic to investigate the efficiency of new initiators for ATRP. In this work, undecenyl bromopropionate (**UBP**) and allyl bromopropionate (**ABP**) initiators were synthesized and applied as initiators on ATRP of styrene under different conditions and the effect of $-CH_2-$ spacer between $CH_2=CH-$ and ester groups of the initiators was investigated.

II. Experimental

Materials: Styrene 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. Finally it was stored in a Schlenk flask at $0^\circ C$ under nitrogen prior to use. Copper (I) bromide was purified by recrystallization in methanol and washed with ether. Bipyridine from Fluka, 2-bromopropenyl bromide, allyl alcohol and 10-undecen-1-ol were purchased from Aldrich and used without further purification. Triethylamine was distilled over CaH_2 . All solvents were purified by distillation followed by refluxed with sodium and benzophenone.

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 CuBr 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 at the desired temperature and the reaction mixture was stirred for certain time. At timed intervals, 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 6 h.

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, cluent, $CDCl_3$ as solvent and calibrated by polystyrene standards. 1H and ^{13}C 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 ^{13}C) was used as internal reference.

Synthesis of Initiators: Allyl-2-bromopropionate (ABP): A 5 g (8.6 mmol) of allyl alcohol 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 1 mL (9 mmol) of 2-bromopropionyl bromide in 20 mL of THF. The mixture was stirred for another 2 h at room temperature. Triethylamine hydrogen bromide salt was filtered out. THF in the filtrate was removed under vacuum at room temperature. The residual was dissolved in $CHCl_3$ and washed with 50 mL of water three times. The aqueous parts were combined and shaken with 50 mL of fresh $CHCl_3$. The total $CHCl_3$ solution was then dried over anhydrous $CaCl_2$ for overnight. After filtering off the drying agent, $CHCl_3$ was distilled out under vacuum. A brown liquid was obtained. A further distillation under high vacuum gave a colorless liquid; yield 3.5g (70 %).

1H NMR ($CDCl_3$): 5.92 ppm (m, 1H, $CH_2=CH-$); 5.45 ppm (dd, 2H, $=CH_2$); 4.71 ppm (d, 2H, $-O-CH_2CH-$); 4.4 ppm (q, 1H, $CH_3CH(Br)-OC(O)-$); 1.80 ppm (d, 3H $-CH(Br)-CH_3$),

^{13}C NMR ($CDCl_3$): 167.21 ppm ($-O-C(O)-$); 128.72 ppm ($CH_2=CH-$); 116.25 ppm ($CH_2=CH-$); 63.70 ppm ($-O-CH_2CH-$); 37.31 ppm ($CH_3CH(Br)-$); 19.07 ppm ($CH_3CH(Br)-$).

Undecen-2-Bromopropionate (UBP): A 5.0 g (30 mmol) of 10-undecen-1-ol and 5 mL (36 mmol) of triethylamine were dissolved in 80 mL of THF. This solution was cooled in an ice-water bath. To this solution was added drop-wise 3.20 mL (30 mmol) of 2-bromopropenyl bromide in 20 mL of THF. The mixture was stirred for 2 h at room temperature. The reaction mixture was worked-up according to the same method used for ABP synthesis. Finally, a colorless liquid was obtained; yield 7.60 g (82 %).

1H NMR ($CDCl_3$): 5.72 ppm (m, 1H, H-b); 4.85 ppm (dd, 2H, H-a); 4.41 ppm (q, 1H, H-l); 4.1 ppm (t, 2H, H-k); 2.00 ppm (q, 2H, H-c); 1.80 ppm (d, 3H, H-m), 1.55 ppm (t, 2H, H-j); 1.2 – 1.4 ppm (m, 14H, H-d-i).

^{13}C NMR ($CDCl_3$): 167.46 ppm (C-l); 136.34 ppm (C-b); 111.47 ppm (C-a); 63.30 ppm (C-k); 37.48 ppm (C-m); 31.10 ppm (C-c); 25.71 - 26.73 ppm (C-d-h, j); 23.05 ppm (C-i); 18.97 ppm (C-n).

III. Results and Discussion

The initiators **ABP** and **UBP** were synthesized from the reaction between 2-bromopropenyl bromide and allyl alcohol or 10-undecene-1-ol, respectively, in the presence of triethylamine. The both initiators **ABP** and **UBP** were characterized by 1H NMR and ^{13}C NMR analysis. In the 1H NMR spectrum and ^{13}C NMR spectrum of the initiators, the signals correspond to all protons and carbons were assigned clearly.

Styrene was polymerized by ATRP at 110 °C initiated by **ABP** and **UBP** at three different ratio of styrene and initiator (St/In) in conjunction with copper (I) bromide and bipyridine as a catalyst under nitrogen atmosphere. The results of the polymerization are listed in Table 1. The ratio of styrene and initiator significantly affects the results of the polymerization. In both cases, the yield of polymer was increased with increasing the ratio St/In. The yield of polymer was higher for **UBP** than that of **ABP** system at similar polymerization conditions. The molecular weight of the polymers obtained was measured with gel permeation chromatography (GPC) and the GPC curves obtained polymers are displayed in Figure 1. In the both catalysts system, the polymers obtained with high molecular weight which is increased with increasing St/In ratio. The molecular weight of the polymer obtained by **UBP** system was higher than that of the polymer obtained by **ABP** system. The **UBP** system showed better catalytic efficiency that could be explained as; the free radical (**ii**) formed in **UBP** system is more stable because it does not form cyclic structure due to longer $-CH_2-$ spacer between carbon free radical and $CH_2=CH-$ group. On the other hand, the free radical (**i**) formed in **ABP** system might have a possibility to form a six member cyclic structure which causes slow initiation during polymerization.

Table 1: Polymerization of styrene using ABP or UBP as initiator with CuBr/Bipyridine.^a

entry	initiator	St/initiator (mmol)	yield (g)	M_n^b	M_w/M_n^b
1	ABP	800	0.82	7479	1.52
2	„	400	0.68	5017	1.38
3	„	200	0.31	3096	1.30
4	UBP	800	1.22	18864	1.47
5	„	400	0.96	9759	1.50
6	„	200	0.61	4863	1.50

^aPolymerization conditions: CuBr = 0.08 mmol, BiPy = 0.24 mmol, temperature = 110 °C, time = 2h. ^bNumber average molecular weight and molecular weight distribution were measured by GPC analysis using polystyrene standard.

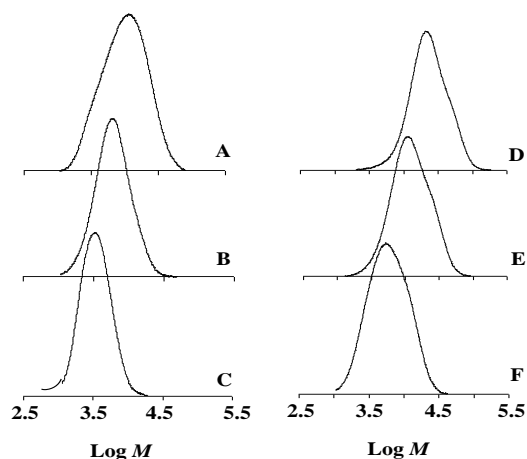
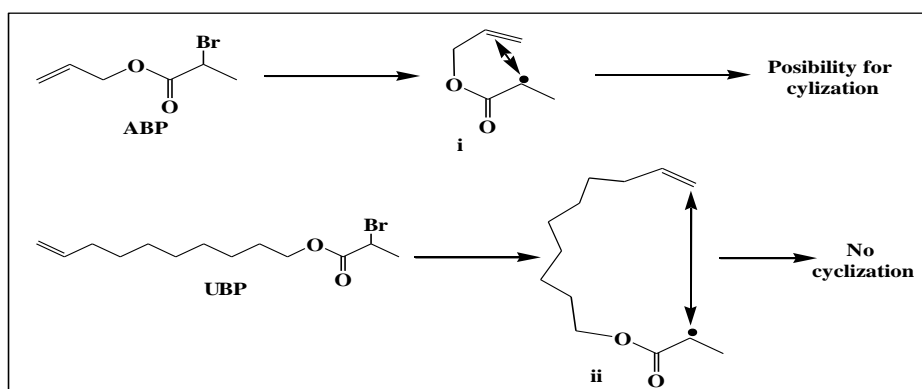


Figure 1: GPC curves of ABP (A, B & C) and UBP (D, E & F)



Scheme 2: Cyclization possibility

^1H NMR spectra of polystyrene and ABP were compared in Figure 3. In the ^1H NMR spectrum of polystyrene, the presence of a double doublet at 5.4 and 5.9 ppm assignable to vinyl protons and a signal at 4.5 ppm assignable to CH proton α - to Br indicate that the polymerization was initiated with ABP. A broad signal at 7.26 ppm was assigned to aromatic protons (*meta*- and *para*-position) of styrene unit labeled as l and m, and at 6.75 ppm for ortho-proton labeled as n. The signals observed at 1.50 and 2.00 ppm were assigned for the CH_2 and CH protons of main chain of polystyrene labeled as h, j, g and i, respectively.

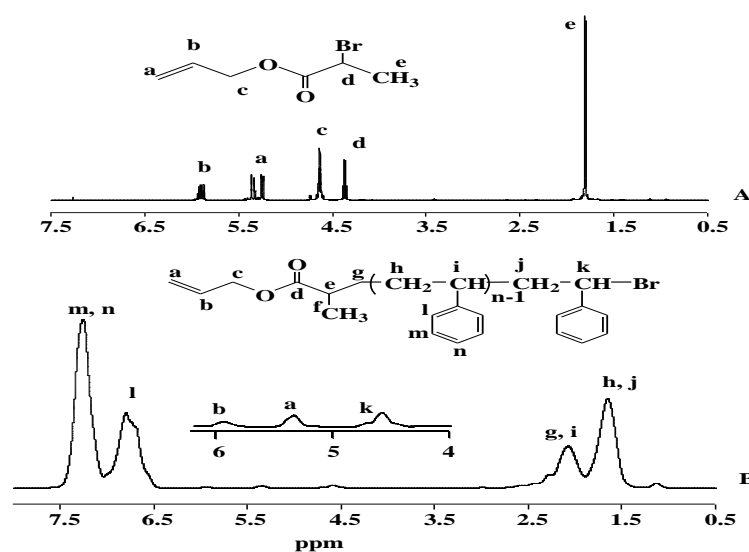


Figure 2: NMR of ABP and ABP end functional Polystyrene

The ^1H NMR spectra of the **UBP** initiator and the polystyrene obtained by **UBP** initiator were compared in Figure 4. In the ^1H NMR spectrum of the polystyrene (Figure 3B), the signals observed at 5.6 and 6.3 ppm assignable to $\text{H}_2\text{C}=\text{CH}$ - protons (H-a and H-b), at 4.7 ppm for CH proton of α to Br (H-r) and at 4.0 ppm for H-l and H-k. These assignments indicate the presence of undecenyl group in the polymer. Two broad signals observed at 7.28 ppm assignable to aromatic protons H-t and H-u (meta- and para-position) and at 6.75 ppm for ortho-proton H-s of styrene unit. The signals observed at 1.50 and 2.00 ppm assignable to CH_2 and CH protons (H-o and H-p) of main chain of polystyrene.

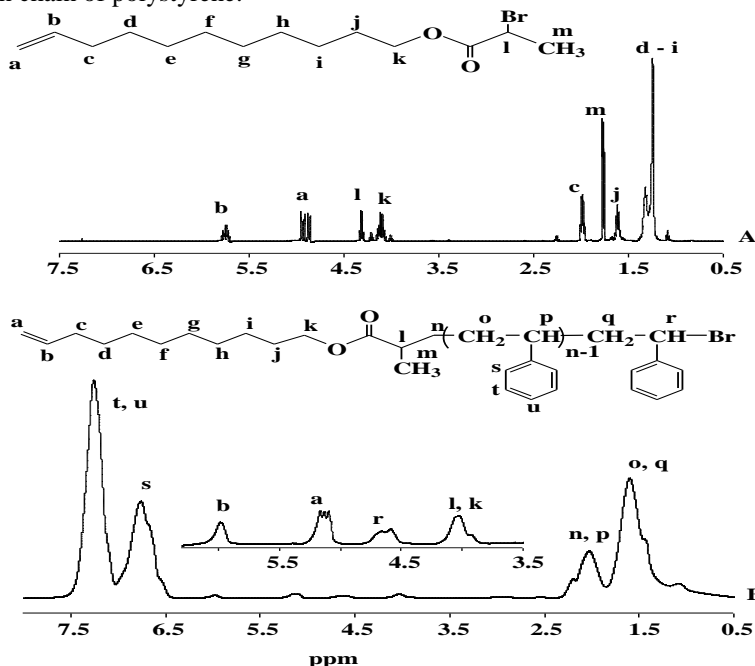


Figure 3: NMR of UBP and UBP end functional Polystyrene

IV. Conclusion

Allyl bromopropionate (**ABP**) and undecenyl bromopropionate (**UBP**) were used as initiator for styrene polymerization by Cu-bipyridine mediated atom transfer radical polymerization. The yield and the molecular weight of the polymer obtained by **UBP** system was higher than the polymer obtained by **ABP** system. The free radical formed from longer spacer containing **UBP** system is assumed to be more stable than the free radical formed from the shorter spacer containing **ABP** system. The $\text{CH}_2=\text{CH}$ - end-functional polystyrenes were obtained from both catalysts system.

V. References

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