Polymer Bulletin 58, 873–879 (2007)
DOI 10.1007/s00289-007-0729-1

Polymer Bulletin

Controlled radical polymerization of methyl methacrylate in the presence of 2-bromoethanol

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Received: 29 October 2006 / Revised version: 20 December 2006 / Accepted: 29 December 2006

Summary

The radical polymerization of methyl methacrylate (MMA) and styrene (St) initiated by 2,2'-azobis(isobutyronitrile) (AIBN) at 60°C in the presence of haloalkyl alcohol are studied. The influence of structure and concentration of haloalkyl alcohol as a transfer agent are investigated. For the radical polymerization of MMA in the presence of large amount of 2-bromoethanol, controlled radical polymerization is proceeded. The 2-bromoethanol is, thus, one of the transfer agents for radical polymerization to control the molecular weight and the structure of poly(MMA).

Introduction

Controlled/living radical polymerization [1-3] is one of the most effective routes to prepare well-defined polymers (e.g. determined molecular weight, narrow distribution, and tailored architectures). It is also used in a wide range of fields such as surfactants, dispersants, coatings, membranes, adhesives to biomaterials, drug delivery, and microelectronics. Since Otsu and coworkers were the first suggested the idea of stable radical (persistent radical) [4,5] for precision polymerization, many kinds of controlled radical polymerization have been found, where the most efficient methods were nitroxide-mediated polymerization (NMP)[6,7], atom transfer radical polymerization (ATRP) [8-10], degenerative transfer (DT) polymerization with alkyl iodide [11-14], and reversible addition-fragmentation chain transfer (RAFT) polymerization [15,16].

For NMP and ATRP process, a reversible termination mechanism is used in which the propagating radical reacts with the control agent to give a dormant chain. It is controlled by the persistent radical effect. In DT and RAFT, the controls of polymerization are achieved through degenerative chain transfer typically from iodoalkyls and dithioesters. The dormant chain can be transferred into actives chain via physical or chemical stimulus.

In recent years, the DT polymerization used mostly the iodoalkyl compounds as the chain transfer agent such as 2-iodofluoropropane, 1-iodo-perfluorohexane, 1-iodo-1-chloroethane, 1-phenylenyl iodide, methyl-2-iodopropionate, and iodoacetonitrile, which are unstable due to weak C-I bond and thus prone to alteration upon storage.

Furthermore, the monomers involving tertiary propagation such as methacrylates was not successful because it would require iodoalkyl compounds with a better leaving group such as ethyl 2-iodo-2-methyl-propionate, although such compounds are inherently more unstable. To solve the problems, we investigated controlled radical polymerization using stable haloalkyl alcohol which can easily dissolve into water and conventional organic solvents. This paper describes about the controlled radical polymerization of MMA and St as a monomer using various haloalkyl alcohols as a chain transfer.

Experimental Section

Materials

MMA and St were purified by distillation under reduced pressure over calcium hydride and stored in ampoules prior to use. AIBN (Wako) was recrystallized twice from methanol and used as initiator. Benzene was distilled as usual. The haloalkyl alcohols of 2-iodoethanol (Tokyo Kasei), 2-chloroethanol (Wako), and 2-bromoethanol (Wako) were used as received.

Polymerization Procedures

MMA/St, benzene and haloalkyl alcohol were added into brown test tube for light protection. After three freeze-thaw-pump cycles, the flask was filled with nitrogen and sealed. The tubes were finally immersed in an oil bath and heated at the desired temperature under stirring. After a certain time, the tube was cooled, opened, and diluted with dichloromethane in turn. The product polymer was recovered from organic layer by evaporation of the solvents under reduced pressure and vacuum dried overnight. The monomer conversion was determined by gravimetry.

Characterization

The molecular weight of the polymers was measured by size exclusion chromatography (SEC) in tetrahydrofuran at 38°C on two polystyrene gel [TSK gel G-MH$_{HR}$-M × 2 (exclusion limit: 4×10^6 (polystyrene, PSt)); 7.8 mm i.d. × 300 mm each; flow rate 1.0 mL/min] connected to Tosoh CCPS dual pump and a RI-8011 refractive detector. The number-average molecular weight (M_n) and M_w/M_n were calculated from SEC curves on the basis of a PSt calibration. ^{1}H-NMR spectrum for the structure such as triad tacticity ratio of poly(MMA) was recorded on a JEOL JNM-EX 500 (500 MHz) spectrometer.

Results and discussion

Radical polymerization of MMA or St with/without haloalkyl alcohol

The polymerizations of MMA and St in the presence of haloalkyl alcohol as a chain transfer agent under different condition were studied. For comparison, the polymerizations without haloalkyl alcohol for these monomers were also examined. The polymerization results are summarized in Table 1, Table 2, and Table 3.

Table 1. Conventional Radical Polymerization of MMA or St without Haloalkyl Alcohol [a]

Monomer	Time (h)	Conv. (%)	$M_n \times 10^{-4}$	M_w/M_n
MMA	7	73.6	7.9	1.7
St	8	20.8	4.5	1.7

[a] $[MMA]_0 = 5.0$ M, $[St]_0 = 5.0$ M, $[AIBN]_0 = 1.0 \times 10^{-2}$ M in benzene at 60°C.

Table 2. Polymerization of MMA in the Presence of Haloalkyl Alcohol [a]

Additive	Conc. [M]	Time (h)	Conv. (%)	$M_n \times 10^{-4}$	M_w/M_n
2-Iodoethanol	4.0		no polym.		
	0.1	2.5	27.5	7.9	1.71
		5.0	47.4	8.4	1.78
		10.0	99.1	7.0	1.81
		22.0	100	5.7	1.93
2-Chloroethanol	4.0	3.0	50.1	9.2	1.94
		6.0	80.7	9.4	2.01
		7.0	86.8	12.5	1.92
		8.0	100	10.9	2.09
	0.1	2.5	33.1	13.6	1.46
		8.0	30.7	10.3	1.64
		9.0	50.8	17.0	1.52
2-Bromoethanol	4.0	3.0	15.0	0.7	1.94
		7.0	39.9	2.2	1.84
	0.1	2.5	42.3	14.0	1.95
		22.0	100	30.0	1.98

[a] $[MMA]_0 = 5.0$ M, $[AIBN]_0 = 1.0 \times 10^{-2}$ M in benzene at 60°C.

Table 3. Polymerization of St in the Presence of Haloalkyl Alcohol [a]

Additive	Time (h)	Conv. (%)	$M_n \times 10^{-4}$	M_w/M_n
2-Iodoethanol [b]	3	7.5	3.7	1.89
	7	26.1	4.2	1.72
	24	66.0	5.0	1.68
	28	70.4	5.1	1.74
2-Chloroethanol	4	16.8	4.1	1.66
	8	30.3	5.0	1.66
	23	51.3	4.9	1.63
	28	75.0	6.3	1.72
2-Bromoethanol	3	12.7	5.4	1.57
	8	25.2	5.5	1.62
	24	53.2	6.1	1.56
	30	67.7	5.5	1.67

[a] $[St]_0 = 5.0$ M, $[AIBN]_0 = 1.0 \times 10^{-2}$ M, $[additive]_0 = 4.0$ M in benzene at 60°C.
[b] $[additive]_0 = 0.1$ M. (In the case of 4.0 M, no polym)

Table 1 shows the results of the conventional radical polymerization of MMA or St in the absence of haloalkyl alcohol. Both polymerizations yielded high conversion, and common polymers with much higher molecular weights and broader molecular weight distributions were obtained. Furthermore, the polydispersities among the polymers were not different and the active order of MMA > St were also observed.

When 2-iodoethanol (0.1 M) was used as a chain transfer agent, the conversion of poly(MMA) was increased with the time but the molecular weight did not increase with the conversion, while the molecular weight distribution was still broader (M_w/M_n ~ 1.8) as summarized in Table 2. This means that, this polymerization is not a controlled radical polymerization but that is called a conventional chain polymerization with transfer agent [17]. On the other hand, a polymerization grew with time for St polymerization, unlike MMA polymerization, the molecular weight increased and molecular weight distribution became slightly narrow (M_w/M_n ~ 1.7) (see Table 3). On the basis of these results, 2-iodoethanol was more effective in St than MMA, although the radical could not control sufficiently the polymerization. Furthermore, 2-iodoethanol increased the molecular weight in the early period of polymerization.

When the 2-chloroethanol, which is more electronegative than 2-iodoethanol, was used, the polymerization of MMA and St grew with the time as shown in Table 2 and 3. The molecular weight of MMA became higher than before and molecular weight distributions became slightly narrow. The similar results were also obtained in St. From the results, the carbon-chlorine bond is strong and can not stabilize (not controlled) the radical center.

When a large amount of 2-bromoethanol, which have the property between 2-iodo- and 2-chloroethanol, was used as a chain transfer agent, the molecular weights could be controlled in MMA polymerization. Meanwhile, there was no changed in polymerization of St. As a result, 2-bromoethanol was more effective than any other chain transfer agents of haloalkyl alcohols. Figure 1 shows (a) the time-conversion curve and (b) M_n-conversion curve for the polymerization of MMA with a large amount of 2-bromoethanol. Interestingly, the polymerization of MMA occurred without induction phase and the M_n of the polymers increased in direct proportion to monomer conversion. In a general DT process, a small amount of transfer agent is effective in controlling molecular weights. It is likely that the large amount of 2-bromoethanol was needed to control polymerization of MMA, due to intermolecular hydrogen bonding in haloalkyl alcohols. Furthermore, the polymerization rate of

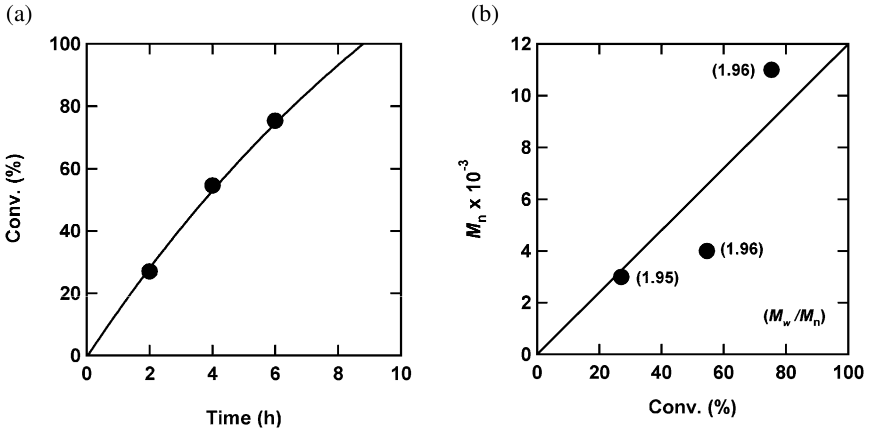

Figure 1. Polymerization of MMA in the presence of 2-bromoethanol in benzene at 60°C: $[MMA]_0$ = 5.0 M, $[AIBN]_0$ = 1.4 × 10^{-2} M, $[\text{2-bromoethanol}]_0$ = 4.0 M. (a) Times-conversion curve, (b) M_n-conversion curve.

MMA was faster than that shown in Table 2 under different concentration of AIBN. Hence, the concentration of AIBN is concerned with the polymerization rate.

Controlled radical polymerization of MMA with 2-bromoethanol: Monomer Addition Experiment

To investigate the "living" nature of MMA polymerization in the presence of 2-bromoethanol, a fresh feed of MMA was added to the reaction mixtures. Figure 2 shows the results of the experiments. The polymerization was not terminated and still

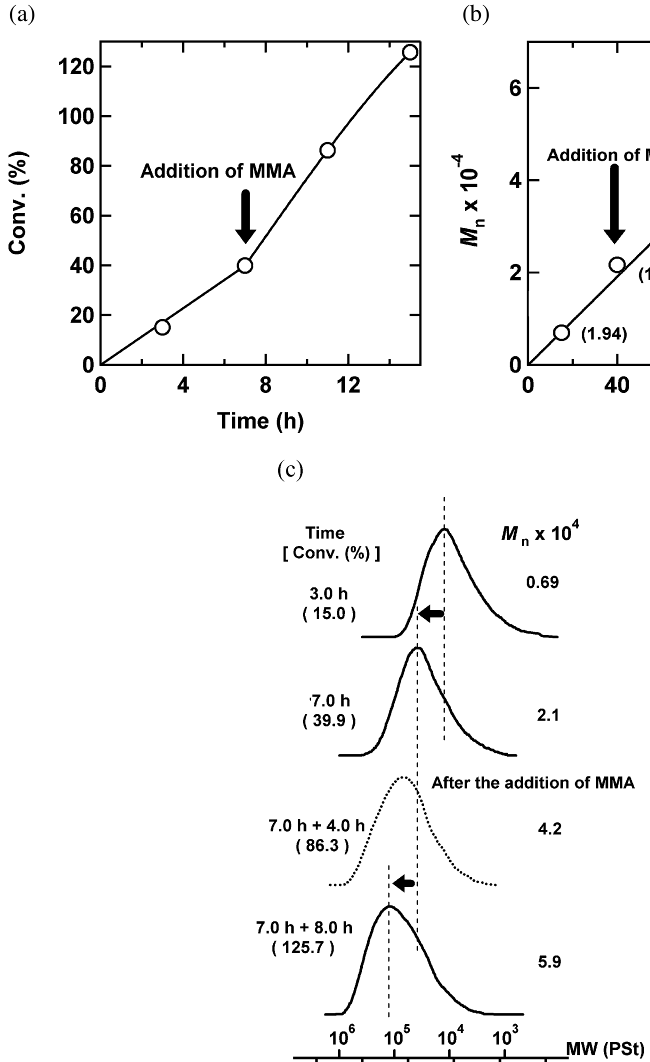

Figure 2. Monomer addition experiments for the polymerization of MMA in the presence of 2-bromoethanol in benzene at 60°C : $[AIBN]_0$ = 1.0 × 10^{-2} M, $[2\text{-bromoethanol}]_0$ = 4.0 M, $[MMA]_0$ = 5.0 M, initial MMA/additional MMA = 5.0/3.3 molar ratio. (a) Time-conversion curves, (b) M_n-conversion curve, and (c) molecular weight distribution.

propagated even after neat MMA addition. Figure 2b shows the relationship between M_n or M_w/M_n and the conversion obtained by the SEC measurement before and after neat MMA addition. The M_n of the polymers increased in direct proportion to monomer conversion. As shown in Figure 2c, the molecular weight distribution was clearly shifted toward higher molecular weight. The quantitative formation of the polymers was determined by the absence of tailing or oligomer peaks in the lower molecular weight regions. From the results, the active chains of the radical polymerization were observed.

^{1}H NMR result of poly(MMA) by controlled radical polymerization in the presence of 2-bromoethanol

Typical ^{1}H NMR spectrum is shown in Figure 3. From the structure of triad tacticity, the structure ratio of isotactics, heterotactics and syndiotactics were I: 0.04, H: 0.35, S: 0.61, respectively. This reveals that the polymers are prepared by radical fashion. The peak α in Figure 3 is a methyl group from AIBN, indicating polymer end groups as the initiator. The peaks of an ethylene group from 2-bromoethanol is behind other peaks. Thus, it is likely that 2-bromoethanol is performed as a degenerative transfer agent after AIBN initiation.

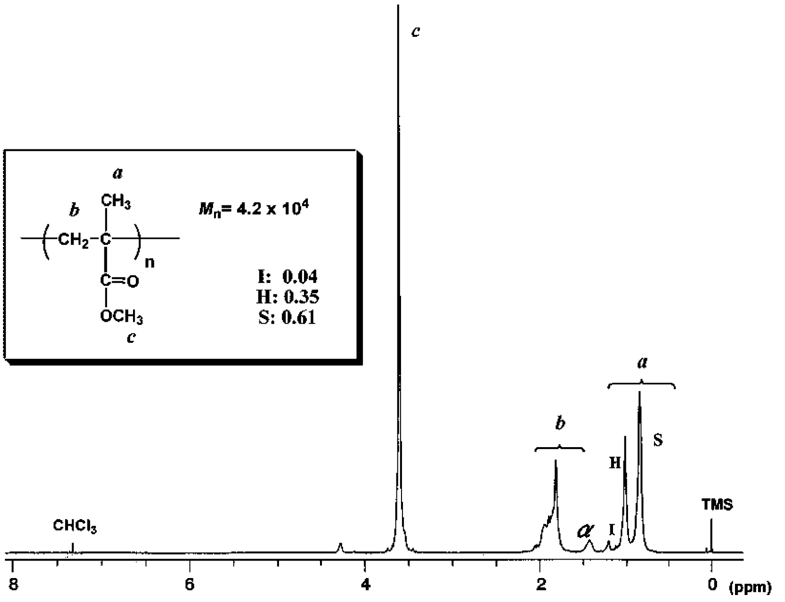

Figure 3. ^{1}H NMR spectrum of the obtained poly(MMA) in $CDCl_3$.

Conclusion

In this paper, we have investigated the new controlled radical polymerization systems of MMA and St using haloalkyl alcohol. Among them, 2-iodoethanol and 2-chloroethanol could not control the radical polymerization of MMA and St. When 2-bromoethanol was used as the chain transfer agent for polymerization of MMA, the M_n of the polymers increased in direct proportion to monomer conversion, and block copolymer (for the same MMA addition experiments) could be obtained. However, this transfer agent was not able to control the polymerization of St. The 2-bromoethanol could be used as one of the transfer agents for radical polymerization to control the molecular weight and the structure of the poly(MMA).

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