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Controlled/Living Radical Polymerization of Methyl Methacrylate in the Presence of 2-Bromoethanol as a Transfer Agent and Comparison with Cumyl Dithiobenzoate as a RAFT Agent

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Abstract: Living polymerization is a process without transfer and termination chain reaction process. It has been developed almost 50 years ago. There are many types of living radical polymerization and the most versatile method is Reversible Addition Fragmentation chain Transfer (RAFT) polymerization. In this study, the controlled/living radical polymerization of methyl methacrylate (MMA) initiated by 2,2'-azobis(isobutyronitrile) (AIBN) in the presence of 2-bromoethanol under different concentration was studied to compare with this established method. Cumyl dithiobenzoate (CDB) was used as a RAFT agent. From the result, in the presence of large amount of 2-bromoethanol, the radical polymerization of MMA is controlled and it is similar with the polymerization using CDB. Furthermore, low molecular weight and relatively narrow molecular weight distributions were also obtained. A fresh feed of MMA was added to the reaction mixtures to observe the living ness in the polymer, which shows that the polymerization was not terminated and still propagated. Typical ^1H NMR spectrum reveals that the polymers are prepared by radical fashion with the sharp signal peak indicates that the polymer was synthesized in the block fashion.

Key words: Controlled/living radical polymerization, conventional radical polymerization, 2-bromoethanol, poly(MMA), RAFT agent

INTRODUCTION

Radical polymerization has is one of the most developed areas in polymer synthesis because of its demanding conditions. Basically, radical reaction use common initiator to polymerize easily many vinyl monomers such as styrene and methyl methacrylate, to give a polymer with the molecular weight about thousands to hundred thousands. However, due to its deficiency of its character including a lack of macromolecular control including end functionalities; it is difficult to prepare a well-defined polymers. Therefore, a controlled/living radical polymerization has emerged as one of the important methods in this field. Living polymerization is a chain growth process without chain breaking reactions. This enables the polymerization of block polymer by sequential monomer addition. The success methods in controlled/living such as Reversible Addition Fragmentation Chain Transfer (RAFT), Nitroxide Mediated Polymerization (NMP), Atom Transfer Radical Polymerization (ATRP) and Reversible Iodine Transfer Polymerization (RITP), depends on their chain transfer agents which give a new defined polymers from a wide range of monomers under simple reaction conditions. The

aim of this study is to develop a new system of controlled radical polymerization using 2-bromoethanol which has a function as a transfer agent. As the comparison, this novel method is compared to the versatile method using cumyl dithiobenzoate (CDB) as a RAFT agent.

MATERIALS AND METHODS

Monomer: MMA was washed once by 5 wt. % of NaOH, then by several times of water until it was confirmed neutral by using the pH test paper. MMA was dried overnight under the calcium chloride. The crude MMA was then distilled once under reduce pressure over calcium hydride and stored in brown ampoules prior to use [b.p. $50^\circ\text{C}/50\text{ mmHg}$].

Solvent: Benzene was washed with 5 vol. % of H_2SO_4 (three times), water and 5 wt. % of aqueous NaOH solution, successively and then was finally washed by water until neutral and was confirmed by using the pH test paper. Benzene was then dried overnight under the calcium chloride. Benzene was purified and distilled once over calcium hydride and stored in the flask with molecular sieves 3 \AA .

Initiator and other material: 2,2'-azobis(isobutyronitrile) (AIBN) and 2-bromoethanol was used as received. Cumyl dithiobenzoate (CDB) was synthesized according to literature methods (Brouwer, 2001; Guo *et al.*, 2006). All glassware was dried before use at 130°C overnight. Bromobenzene was mixed slowly with dried diethyl ether in 100 mL dropping funnels and then the solution was added to warm magnesium turnings (in diethyl ether) in a three-necked 1 L round bottom flask under a nitrogen atmosphere. The mixture was stirred and heated to reflux. The sudden appearance of the brownish iodine color indicated the starts of the reaction. Both bromobenzene and diethyl ether were the added dropwise at such rates that the reaction kept on going and that the temperature remained between 30 to 35°C. An ice bath was used to remove the heat of reaction. Upon completion of the addition, the mixture was left to stir until no energy was produced anymore. The mixture possessed the dark greenish translucent shade of black, typical for such Grignard compounds. The empty dropping funnels were recharged with carbon disulfide. The ice bath was reapplied to keep the temperature at 0°C while carbon disulfide was added. The mixture was kept stirring for about 3 h and then carefully poured into iced water and the product was extracted with diethyl ether. After removal of the ether by using HCl, the crude dithiobenzoate acid was obtained as dark-red brown oil. Dithiobenzoate acid, α -methylstyrene, carbon tetrachloride and a small amount of acid catalyst (p-toluenesulfonic acid) were combined under nitrogen and heated at 70°C for 5 h. After evaporation of the solvent and excess monomer using a rotary evaporator, the residue was purified twice by column chromatography on silica gel with petroleum ether as the eluent to give cumyl dithiobenzoate as dark-purple oil (yield ca. 3%). The Rf value of TLC was 0.42 in hexane.

Polymerization procedure: Polymerization was carried out at 60°C under a dry nitrogen atmosphere in a brown test tube for light protection equipped with three-way stopcock that was first degassed. MMA, 2-bromoethanol or CDB and benzene were added into the test tube using dry medical syringe. After three freeze-thaw-pump cycles, AIBN was added, filled with nitrogen gas and sealed. The test tubes were finally immersed in an oil bath and heated at 60°C under stirring. After a certain time, the tube was cooled by liquid nitrogen, opened, successively diluted with chloroform. The 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. The molecular

weight of the polymers was measured by Size Exclusion Chromatography (SEC) in tetrahydrofuran at 38°C. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were calculated from SEC curves on the basis of a PSt calibration.

RESULTS

Polymerization of MMA using 2-bromoethanol as transfer agent: The polymerizations of MMA in the presence of 2-bromoethanol as a chain transfer agent under different condition were studied. For comparison, the polymerizations without haloalkyl alcohol for these monomers were also examined. The results are summarized in Table 1.

From Table 1, the polymerization without transfer agent yielded higher conversion and common polymers with much higher molecular weights and broader molecular weight distributions were obtained. In the other hand, when 2-bromoethanol was used, the polymerization grows in the direct proportion with the time without induction phase. Figure 1 shows (a) time-conversion curves and (b) M_n -conversion curves for the polymerization of MMA with a large amount of 2-bromoethanol. The molecular weight of MMA was also increased gradually with the monomer conversion. Compare to the well and versatile transfer agent, a large amount of 2-bromoethanol was needed to control polymerization of MMA, due to intermolecular hydrogen bonding in haloalkyl alcohol.

Typical ^1H NMR spectrum which is shown in Fig. 2 shows that 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 Fig. 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, 2-bromoethanol can be performed as a degenerative transfer agent after AIBN initiation.

From the Fig. 2, the polymerization reaction of MMA carried out in the presence of 2-bromoethanol can be summarized as follows (Scheme 1). In the early stages of the polymerization, the reagent (2-bromoethanol) is reacting with the initiator radical to form a propagating

Table 1: Polymerization results of MMA ([MMA] = 5.0 M, [AIBN] = 1.0×10^{-2} M, [X] = 4.0 M in benzene at 60°C)

Additive X	Time (h)	Conv. (%)	$M_n \times 10^{-4}$	M_w/M_n
-	7.0	73.6	7.9	1.71
2-bromoethanol	2.0	25.4	0.3	1.95
	4.0	54.6	0.4	1.96
	6.0	97.1	1.1	1.96

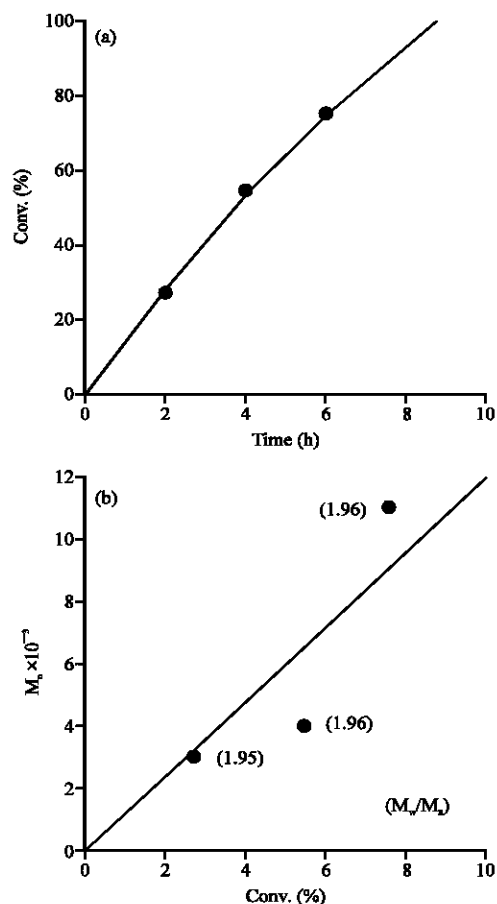


Fig. 1: Polymerization of MMA in the presence of 2-bromoethanol in benzene at 60°C: [MMA] = 5.0 M, [AIBN] = 1.4×10^{-2} M, [2-BrCH₂CH₂OH] = 4.0 M. (a) Times-Conversion curve, (b) Mn-Conversion curves

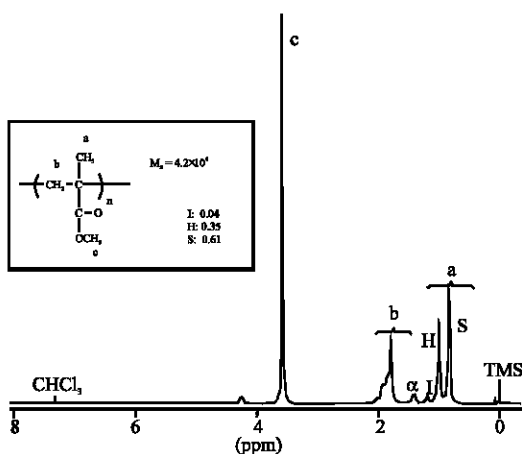
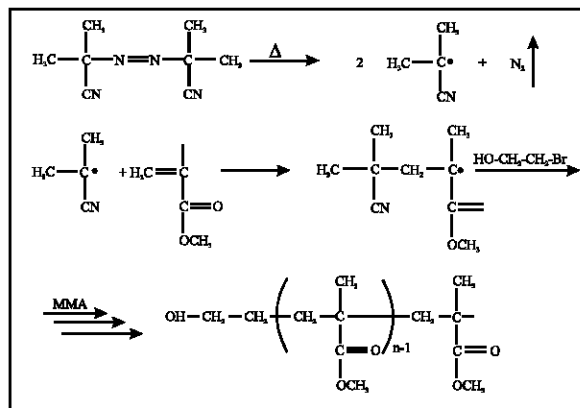
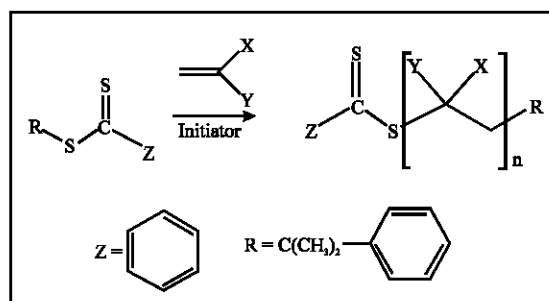


Fig. 2: ¹H NMR spectrum of the obtained poly (MMA) in CDCl₃



Scheme 1: Polymerization of MMA by 2-bromoethanol



Scheme 2: Overall reaction

Table 2: Polymerization results in Benzene at 60°C ([MMA] = 7.02 M, [AIBN] = 6.1×10^{-3} M, [X] = 1.16×10^{-2} M)

Additive X	Time (h)	Conv. (%)	$M_n \times 10^{-4}$	M_w/M_n
CDB	11	26.8	0.90	1.26
	24	87.7	2.03	1.15
	30	90.4	2.22	1.12

radical. Because of the majority of chains in the product polymer possess Br and OH groups, polymerization can be continued in the presence of a second monomer to give a block polymer.

Polymerization of MMA using CDB as RAFT agent: The polymerization result can be summarized in Table 2.

For the synthesis of CDB, bromobenzene and dithiobenzoate acid were added as a starting reagent (Scheme 2), which is an effective way to get the target product, but the drawback of this reaction is the lower of 3%. The last product also is not easily cleaned.

The polymerization of MMA in benzene was carried out using CDB as the RAFT agent and AIBN as the initiator and from the results; it shows that, with the small amount, CDB can controlled the polymerization of MMA effectively with a low molecular weight and narrow molecular weight polydispersities. The plot of conversion

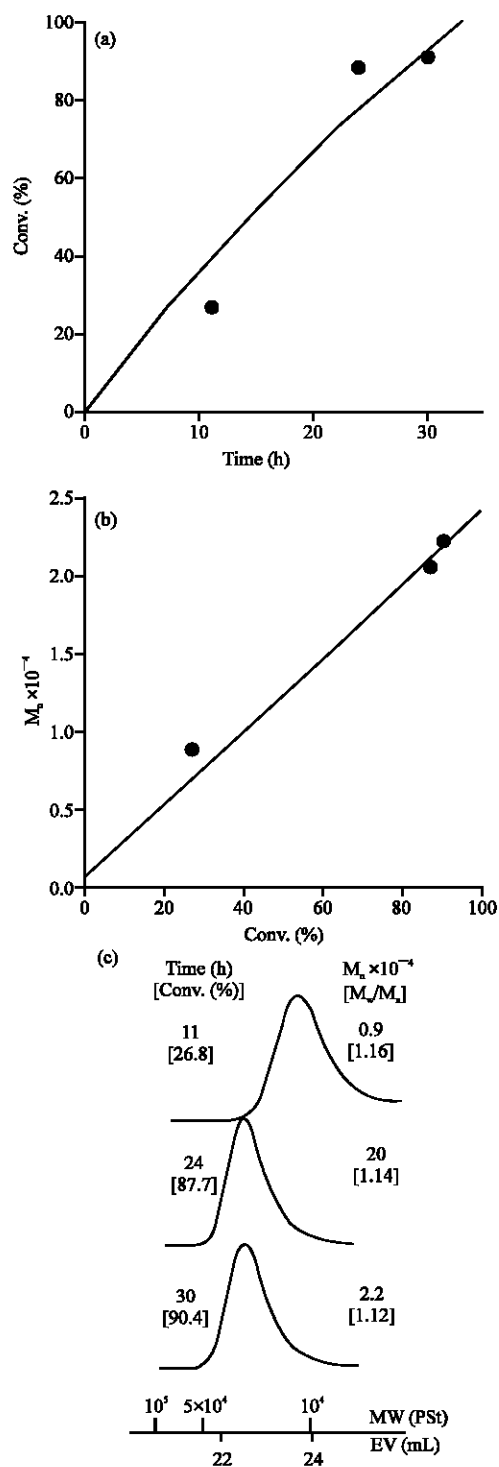


Fig. 3: Polymerization of MMA in the presence of cumyl dithiobenzoate in benzene at 60°C: [AIBN] = 6.1×10^{-3} M, [CDB] = 1.16×10^{-2} M, [MMA] = 7.02 M. (a) Time-conversion curves, (b) M_n -conversion curves and (c) Molecular Weight Distributions (MWD)

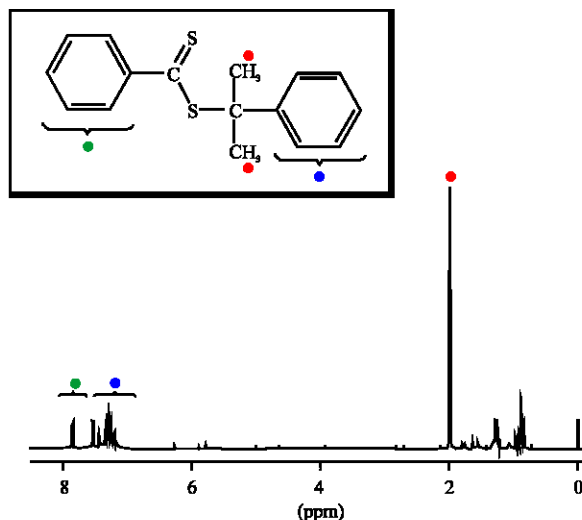


Fig. 4: ^1H NMR spectrum of the obtained cumyl dithiobenzoate in CDCl_3

versus time, M_n versus conversion and SEC traces are shown in Fig. 3.

The CDB and poly (MMA) were characterized by using ^1H NMR spectroscopy (Fig. 4). From the result, the signal can be assigned in the region 1.99, 7.2-7.6 and 7.85 ppm. Since, the signals that are shown between 0.1-1.8 ppm which is the eluent in column chromatography, that is petroleum ether, the evidence that shows that CDB couldn't be easily purified. However, this factor couldn't influence the polymerization rate of MMA, since another factor such as oxygen and purity of monomer that playing an important role on polymerization rate.

CONCLUSION

In this study, the new controlled radical system of MMA using haloalkyl alcohol was investigated. When 2-bromoethanol was used as the chain transfer agent for polymerization of MMA, surprisingly, 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).

We also synthesized cumyl dithiobenzoate (CDB) as one of the RAFT agent to compare this system with the 2-bromoethanol system. RAFT polymerization using CDB as the chain transfer agent definitely proves to be an excellent and versatile method which provides controlled

molecular weight polymers with very narrow polydispersities ($M_w/M_n < 1.2$). However, it is difficult to synthesize the oily RAFT agent such as CDB with a large amount of reagents were needed and less than 5% was obtained from the reactions. In addition, it was also complicated to purify the RAFT agent completely.

The polymerization with 2-bromoethanol may not be very good as the current systems, but it is available commercially and can be used without any further purification. Therefore, this reagent is perhaps to be one of the versatile methods in polymer industry.

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