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# Preparation of poly(methyl methacrylate) macromonomer by radical polymerization in the presence of methyl α-(bromomethyl)acrylate and copolymerization of the resultant macromonomer

**Bunichiro Yamada, Eiichi Kato, Seiya Kobatake, and Takayuki Otsu***

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

## Summary

Radical polymerization of methyl methacrylate (MMA) in the presence of methyl α-(bromomethyl)acrylate yielded poly(MMA) bearing the 2-methoxycarbonylallyl end group through chain reaction involving bimolecular termination. The molecular weight of the resultant polymer was effectively controlled with a small amount of the bromomethylacrylate added; the chain transfer constant was estimated to be 0.9. The poly(MMA) with the unsaturated end group ($\overline{M}_n$= 2800 and $\overline{M}_w/\overline{M}_n$ = 1.39) was used as a macromonomer for copolymerization with various monomers. The monomer mixture containing styrene and less than 10 mole-% of the macromonomer produced a corresponding copolymer. Copolymers with non-conjugated monomers were also obtained. The macromonomer was less reactive toward poly(MMA) radical than poly(styrene) radical. The radical produced by an addition of poly(styrene) radical to the macromonomer was detected using ESR spectroscopy at room temperature.

## Introduction

In radical polymerization, that is a typical chain reaction, the degree of polymerization of the product polymer is principally determined by a ratio of the propagation rate to termination rate. Being sufficiently faster than the bimolecular termination, chain transfer or primary radical termination can be used to regulate the molecular weight of the polymer. In particular, an initiator, functioning as a chain transfer agent and/or terminator, has been noted as *iniferter* to control radical polymerization (1). Meijs and coworkers (2) have found that α-(tert-butylthiomethyl)vinyl monomers are highly reactive during chain transfer involving an addition followed by fragmentation to the tert-butylthiyl radical and the substituted allyl groups prevailing bimolecular termination to control molecular weight and the end group, simultaneously.

Alternatively we have revealed that among the α-(halomethyl)acrylates, ethyl α-(bromomethyl)acrylate (EBMA), which does not homopolymerize, reacts with the propagating radical of methyl methacrylate (MMA) to yield the polymer of a reduced molecular weight bearing the alkoxycarbonylallyl group through the addition-fragmentation chain transfer (3).

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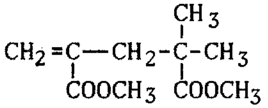
*To whom offprint requests should be sent

Consequently, the polymerization in the presence of EBMA could be used as a synthetic route to macromonomers of controlled chain lengths bearing a similar end group.

However the alkoxycarbonylallyl end group, which is also introduced by disproportionation of poly(MMA) radical, has been deduced to act as a chain terminator as well as dimethyl 4-methyl-1-pentene-2,4-dicarboxylate, I:



$$CH_2{=}\underset{COOCH_3}{\underset{|}{C}}{-}CH_2{-}\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}}{-}CH_3$$

I

Since I is difficult for polymerization (4), the macromonomer could not undergo homopolymerization.

The poly(MMA) and the polymers from methacrylic monomers with a similar allyl end group have been prepared by catalytic chain transfer with cobalt complexes (5-7), and copolymerizations of the poly(MMA) bearing the substituted allyl group with MMA, ethyl acrylate, styrene (St), and vinyl acetate (VAc) were carried out (8). However, the reported behavior of the alkoxycarbonylallyl compound seems to be inconsistent with each other. The inhibition of I and the poly(MMA) bearing the allyl end group (4), almost the same reactivity of I ($M_2$) as St ($M_1$) in copolymerization ($r_1$ = 0.975 and $r_2$ = 0.000) over a wide range of comonomer composition (9), and incorporation of a small amount of the macromonomer in the copolymer with St (8) have been reported.

In this article, polymerization of MMA in the presence of a small amount of MBMA to the poly(MMA) macromonomer (MCRM) with a controlled molecular weight and characteristics in the copolymerization of MCRM with various monomers are described.

## Experimental

MBMA was prepared by bromination of methyl $\alpha$-(hydroxymethyl)acrylate with phosphorous tribromide (10-12), and was distilled under reduced pressure. $^1$H-NMR ($CDCl_3$); $\delta$ = 3.72 (3H, $OCH_3$), 4.14 (2H, $CH_2Br$), 5.85 (1H, CH=C), and 6.18 ppm (1H, CH=C). EBMA was prepared as described previously (3). MMA, St, VAc, and divinylbenzene (DVB) were commercially available and distilled under reduced pressure in a nitrogen atmosphere before use. Vinyl chloride (VC) was used as supplied. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. tert-Butyl peroxide (TBP) was distilled under reduced pressure.

All the polymerizations were carried out in sealed tubes using AIBN as initiator at 60 °C. After a certain polymerization time, the contents of the tube were poured into a large amount of methanol or n-hexane, and the conversion was calculated from the weight of the polymer or the polymeric product. MCRM was purified by reprecipitation with benzene/n-hexane.

Copolymerizations of MCRM were also carried out in the sealed tubes; 0.2 g of MCRM, 2 mL of a monomer, and a desired amount of AIBN were dissolved in 3 mL of benzene.

The copolymer was precipitated with a large amount of methanol or n-hexane. MCRM that did not copolymerize was separated by extraction with hot methanol, except for the copolymer with VAc which is soluble in methanol.

Number average molecular weight ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$) were measured by a TOSO 8000 series GPC calibrated with the standard poly(St), and THF was used as the eluent. NMR spectra were recorded on a JEOL GX 400 or a Hitachi R24B spectrometer, and deuterochloroform was used as the solvent. ESR spectra were recorded on a Bruker ESP 300 spectrometer at room temperature and the polymerization mixture containing TBP was irradiated with an Ushio 500 W xenon lamp in the cavity.

## Results and Discussion

### Polymerization to MCRM

The effect of MBMA on MMA polymerization is shown in Fig. 1. Affecting the overall rate of polymerization ($R_p$) to a small extent within the concentration range in Fig. 1, a small amount of MBMA effectively reduced the $\bar{M}_n$ of MCRM as well as EBMA (3). The polymerization of MMA in the absence of MBMA yielded poly(MMA) of $\bar{M}_n$ = 131000 and $\bar{M}_w/\bar{M}_n$ = 1.86 at the same concentrations of MMA and AIBN. The rate of MMA consumption in the polymerization regulated by MBMA was

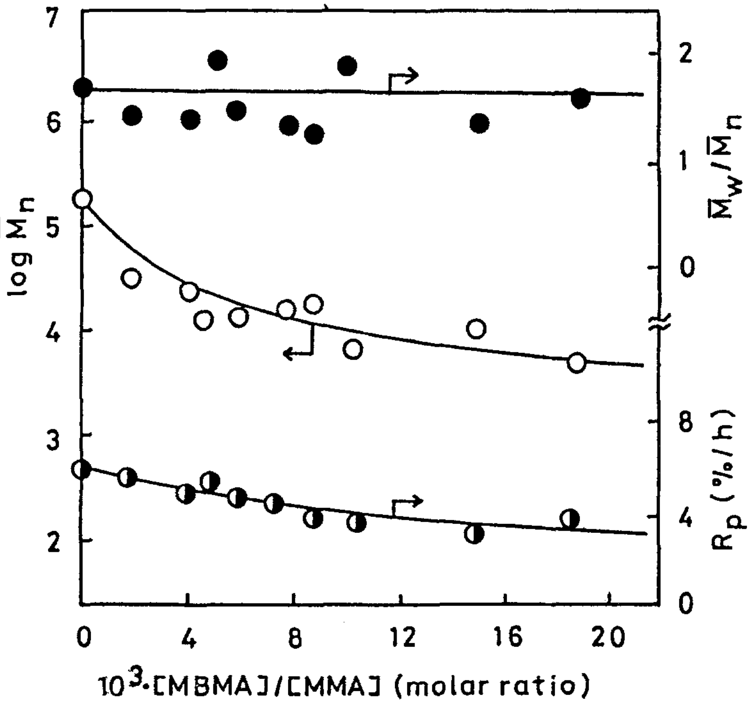


Fig. 1. Polymerization of MMA in the presence of MBMA in benzene for 6.5 h at 60 °C: [MMA] = 3.74 mol/L and [AIBN] = 0.005 mol/L.

found to be proportional to the square root of the AIBN concentration. We can conclude that MCRM is produced by a radical chain reaction involving bimolecular termination of the chain carrier.

Based on these data, the chain transfer constant of MBMA in MMA polymerization was evaluated to be 0.9 by the conventional Mayo plot. However a further addition of MBMA to the polymerization mixture brought about a decrease in $R_p$, and the addition to MBMA and/or reinitiation seems to be slightly slower than the propagation.

The structure of MCRM prepared with EBMA has been confirmed by NMR spectroscopy and bromine analysis(3). The $^1$H-NMR spectrum of MCRM obtained by the polymerization in the presence of MBMA shows resonances of the allylic protons (2.45 ppm) and of the olefinic protons (5.39 and 6.10 ppm) which are distinctly differentiated from the resonances of the same type of the protons in MBMA (5.85 and 6.18 ppm) as in Fig. 2A. Either of the resonances at ca. 3.7 ppm would

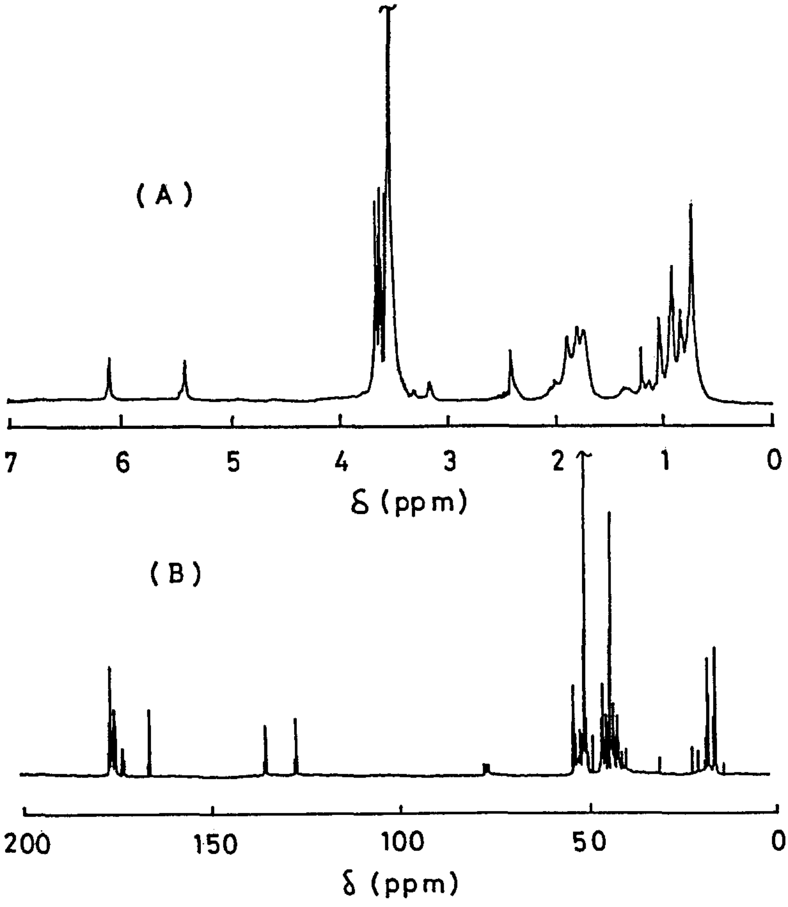
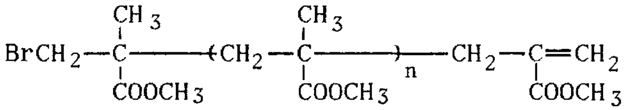


Fig. 2. $^1$H- and $^{13}$C-NMR spectra (A and B, respectively) of MCRM ($\bar{M}_n$ = 900 and $\bar{M}_w/\bar{M}_n$ = 1.66).

be assigned to the $BrCH_2$ group of the terminal MMA unit produced by re-initiation with bromine atom (3). Resonances of the olefinic carbons (127.9 and 135.9 ppm) and the carbonyl carbon (163.8 ppm) in the $^{13}$C-NMR spectra (Fig. 2B), and the absence of the resonance due to $CH_2Br$ group which appears at 28.9 ppm in the spectrum of MBMA corroborate the structure II:



$$BrCH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}})_n-CH_2-\underset{COOCH_3}{C}=CH_2 \qquad II$$

While the terminus of MCRM involves a carbon-carbon double bond, the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ did not change with an increase in the conversion of MMA as shown in Table 1. This is reasonable tendency, because the same unsaturated end group produced by disproportionation is conserved throughout polymerization of MMA.

Table 1. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of MCRM prepared at 60 ℃ a)

| Time (h) | Convn. (%) | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|
| 4 | 10.2 | 11800 | 1.43 |
| 10 | 32.0 | 12000 | 1.34 |
| 12 | 37.9 | 13000 | 1.39 |

a) [MMA] = 3.76 mol/L, [MBMA]/[MMA] = 0.01, and [AIBN] = 0.005 mol/L.

### Copolymerization of MCRM

MCRM ($\bar{M}_n$ = 2800 and $\bar{M}_w/\bar{M}_n$ = 1.39) prepared by the polymerization in the presence of 0.05 molar ratio of MBMA to MMA was copolymerized with various monomers as summarized in Table 2. Considering the structural similarity of MCRM and poly(MMA), we estimated the amount of unchanged MCRM in the copolymerization with MMA based on the RI responce of GPC before the extraction. It was found that MCRM exhibits

Table 2. Copolymerization of MCRM at 60 °C a)

| [Monomer] (mol/L) | [Monomer]/[MCRM] | Time (h) | $\bar{M}_n \times 10^{-4}$ | $\bar{M}_w/\bar{M}_n$ | Convn. b) (%) | [Monomer] c)/[MCRM] |
|---|---|---|---|---|---|---|
| MMA 3.76 | 269 | 31 | 5.2 | 2.43 | 94 | 520/1 d) |
| St 3.46 | 247 | 23 | 5.4 | 1.50 | 32 | 520/2 |
| St/DVB 3.42/0.036 | 246 | 23 | 3.1 | 5.10 | 31 | 300/2 |
| VC 6.06 | 433 | 16 | 2.0 | 2.21 | 40 | 290/2 |
| VAc 4.33 | 309 | 31 | 10.4 | 3.06 | 71 | 1100/5 |

a) [MCRM] = 0.014 mol/L and [AIBN] = 0.005 mol/L. b) Conversion of monomer. c) Average numbers of the respective units per copolymer chain. d) Estimated from a decrease in $\bar{M}_n$

quite low reactivity in the copolymerization; poly(MMA) radical preferentially adds to MMA itself. The $\bar{M}_n$ of the product of the copolymerization with MMA was less than that of poly(MMA) prepared in the absence of MCRM ($\bar{M}_n$ = 131000), showing that MCRM terminates the propagating radical.

After the copolymerizations of MCRM with monomers other than MMA, the GPC curves did not show any presence of large amounts of unchanged MCRM. In Table 2, the molar ratio of MCRM to the monomer units in each copolymer chain was calculated from the composition of the product determined by intensity ratio of the characteristic resonances in the $^1$H-NMR spectrum and the $\bar{M}_n$ estimated by GPC.

Comparison of the feed composition with that of the St copolymer in Table 2 reveals that MCRM is more reactive than St. The copolymerization with St was examined further at higher MCRM contents in the feed, and the results are shown in Fig. 3. With an increase in the MCRM content of the feed below 10 mole-%, a decrease in $\bar{M}_n$ and an increase in the MCRM content of the copolymer are observed. Considering the inhibition effect of I observed (4) and a decrease in $\bar{M}_n$ of the copolymer with an increase in the MCRM content in Fig. 3, we can conclude that MCRM is about twice as reactive as St toward poly(St) radical and that MCRM radical which does not react with MCRM itself adds to St quite slowly. The copolymerization in the presence of a small amount of DVB ([St]/[DVB] = 95 molar ratio) resulted in the benzene soluble copolymer with a larger $\bar{M}_w/\bar{M}_n$. This finding implies that a relatively short poly(St) branch from the DVB unit was terminated with MCRM prior to cross-linking.

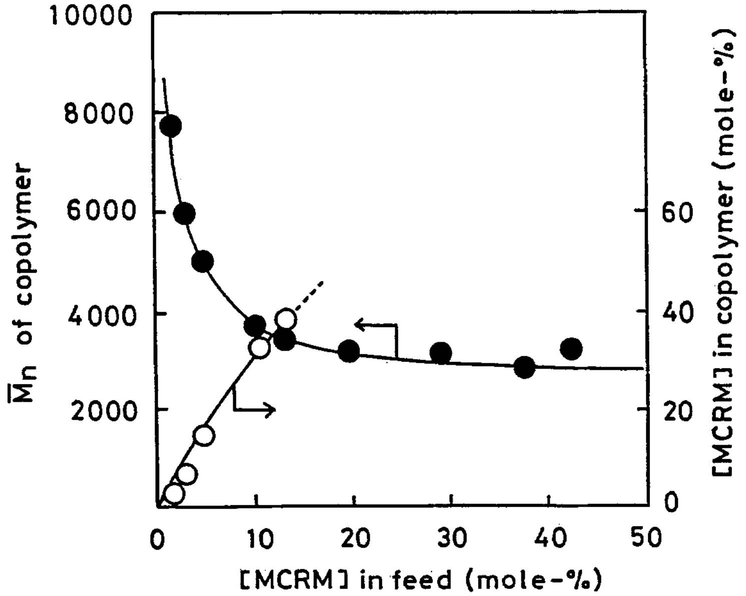


Fig. 3. Dependencies of $\bar{M}_n$ and MCRM content in copolymer with St on comonomer composition.

Copolymerizations of VC and VAc with MCRM yielded products containing larger amounts of MCRM unit than the comonomers as shown in Table 2; MCRM being more reactive than VC or VAc. Since the two units of MCRM correspond to an average of 56 MMA units, the copolymer consists of 290 VC units and 56 MMA units. Probably these figures mean that two of the MCRM units are involved separately in the poly(VC) chain. VAc that is a non-conjugated and electron donating monomer favored the fast copolymerization, and resulted in a copolymer involving the largest MCRM amount. Due to highly reactive nature of poly(VAc) radical as well as poly(VC) radical in chain transfer to the polymer, MCRM unit could be involved in each branch. Copolymerization of MCRM with ethylene gave a copolymer consisting of poly(MMA) and poly(ethylene) chains.

For copolymerization of monomeric MMA with VAc and VC, much greater monomer reactivity ratios have been evaluated for MMA: $r_{MMA}$ = 26 and $r_{VAc}$ = 0.03 for MMA copolymerization with VAc, and $r_{MMA}$ = 12.5 and $r_{VC}$ = 0 for MMA copolymerization with VC (13). Based on the $r_{MMA}$ and $r_{VC}$, the MMA copolymer containing more the 50 mole-% of VC unit could not be prepared. To obtain a copolymer containing 89 mole-% of VAc unit as well as the MCRM-VAc copolymer, the monomer feed should consist of more than 99 mole-% of VAc. Therefore copolymerization of MCRM with VAc and VC could have significance as a convenient mean to prepare a copolymer containing a large amount of the unit from the non-conjugated monomer.

## Radical Addition to MCRM

When a benzene solution of MCRM ($\bar{M}_n$ = 2400 and $\bar{M}_w/\bar{M}_n$ = 1.72) prepared in the presence of EBMA (0.04 molar ratio) and TBP was UV irradiated, the spectrum in Fig. 4A was observed at room temperature. The spectrum can be accounted for by splitting due to two pairs of the $\beta$-protons, and the spectrum coincides with those of the radicals produced by an addition of low molecular weight radicals to I (4) except for the difference in line width. Prolonged irradiation did not affect the splitting pattern and the line width of the spectrum from MCRM. Based on the decay of the signal,

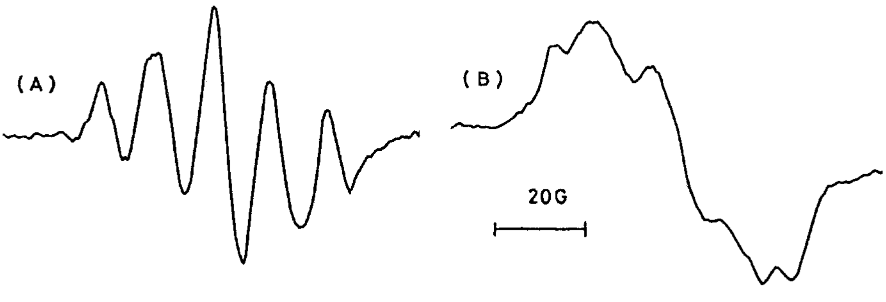


Fig. 4. ESR spectra of radicals produced by addition of tert-butoxy and poly(St) radicals to MCRM with UV irradiation: A, MCRM (0.15 g) and TBP (0.01 g) in benzene (0.3 mL); B, MCRM (0.15 g), St (0.05 mL), and TBP (0.01 mL) in benzene (0.25 mL).

the rate constant for bimolecular termination of the radical at room temperature was evaluated to be $3 \times 10^5$ L/mol•s, which is less than that of poly(MMA) radical by two orders.

However, the solution containing St gave the broad signal as shown in Fig. 4B after irradiation for a longer period. Copolymerization of MCRM with St occurred producing a radical from MCRM with poly(St) chain. After the ESR measurement, GPC analysis of the recovered polymer showed binding of poly(St) chain to MCRM resulting in $\overline{M}_n$ = 4900 and $\overline{M}_w/\overline{M}_n$ = 2.07.

## References

1. T. Otsu, T. Matsunaga, A. Kuriyama, M. Yoshioka, Europ. Polym. J., 25, 643 (1989)
2. G. F. Meijs, E. Rizzardo, S. H. Thang, Macromolecules, 21, 3122 (1988)
3. B. Yamada, T. Otsu, Makromol. Chem., Rapid Commun., 11, 531 (1990).
4. H. Tanaka, H. Kawai, T. Sato, T. Ota, J. Polym. Sci.: Part A: Polym. Chem., 27, 1741 (1989)
5. N. S. Enikolopyan, B. R. Smirnov, G. V. Ponomarev, I. M. Belgovskii, J. Polym. Sci., Polym. Chem. Ed., 19, 879 (1981).
6. A. F. Burczyk, K. F. O'Driscoll, G. L. Rempel, J. Polym. Sci., Polym. Chem. Ed., 22, 3255 (1984).
7. R. A. Sanayei, K. F. O'Driscoll, J. Macromol. Sci.-Chem., A26, 1137 (1989).
8. P. Cacioli, D. G. Hawthorne, R. L. Laslett, E. Rizzardo, D. H. Solomon, J. Macromol. Sci.-Chem., A23, 839 (1986).
9. F. Shinagawa, K. Naruchi, M. Kudoh, F. Akutsu, M. Miura, Polym. Prepr., Jpn., 39, 134 (1990).
10. H. M. R. Hoffmann, J. Rabe, Angew. Chem., Int. Ed. Engl., 22, 795 (1983).
11. A. O. Kress, L. J. Mathias, G. Cei, Macromolecules, 22, 537 (1989).
12. J. Villieras, M. Rambaud, Synthesis, 924 (1982)
13. R. Z. Greenely, "Polymer Handbook", 3rd Ed., J. Brandrup, E. H. Immergut, ed., Wiley, 1989, p. II/267.

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