GPC Observations of Branching Effects in Anionic Polymerization of Methyl Methacrylate: A Preliminary Study

Yuhsin Tsai,[1] Jyh-Horng Wu,[2] Fuu-Jen Tsai[1,3,4]

[1]Graduate Institute of Chinese Medical Science, China Medical University, Taichung, Taiwan
[2]Nano-Powder & Thin Film Technology Center, Industrial Technology Research Institute, Tainan, Taiwan
[3]Department of Medical Genetics, Pediatrics and Medical Research, China Medical University Hospital, Taichung, Taiwan
[4]Department of Biotechnology and Bioinformatics, Asia University, Taichung, Taiwan

ABSTRACT: The anionic polymerization of methyl methacrylate was performed in tetrahydrofuran (THF) at $-78°C$, using *sec*-butyllithium/1,1-diphenylethylene (DPE) as the initiation system. The effects of polymerization time and initiator concentration on the branching reaction were studied. High vacuum was used to prevent contamination during the polymerization. Gel permeation chromatography (GPC) was used to characterize the branching effect qualitatively. Experimental results indicated that the monomer conversion reached more than 98% in a polymerization time of 10 min. The branching reaction occurred after high monomer conversion, resulting in a tail of high molecular weight in the GPC trace. This branching effect, observed by GPC, increased with polymerization time. Rapid termination was thus probably required immediately after all of the monomer was consumed in the preparation of a well-defined PMMA without a high-molecular-weight tail in this diphenylbutyllithium/THF/$-78°C$ system. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2099–2103, 2009

Key words: anionic polymerization; gel permeation chromatography; branching reaction; polymethyl methacrylate; butyllithium

INTRODUCTION

The controlled anionic polymerization of methyl methacrylate (MMA) has seen revolutionary advances over the last decade. The anionic polymerization of MMA proceeds in a controlled manner only under some judiciously chosen reaction conditions, because the initiating and propagating species undergo side reactions with the ester group.[1,2] The addition reaction occurs and polymerization proceeds when the initiating and propagating species react with the unsaturated double bond of the MMA monomers. However, a substitution reaction which causes chain termination occurs, when the initiating and propagating species react with the carbonyl carbon of either monomers or polymers, as shown in Figure 1.

Many systems for the ideal anionic polymerization of MMA to eliminate the termination reaction have been reported, including *sec*-butyllithium/1,1-diphe-nylethylene (DPE) systems,[3,4] silyl ketene acetal initiating systems,[5] metal-free initiators,[6] and the addition of enolate ion pair stabilizers.[7,8] Most reduce the reactivity of ionic species, particularly in the initiation stage. Therefore, the addition reaction, rather than the substitution reaction, dominates. Controlled molecular weights and narrow polydispersities can be obtained using such polymerization techniques.

The major termination reaction of anionic polymerization of MMA is believed to involve the back-biting reaction of the propagating chain-end with the carbonyl group of the antepenultimate unit of the own chain.[9] However, a high-molecular-weight tail is observed in the gel permeation chromatography (GPC) trace of PMMA, which is prepared by controlled anionic polymerization, although the polymer has a polydispersity index (PDI) of less than 1.1.[1,2] This high-molecular-weight tail may result from the branching reaction between the propagating chain-end and the carbonyl group of polymer. To our knowledge, no detailed report on the branching effects has begun to appear, because anionic polymerization of MMA is a fast and complicated reaction. Therefore, the branching effect of controlled anionic polymerization of MMA,

Termination by intramolecular cyclization

Termination by intermolecular branching reaction.
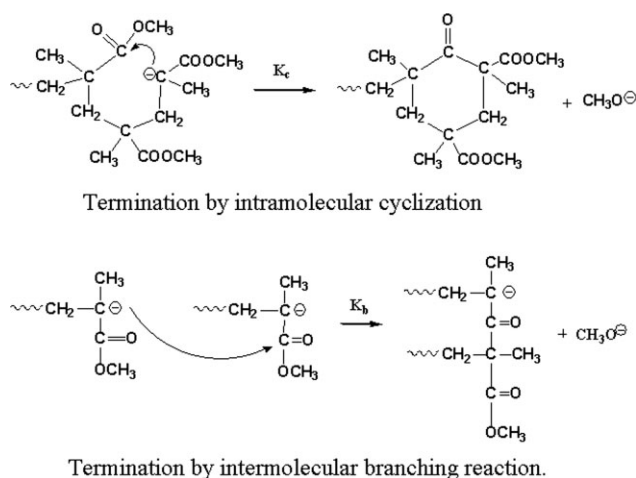
Figure 1 Termination reactions in anionic polymerization of MMA.

particularly in the late stage of the polymerization, is of interest.

In this work, the anionic polymerization of MMA was performed in tetrahydrofuran (THF) at $-78°C$ using *sec*-butyllithium/1,1-DPE as the initiation system. A high vacuum was applied to eliminate contamination during polymerization. The branching effect is characterized qualitatively by GPC, which is calibrated with PMMA standards. Finally, the influence of polymerization time and initiator concentration on the branching reaction is discussed.

EXPERIMENTAL

Materials

THF, 1,1-DPE, MMA, methanol, acetic acid, calcium hydride (CaH₂), triethylaluminum, and benzophenone were purchased from Aldrich. Solutions of *sec*-butyllithium (FMC, Lithium Division, 12.0 wt % in cyclohexane) were used for initiation following titration analysis.[10] DPE was stirred over CaH₂ for 24 h and then the middle fraction was collected by distillation at reduced pressure. THF was dried over CaH₂ for several days and distilled under vacuum into a reservoir containing sodium benzophenone. Measured quantities of purified THF were collected by distilling under vacuum from this reservoir into ampoules which were each equipped with a break seal and heat-sealed with a hand torch for further use.

MMA was passed through a column of neutral aluminum and was dried over CaH₂ for 24 h. Before polymerization, it was further purified by adding triethylaluminum until a yellowish-green color was observed, and then distilled under vacuum into an ampoule which had equipped with a break seal. After the desired amount of MMA was obtained, the monomer was diluted by distillation of THF into the

ampoule. This MMA/THF solution ampoule was used immediately. An MMA/THF solution rather than MMA only was to prevent the formation of a local heat spot during polymerization.[11,12]

The desired amount of acetic acid in an ampoule with a break seal was degassed on the vacuum line and then the required amount of methanol was distilled into this ampoule, which was heat-sealed using a hand torch. This acetic acid/methanol ampoule was adopted as the quenching reagent of anionic polymerization.

Polymerization

All steps of the reaction were performed in an all-glass, sealed reactor using break seals or high-vacuum stopcocks and standard high-vacuum techniques,[13] except for the injection of *sec*-butyllithium and 1,1-DPE into a 500 mL reactor, which was performed under argon. The glass reactor that is presented in Figure 2 is used for the preparation of PMMA. The reactor comprised a solvent (THF) ampoule (A), an MMA/THF solution ampoule (B), an ampoule with the methanol/acetic acid solution (C), an extra ampoule (D), a thick-walled sidearm tube (E), break seals (F), and a magnetic stirrer (G). The reactor assembly was attached to the vacuum line and the side-arm tube was closed using a rubber septum and then evacuated for many hours. Argon gas was introduced into the reactor through the vacuum line. The initiator, 1.4 mL (2.1 mmol) *sec*-butyllithium, and 0.56 mL (3.0 mmol) 1,1-DPE were added through the side arm tube using a syringe under argon gas purging. After the side arm had been closed with a septum, the solvent of the
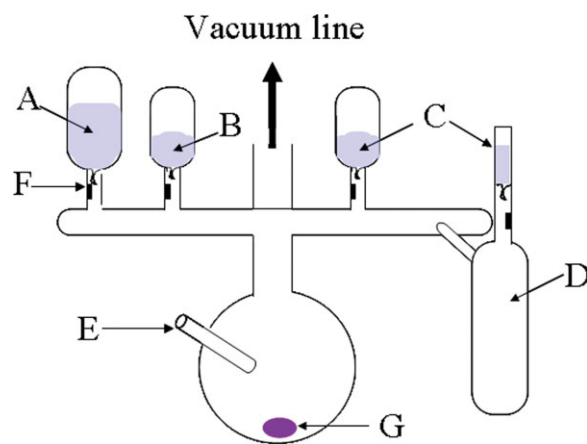
Figure 2 Apparatus for anionic polymerization. (A): solvent (THF) ampoule; (B): MMA/THF solution ampoule; (C): aliquot ampoule with the methanol/acetic acid solution; (D): extra ampoule; (E): thick-walled sidearm tube; (F): breakseal and (G): magnetic stirrer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

initiator was evaporated. The reactor was cooled in a dry ice/isopropanol bath (−78°C), and the side arm tube and reactor were then sealed off from the vacuum line using a hand torch. The break seal of an ampoule of 250 mL THF was broken to introduce the solvent into the reactor; then the MMA/THF solution (13 mL (0.12 mol) MMA in 20 mL THF) was added through the corresponding ampoule. The polymerization was allowed to proceed for the desired period at −78°C. After the reaction, the living polymer was quenched by breaking the ampoule which contained the methanol/acetic acid solution. For the preparation of Samples 2a and 2b, some of the living polymer was taken from the reactor by sealing off the ampoule (D) and quenching its content. The remaining reaction medium was stored overnight before the ampoule that contained the methanol/acetic acid solution at −78°C was broken. All polymers were isolated by solvent evaporation or the precipitation of their THF solutions into excess methanol.

Characterization

GPC analysis of the polymers was conducted at a flow rate of 1.0 mL/min in THF at 30°C using a Waters HPLC component system (RI or Hewlett Packed 1040 diode array detector) that was equipped with ultra-u-styragel columns (two 500, two 10^3, 10^4, and 10^5 A). The calibration curve was obtained using a standard poly(methyl methacrylate) samples (Polymer Laboratories). The weight-average molecular weights of these polymers were determined by coupling a Chromatix KMX-6 photometer with a Waters 150C instrument, both interfaced with a digital computer.

RESULTS AND DISCUSSION

The polymerization of MMA was performed in an all-glass, sealed reactor using break seals and a standard high-vacuum line to eliminate any possible impurity. To avoid the local hot spot during the polymerization, the volume concentration of MMA in THF was kept less than 5% for all experiments in this study (13 mL MMA in 270 mL THF). As soon as the DPE and *sec*-butyllithium were added to the reactor through the side arm tube under argon gas purging, a dark reddish color was observed, corresponding to diphenylbutylllithium (DPHLi). The dark-red solution turned lightly yellowish-green, after the MMA/THF solution ampoule was broken and the first few drops of the MMA/THF solution were added to the initiator solution. This change indicated that DPHLi crossed over to MMA. Two experiments were conducted with different polymerization times of 10 min (Sample la) and 1 h (Sample
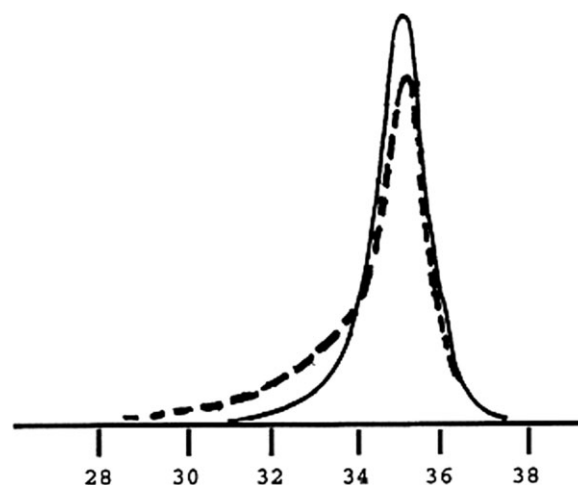
Figure 3 GPC results for Sample la and Sample 1b. Sample 1a (solid-line, 10 min polymerization time): $M_n = 6.4 \times 10^3$ g/mol, $M_w = 7.4 \times 10^3$ g/mol and PDI = 1.16. Sample 1b (dash-line, 1 h polymerization time): $M_n = 6.8 \times 10^3$ g/mol, $M_w = 8.5 \times 10^3$ g/mol and PDI = 1.25.

lb). The polymerization was terminated by breaking an ampoule of the acetic acid/methanol solution under vacuum. After evaporation of solvent, both samples exhibited over 98% monomer conversion. Figure 3 presents the GPC results of these polymers (Samples la and 1b). Figure 3 also indicates that both Samples 1a and 1b have tails of high molecular weight. However, Sample 1a (with the shorter polymerization time) had a shorter high-molecular-weight tail than Sample 1b (with a longer polymerization time). Sample 1b had a PDI = 1.25, and M_w and M_n equal to 8.5×10^3 and 6.8×10^3 g/mol, respectively. Sample 1a (10 min of polymerization) had a lower PDI (1.16) and M_w and M_n were 7.4×10^3 and 6.4×10^3 g/mol, respectively, as shown in Table I.

The monomer conversion exceeded 98% after 10 min of polymerization, in which the result was consistent with the earlier results.[14] Because little monomer was available in this stage (as over 98% monomer was consumed), increasing the polymerization time did not promote polymerization. Therefore, termination by the cyclization and branching reaction, rather than polymerization, dominated. Because termination by cyclization did not increase the molecular weight, the high-molecular-weight tails in these reactions were caused by the branching reaction. Thus, Sample 1b (1 h of polymerization) had a higher PDI than Sample 1a (10 min of polymerization) and a tail with a higher molecular weight.

Another reaction was performed to elucidate the effect of the polymerization time on the branching reaction and eliminate any errors associated with differences between experiments. The reaction medium

TABLE I
Characterization of PMMA Synthesized by Anionic Polymerization

Run	[DPHLi]$_0$ (mmol)	MMA (mol)	$M_n{}^a$	$M_w{}^b$	M_n	M_w	PDI	Reaction time	Conversion
					GPC^c				
Sample1a	2.10	0.12	5700	7900	6400	7400	1.16	10 min	>98%
Sample 1b	2.10	0.12	5700	8800	6800	8500	1.25	60 min	>98%
Sample 2a	2.10	0.12	5700	8100	6700	7600	1.19	10 min	–
Sample 2b	2.10	0.12	5700	NA^d	NA^d	NA^d	NA^d	>12 h	–
Sample 3	1.05	0.12	11,400	14,100	12,900	13,500	1.05	10 min	>98%

^{a} Calculated from [MMA]/[DPHLi]$_0$.
^{b} From light scattering.
^{c} Based on PMMA standards.
^{d} Bimodal distribution.

was separated into two parts under vacuum before it was quenched by the acetic acid/methanol solution. After the split, one part (Sample 2a) was quenched after 10 min polymerization. The other (Sample 2b) was maintained in a dry iced bath overnight in the vacuum state, and then quenched. The GPC result for Sample 2a was the same as for Sample la, as shown in Figure 4. However, a bump at high molecular weight was observed in the GPC result of Sample 2b, indicating that PMMA was formed in Sample 2b with a higher molecular weight than in Sample 1b. These results clearly revealed that a longer reaction time was associated with a more extensive branching reaction.

The branching reaction is a bimolecular reaction and its rate (R_b) is proportional to the concentrations of the propagating chain and the carbonyl group in the system. However, the carbonyl group in the backbone of PMMA is not accessible to the reaction except for that in the chain-end, because of the steric hindrance.[15] Therefore, the rate equation of the branching reaction is,

$$R_b = k_b \text{ [propagating chain]}$$
$$\times \text{ [carbonyl group in the chain} - \text{end]} \quad (1)$$

Intramolecular cyclization is a unimolecular reaction and the rate equation of intramolecular cyclization is,

$$R_b = k_c \text{ [propagating chain]} \quad (2)$$

Because both concentrations of the propagating chain and the carbonyl group in the chain-end are equal to the concentrations of the initiator, eqs. (1) and (2) can be rewritten as

$$R_b = k_b \text{ [initiator]}^2 \quad (3)$$

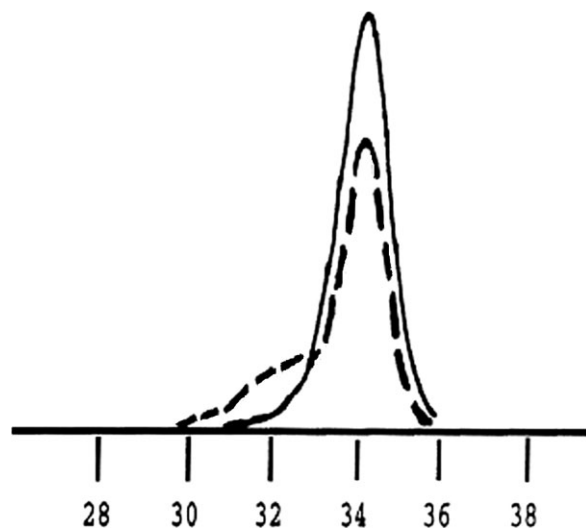$$R_c = k_c \text{ [initiator]} \quad (4)$$

Figure 4 GPC results for Samples 2a and 2b. Sample 2a (solid line, 10 min polymerization time): $M_n = 6.7 \times 10^3$ g/mol, $M_w = 7.6 \times 10^3$ g/mol and PDI = 1.19. Sample 2b (dash-line, > 12 h polymerization time).
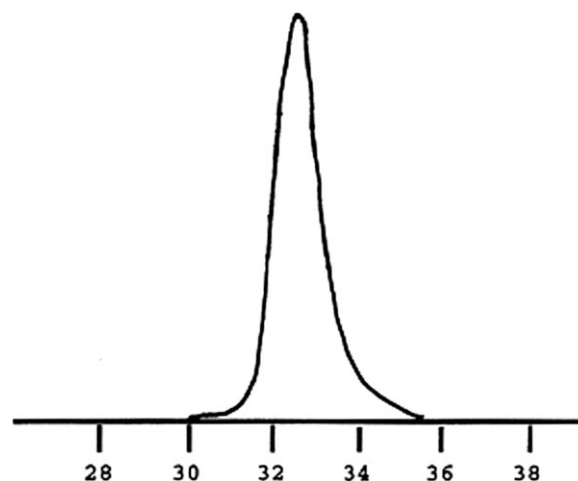

Figure 5 GPC result for Sample 3 (10 min polymerization time): $M_n = 12.9 \times 10^3$ g/mol, $M_w = 13.5 \times 10^3$ g/mol and PDI = 1.05.

From eqs. (3) and (4), reducing the amount of initiator reduces R_b more than it reduces R_c. Sample 3 was prepared by reducing the amount of DPHLi. For this sample, the high-molecular-weight tail almost disappeared. The PDI was 1.05. M_w and M_n were 13.5×10^3 and 12.9×10^3 g/mol, respectively, as presented in Figure 5 and Table I. Because the termination reaction is very complicated and insufficient kinetic data are available, the quantitative relationship among R_b, R_c, and [Initiator] cannot be determined. However, qualitatively, almost no high-molecular-weight tail was observed in Sample 3, which was polymerized by reducing the amount of DPHLi. The kinetic study of intermolecular and intramolecular terminations by using NMR, MALDI-TOF, and/or polymer end group analysis may provide the detailed information for understanding the branching mechanisms, which is undergoing now.

CONCLUSIONS

Experimental results revealed that the branching reaction in the anionic polymerization of MMA occurred especially following the high monomer conversion. This branching reaction completed with intramolecular cyclization. To prepare anionically a well-defined PMMA without a high-molecular-weight tail, rapid termination was probably required immediately after all monomer had been consumed in this DPHLi/THF/−78°C system.

References

1. Baskaran, D. Prog Polym Sci 2003, 28, 521.
2. Vlcek, P.; Lochmann L. Prog Polym Sci 1999, 24, 793.
3. Anderson, B. C.; Andrews, G. D.; Arthur, P., Jr.; Jacobson, H. W.; Melby, L. R.; Playtis, A. J.; Sharket, W. H. Macromolecules 1981, 14, 1601.
4. Andrews, G. D.; Melby, L. R. In New Monomers and Polymers; Culbertson, B. M.; Pittman, C. U., Jr., Eds.; Plenum Press: New York, 1988; p 357.
5. Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. J Am Chem Soc 1983, 105, 5706.
6. Reetz, M. T. Angew Chem 1988, 100, 1026.
7. Baskaran, D.; Chakrapani, S.; Sivaram, S. Macromolecules 1995, 28, 7315.
8. Mahua, G. D.; Baskaran, D.; Swaminathan, S.; Macromol Chem Phys 2003, 12, 204.
9. Warzelhan, V.; Hocker, H.; Schulz, G. V. Makromol Chem 1978, 179, 2221.
10. Trekoval, J.; Kratochvil, P. J Polym Sci Part A-1: Polym Chem 1972, 10, 1391.
11. Rempp, P.; Franta, E.; Herz, J. E. Adv Polym Sci 1988, 86, 145.
12. Tsai, Y.; Wang, W. J Appl Polym Sci 2006, 101, 1953.
13. Morton, M.; Fetters, L. J. Rubber Chem Technol 1975, 48, 359.
14. Hatada, K.; Kitayama, T.; Okahata, S.; Heimei, Y. Polym J 1981, 13, 1045.
15. Von Schreyer, G.; Volker, T. Makromol Chem 1963, 63, 202.