

Kinetic and Molecular Weight Control for Methyl Methacrylate Semibatch Polymerization. II. Open Control

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ABSTRACT: The gel effect will bring a violent increase of conversion for methyl methacrylate (MMA) polymerization in a short time. It will be very dangerous for the reactor, as it causes an increase of molecular weight and broadens the molecular weight distribution. To unify the kinetics, molecular weight, and its distribution, on the basis of the mathematical models for semibatch polymerization of MMA, three controlled objectives that are the heat load distribution index, the change in molecular weight, and molecular weight distribution index are presented. Three materials (monomer,

solvent, and chain transfer agent) and their flow rate and feeding mode are analyzed for the open control of kinetics, molecular weight, and its distribution. The optimum flow rate and mode are obtained. The heat load distribution index and molecular weight distribution index are even less than 2.0 and 2.2, respectively. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4399–4405, 2006

Key words: methyl methacrylate; control; kinetics; molecular weight

INTRODUCTION

In most industrial polymerization, the increase in the polymer concentration during the reaction strongly influences the kinetics and polymer properties. The viscosity increase of the polymerization system results in a mobility reduction of polymer chain and diffusion-controlled of termination and propagation. The gel effect arises because the termination rate constant decreases, comparing with that of propagation rate constant, and causes a large increase in the polymerization rate and a sudden increase in the conversion. It is very dangerous for an industrial reactor. Similarly, at higher conversions, if the polymerization temperature is lower than the glass transition temperature of the polymer/monomer mixture, the propagation rate constant will decrease significantly.

Molecular weight of polymer is related to the kinetic constant (k_p and k_t) and operation conditions. The gel effect on the molecular weight of polymer is very strong, and so the number- or weight-average molecular weight will increase with the free radical accumulation when the gel effect occurs. The glass effect will cause a small decrease of molecular weight. How-

ever, both the gel and glass effects can broaden the molecular weight distribution.

From the heat transfer of the polymerization reactor, the so-called gel effect will be very dangerous. The heat load distribution index (Q_{\max}/Q_{ave}) is very large with the appearance of gel effect, and it will squander the reactor productivity. From the qualities of obtained polymer, the gel effect will cause a change in the final polymer properties. So, the crux of the kinetics and molecular weight problems is in the gel effect. It should be controlled or eliminated in the polymerization process. A semibatch reactor is suitable, with the flow stream of chain transfer agent (CTA), monomer, initiator, or solvent to control or eliminate the gel effect.

A large number of articles can be read about the optimization of polymerization and polymer properties. Louie and Soong¹ distinguished between two categories of partial optimizations: minimizing the reaction time that left the molecular weight uncontrolled, and narrowing the molecular weight distribution that left the reaction time and molecular weight uncontrolled. The optimum reaction time for methyl methacrylate (MMA) solution batch polymerization was determined mathematically by Ponuswamy et al.² Takamatzu et al.³ proposed a new method and simulated to obtain the prescribed MWD by the change in temperature and initiator concentration in the batch reactor. Chang and Lai⁴ presented another new method to obtain a specified MWD by the selection of optimal temperature for

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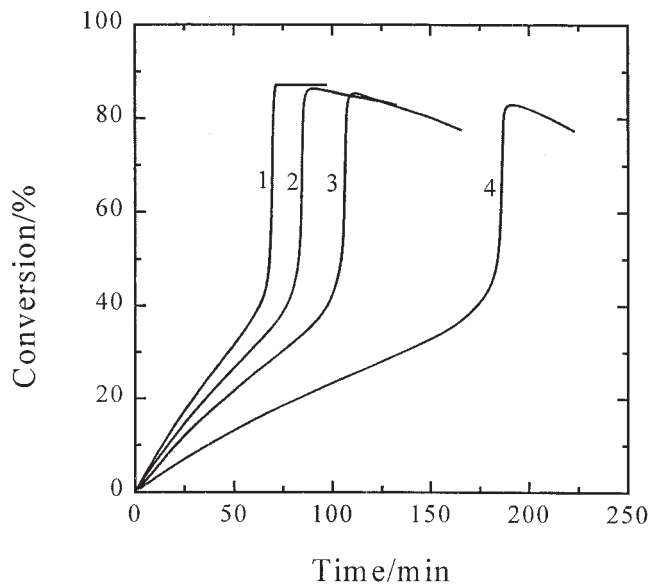


Figure 1 Kinetic simulation data of MMA polymerization at various monomer flow rate ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$).

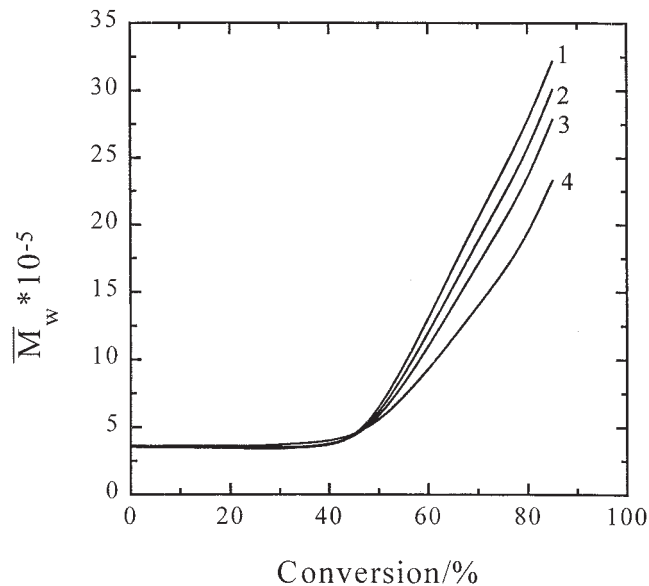


Figure 3 Weight-average molecular weight simulation of MMA polymerization at various monomer flow rate ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$).

bulk or solution batch polymerization. Maschio et al.⁵ developed a mathematical model for the bulk or suspension polymerization of MMA in batch reactors to achieve assigned values of molecular weight and minimum MWD.

On the basis of the previous article,⁶ we present three objectives to control the kinetics, molecular weight, and its distribution in this study: heat load

distribution index ($Q_{\text{max}}/Q_{\text{ave}}$, it is the ratio of the maximum polymerization heat to that of average), change in molecular weight, and molecular weight distribution index (\bar{M}_w/\bar{M}_n). It is different from the former work, because we want to meet the three objects at the same time. The control methods are selection of species type, flow rate, and feed mode.

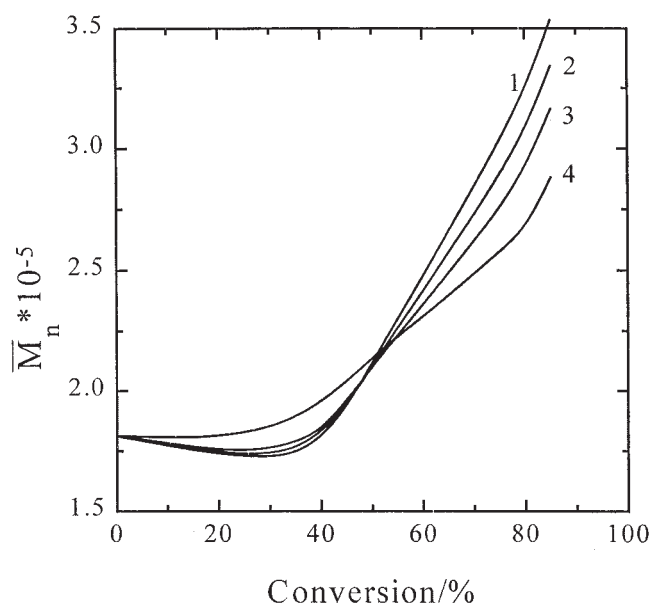


Figure 2 Number-average molecular weight simulation of MMA polymerization at various monomer flow rate ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$).

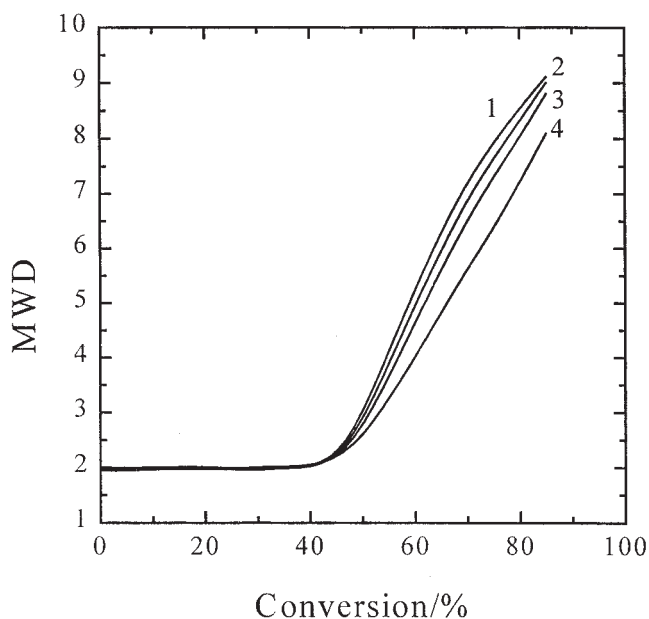


Figure 4 Molecular weight distribution simulation of MMA polymerization at various monomer flow rate ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$).

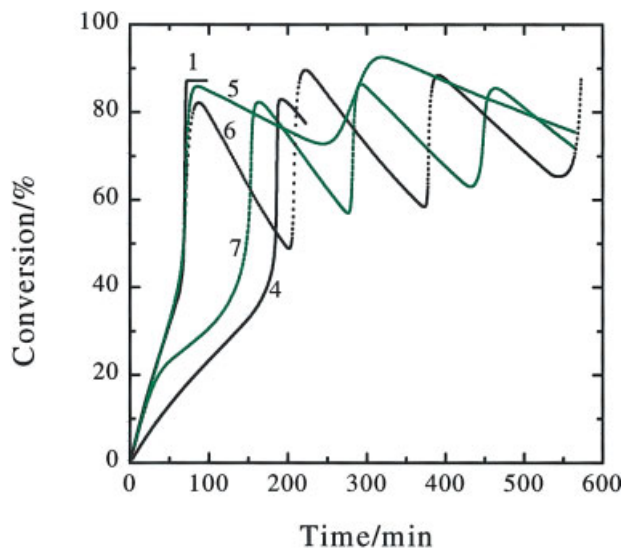


Figure 5 Kinetic simulation data of MMA polymerization at various monomer feeding mode ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

SIMULATION AND CONTROL OF KINETICS AND MOLECULAR WEIGHT

By monomer flow rate and feeding mode

When we consider an industrial preparation of polymer, the bulk polymerization is usually selected at first for its simplicity and cheapness. No matter how large amount of monomer or how many kinds of feeding modes, it is always a “pure” system without separation. So, we first select monomer to add into the polymerization system.

At different monomer flow rate (modes 1–4), we obtain the simulation results of kinetics, molecular weight, and its distribution (see Figs. 1–4). Although the polymerization time when the gel effect occurs is delayed with the increase of the monomer flow rate, the gel effect will always appear at 40–50% polymer content (see Fig. 1). The change in molecular weight and its distribution become small with the increase of the monomer flow rate (see Figs. 2–4), but the results are too far away from our object (molecular weight distribution index, \bar{M}_w/\bar{M}_n , should be controlled in the range of 2–3).

If we change the monomer feeding mode (like if the monomer is added after 0.5 and 1 h), the gel effect can not be eliminated and will still be caused at 40–50% polymer content. More dangerous is the appearance of the multiple gel effects when the monomer is added after an interval of polymerization (Fig. 5). Meanwhile, the molecular weight and its distribution show the multiple increases, and a designed value can not be retained.

The heat load distribution index can be used to judge the productivity of the reactor and the suitability

TABLE I
Monomer Feeding Flow Rate and Mode and the Heat Load Distribution Index

No.	Feeding flow rate and mode	Q_{\max}/Q_{ave}
1	Without adding monomer	26.455
2	Monomer flow rate is 0.5 mol/h from the beginning to the end	20.042
3	Monomer flow rate is 1 mol/h from the beginning to the end	18.783
4	Monomer flow rate is 2 mol/h from the beginning to the end	28.844
5	Monomer flow rate is 0.5 mol/h from 3600 s to the end	18.779 ^a
6	Monomer flow rate is 2 mol/h from 3600 s to the end	13.330 ^a
7	Monomer flow rate is 2 mol/h from 1800 s to the end	31.298 ^a

$M_0 = 8.8835 \text{ mol}$, $\text{AIBN}_0 = 0.01548 \text{ mol}$, $T = 70^{\circ}\text{C}$.

^a Only calculated to the first gel effect peak.

of the selected recipe and operation conditions. The more it is near to 1, the higher is the productivity of the polymerization reactor. Comparing the Q_{\max}/Q_{ave} in the Table I, there is an optimum monomer flow rate (modes 1–4) and feeding point (modes 4, 7, and 6) to obtain a minimum heat load distribution index. This result is proved by the experimental phenomena of Louie.^{1,7} However, no matter which method is selected, Q_{\max}/Q_{ave} is always far from 3.0.

Both the heat load and molecular weight distribution indexes are far from that of our objects, and the molecular weight of PMMA always change ten times in the polymerization process. So, it is impossible to eliminate the gel effect and unify the kinetics, molecular weight, and its distribution, though there is change in the monomer flow rate or the feeding mode.

By solvent flow rate and feeding mode

When the monomer addition can not meet the industry needs, the second selection is to add a small

TABLE II
Solvent Feeding Flow Rate and Mode and the Heat Load Distribution Index

No.	Feeding flow rate and mode	Q_{\max}/Q_{ave}
1	Without adding benzene	26.455
2	Benzene flow rate is 2 mol/h from 3600 s to the end	23.583
3	Benzene flow rate is 1 mol/h from the beginning to the end	6.283
4	Benzene flow rate is 1.2 mol/h from the beginning to the end	2.142
5	Benzene flow rate is 2 mol/h from the beginning to the end	3.084

$M_0 = 8.8835 \text{ mol}$, $\text{AIBN}_0 = 0.01548 \text{ mol}$, $T = 70^{\circ}\text{C}$.

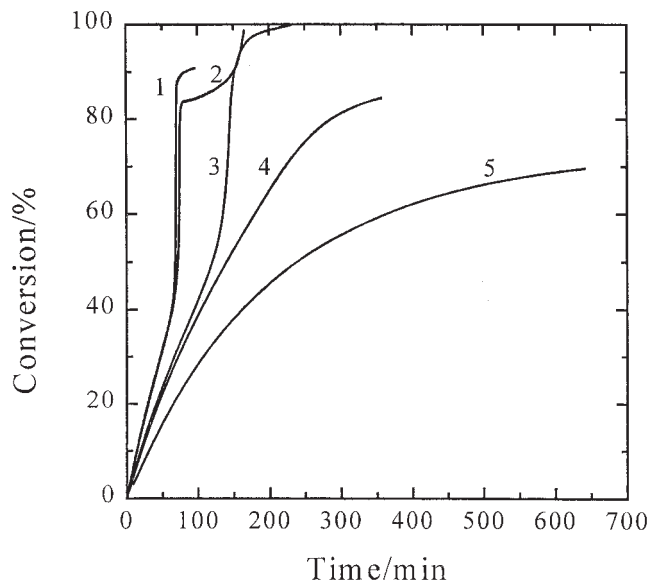


Figure 6 Kinetic simulation data of MMA polymerization at various benzene feeding flow rate and mode ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$).

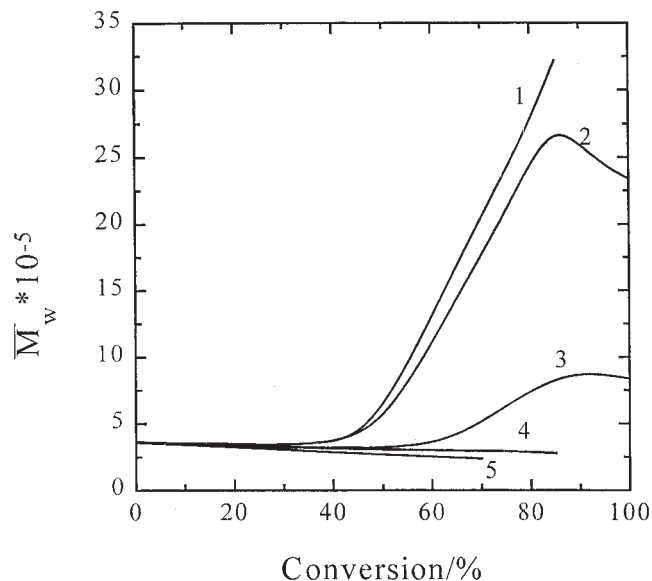


Figure 8 Weight-average molecular weight simulation of MMA polymerization at various benzene feeding flow rate and mode ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$).

amount of solvent in the bulk polymerization system. Because the addition of solvent can increase the mobility of the macroradicals and decrease the change in ψ , the gel effect will be delayed or eliminated with the increase of solvent concentration. But a large amount of solvent will bring many problems, such as separation of the polymer and solvent, reduction of the polymerization rate, and descent of the molecular weight; a suitable solvent flow rate and feeding mode

should be important for the elimination of gel effect and succession of our three objectives (Table II).

Figures 6–9 present the effects of solvent feeding flow rate and mode on the kinetics, molecular weight, and distribution.

Comparing the mode 2 and 5, the solvent should be added at a suitable time. The gel effect will not be controlled if the solvent is added at the time closer to the appearance of the gel effect. The results,

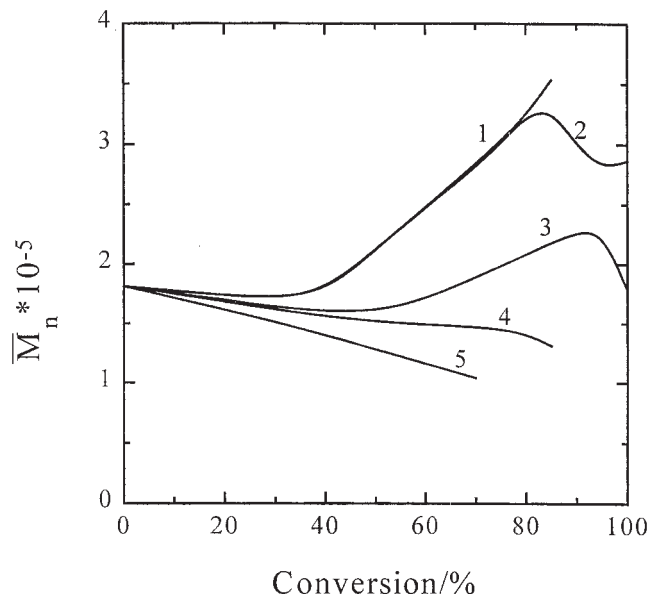


Figure 7 Number-average molecular weight simulation of MMA polymerization at various benzene feeding flow rate and mode ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$).

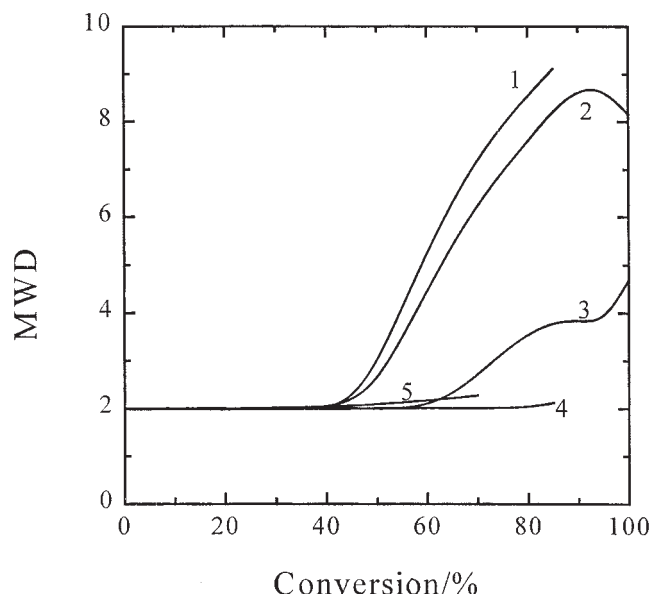


Figure 9 Molecular weight distribution simulation of MMA polymerization at various benzene feeding flow rate and mode ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$).

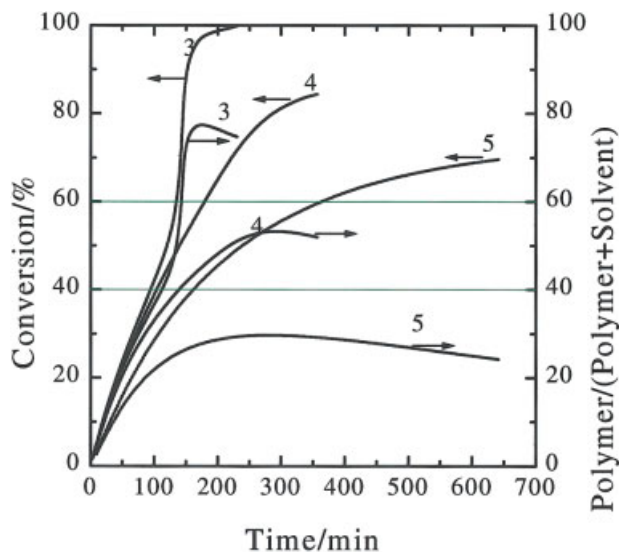


Figure 10 Conversion and polymer weight fraction in the MMA polymerization system at various benzene flow rate ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

kinetics, molecular weight, and its distribution, and heat load distribution index are largely different.

At different solvent flow rates (mode 1, 3, 4, and 5), we find that there is an optimum solvent feeding flow rate for molecular weight distribution and heat load distribution indexes. In a small solvent feeding flow rate (mode 3), the gel effect is delayed with the conversion of 55–65%, but it will still occur sometime; the molecular weight and its distribution will increase after the gel effect, and the heat load distribution index will not be a small value. On the other hand, in a large solvent feeding flow rate (mode 5), the gel effect is eliminated, but it will take more time to react; the molecular weight and its distribution will decrease in the polymerization process. When a large amount of solvent is added into the polymerization system, the productivity of the reactor is low, and the heat load distribution index will not be a minimum value. The optimum solvent feeding flow rate to eliminate the gel effect and to unify molecular weight and its distribution and heat

load distribution indexes for MMA polymerization at 70°C and $[\text{AIBN}] = 0.01548 \text{ mol/L}$ is 1.2 mol/h. From Figure 10, the polymer weight fractions of mode 4 are always in the range of 40–50% when the conversion is higher than 40%. The 40–50% of polymer weight concentration is in agreement with the results.⁶ So, mode 4 is the most efficient method to control the gel effect; its heat load distribution index is even less than 2.0, number- or weight-average molecular weight is retained at 1.8×10^5 – 1.3×10^5 or 3.6×10^5 – 2.8×10^5 , and molecular weight distribution index is even in the range of 2.0–2.2.

So, it is a good method to eliminate the gel effect, unify the kinetics, molecular weight, and its distribution, and enhance the efficiency of the reactor, though there is change in the solvent flow rate and feeding mode.

By CTA flow rate and feeding mode

CTA can control the kinetics, molecular weight, and its distribution, because the CTA will deactivate some of the macroradicals, keep the radical concentration in a low normal level ($\sim 10^{-7} \text{ mol/L}$), will transfer to the macroradicals, and keep the molecular weight and its distribution at a constant.

The CTA could be added at the fixed time (such as at the beginning or after reacting one hour) or in a continuous feeding mode at a interval time. The best time of adding CTA is after 1 h polymerization at 70°C and $[\text{AIBN}] = 0.01548 \text{ mol/L}$, because the gel effect will occur after that time. So, six methods (see Table III) are designed to compare the effects of CTA feeding flow rate and mode on the kinetics, molecular weight, and its distribution.

Figures 11–14 present the results with the participation of CTA. It is obvious that the heat load distribution index decreases largely when CTA is added into the polymerization system. The heat load distribution index decreases even less than 2.0.

Comparing mode 6 with 4 and 5, which are added with the same total CTA applied quantity, the molecular weight of PMMA controlled by mode 6 is more less than those by mode 4 and 5, though its molecular weight distribution is very small (not more than 2.1). If

TABLE III
CTA Feeding Flow Rate and Mode and the Heat Load Distribution Index

No.	Feeding flow rate and mode	Total mole	$Q_{\text{max}}/Q_{\text{ave}}$
1	Without CTA	0	26.455
2	DDM flow rate is 0.1 mol/h from 3600 s to 4600 s	0.02778	2.451
3	DDM flow rate is 0.2 mol/h from 3600 s to 4100 s	0.02778	2.181
4	DDM flow rate is 0.2 mol/h from 3600 s to 4600 s	0.05556	1.765
5	All of the 0.05556 mol DDM is added at 3600 s	0.05556	1.823
6	All of the 0.05556 mol DDM is added at 0 s	0.05556	1.835

$$M_0 = 8.8835 \text{ mol}, \text{AIBN}_0 = 0.01548 \text{ mol}, T = 70^{\circ}\text{C}.$$

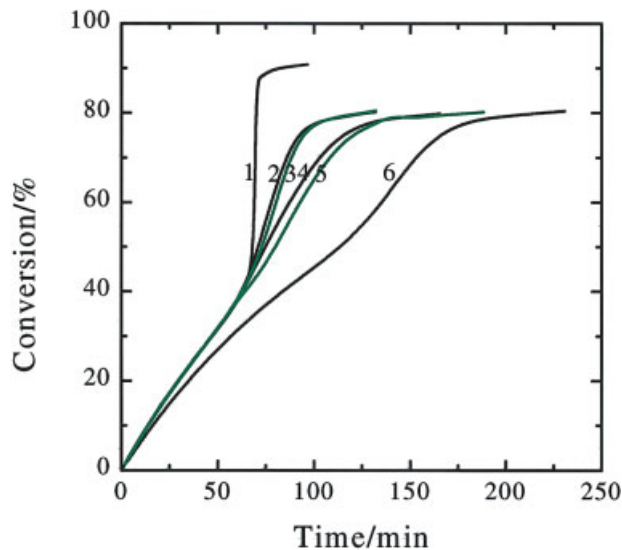


Figure 11 Kinetic simulation data of MMA polymerization at various CTA feeding rate and mode ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$, n -dodecyl mercaptan as CTA). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

we want to produce a high molecular weight PMMA, the mode 6 is not suitable, and the CTA should be added by a continuous or after an interval mode.

Both the modes 2 and 3 have the small heat load distribution and molecular weight distribution and are suitable to control the kinetics, molecular weight, and its distribution.

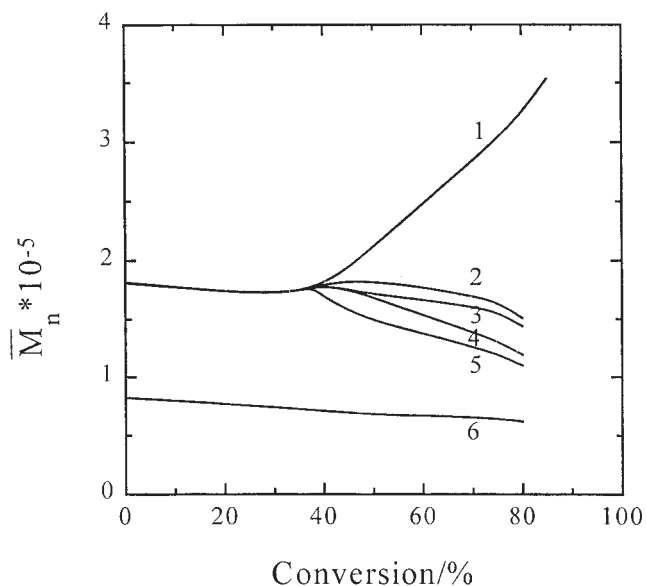


Figure 12 Number-average molecular weight simulation of MMA polymerization at various CTA feeding rate and mode ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$, n -dodecyl mercaptan as CTA).

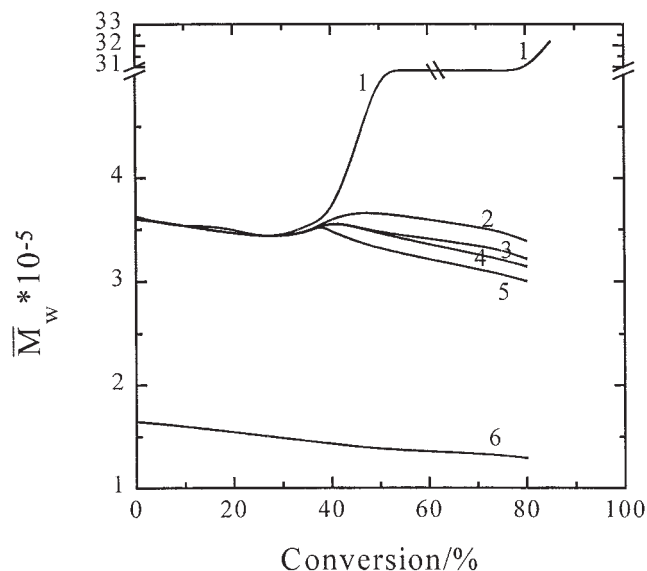


Figure 13 Weight-average molecular weight simulation of MMA polymerization at various CTA feeding rate and mode ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$, n -dodecyl mercaptan as CTA).

CONCLUSIONS

On the basis of the three control objectives: heat load distribution index, change in molecular weight, and molecular weight distribution index, the effects of the flow rate and feeding mode of monomer, solvent, and CTA on the three control objectives are investigated, respectively.

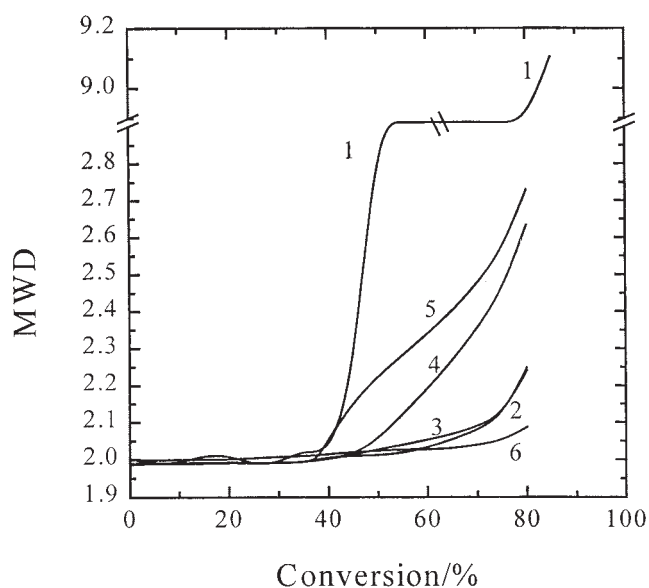


Figure 14 Molecular weight distribution simulation of MMA polymerization at various CTA feeding rate and mode ($T = 70^{\circ}\text{C}$, $[\text{AIBN}] = 0.01548 \text{ mol/L}$, n -dodecyl mercaptan as CTA).

Because the gel effect can not be eliminated by the change in monomer flow rate, changing feed mode will bring a multiple violent increase of conversion, the molecular weight will increase with the appearance of gel effect, and the control method of changing monomer flow rate and feed mode can not meet the demand of three control objects to unify the kinetics, molecular weight, and its distribution.

The molecular weight of polymer prepared in solution polymerization or with the participation of CTA is always smaller than that in bulk polymerization. However, with the change of solvent or CTA flow rate and feed mode, not only the molecular weight can be equal to that of bulk polymerization but also the gel effect can be eliminated, and kinetics, molecular weight, and its distribution can be controlled. The optimum heat load distribution index is even less than 2.0, the change in molecular weight is lower than 10%,

and molecular weight distribution index is even in the range of 2.0–2.2.

Using the change of solvent and CTA flow rate and feed mode, combining with the effects of temperature, and initiator concentration on the kinetics, molecular weight, and its distribution, any kinds of kinetic curves and any molecular weight and its distribution can be obtained.

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