The multiple-component initiator technique for constant-rate free-radical homopolymerization

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The multiple initiator method of controlling polymerization at a prescribed rate is studied. A correlation of the auto-acceleration function with the kind and concentration of the initiator is assumed. The equations for the determination of the kind and concentration of the initiator to control polymerization at a constant rate are then derived. Bulk polymerization of methyl methacrylate is chosen for verification. Using the method proposed and binary initiator systems, we determine several sets of initiator pairs and their concentrations for polymerization of methyl methacrylate at rates of 0.1 and 0.2 h^{-1} for various reaction temperatures. The results indicate that the polymerization rates obtained with the given initiator pairs and concentrations are what we have prescribed.

(Keywords: auto-acceleration function; multiple initiators; constant polymerization rate)

INTRODUCTION

Increasing the rate of a reaction is a method for reducing batch time to a minimum. The allowable reaction rate in many bulk radical polymerizations is, however, limited by the gel effect. This effect induces auto-acceleration and leads to the generation of a large amount of heat. The critical condition for minimum batch time, therefore, is that the heat generation rate at any point in the reaction should be equal to the rate of removal of heat from the system via the heat of reaction. This can be attained by controlling polymerization so that it occurs at an appropriate reaction rate. Temperature programming techniques[1,2] and multiple-component initiator methods[3] have been suggested for obtaining constant-rate polymerization. For temperature programming techniques, a somewhat complex reactor is required, which may produce a wider dispersity of polymer product. Multiple-component initiator methods do not involve such problems and thus may be better for obtaining constant-rate polymerization. However, in the method, a quantitative way of determining the kind and concentration of the initiators needed to obtain a prescribed rate is still a problem worthy of study.

THEORY

Rate expressions

The mechanism of bulk radical polymerization that has been used in most standard polymer texts[4,5] is used in this study. There is an initiation step, a propagation step and a termination step, while the chain-transfer reactions to monomer, to initiator and to dead polymers are assumed to be negligible. Thus the reactions are given as follows:

$$\textit{Initiation}\quad I_\alpha \xrightarrow{k_{d\alpha}} 2R_{c\alpha}\ (\alpha=1,2\ldots)$$

$$R_{C\alpha}+M \xrightarrow{k_{a\alpha}} R_1$$

$$\textit{Propagation}\quad R_i+M \xrightarrow{k_p} R_{i+1}$$

$$\textit{Termination}\quad R_i+R_j \xrightarrow{k_{tc}} P_{i+j}\ (i,j=1,2,\ldots)$$

$$R_i+R_j \xrightarrow{k_{td}} P_i+P_j$$

where R_i and P_i denote the species and concentration of active and dead polymers of chain length i, respectively.

If the dissociation of initiators is assumed to be the rate-determining step, the rate expressions for the reactions mentioned above are given by

$$I_\alpha = I_{\alpha 0}\exp(-k_{d\alpha}t) \tag{1}$$

$$r_I = 2\sum_\alpha^\infty f_\alpha k_{d\alpha} I_\alpha \tag{2}$$

$$r_P = -dM/dt = k_p M_0(1-m)\mu_0 + 2\sum_\alpha^\infty f_\alpha k_{d\alpha} I_\alpha \sim k_p M_0(1-m)\mu_0 \tag{3}$$

$$d\mu_0/dt = d\left(\sum_{i=1}^\infty R_i\right)\Big/ dt = 2\sum_\alpha^\infty f_\alpha k_{d\alpha} I_\alpha - k_t\mu_0^2 \tag{4}$$

$$d\mu_1/dt = d\left(\sum_{i=1}^\infty iR_i\right)\Big/ dt = 2\sum_\alpha^\infty f_\alpha k_{d\alpha} I_\alpha + k_p M_0(1-m)\mu_0 - k_t\mu_0\mu_1 \tag{5}$$

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$$d\mu_2/dt = d\left(\sum_{i=1}^{\infty} i^2 R_i\right)\Big/ dt = 2\sum_{\alpha}^{\infty} f_\alpha k_{d\alpha} I_\alpha + k_p M_0(1-m)(2\mu_1+\mu_0) - k_t\mu_0\mu_2 \quad (6)$$

$$d\sigma_0/dt = d\left(\sum_{i=1}^{\infty} P_i\right)\Big/ dt = \tfrac{1}{2}(2-\beta)k_t\mu_0^2 \quad (7)$$

$$d\sigma_1/dt = d\left(\sum_{i=1}^{\infty} iP_i\right)\Big/ dt = k_t\mu_0\mu_1 \quad (8)$$

$$d\sigma_2/dt = d\left(\sum_{i=1}^{\infty} i^2 P_i\right)\Big/ dt = k_t\mu_0\mu_2 + k_t\mu_1^2 \quad (9)$$

where

$$\mu_k = \sum_{i=1}^{\infty} i^k R_i \quad \text{and} \quad \sigma_k = \sum_{i=1}^{\infty} i^k P_i$$

r_I and r_P denote the rates of initiation and polymerization, respectively, m is the monomer conversion, which is defined by $(M_0 - M)/M_0$, where M_0 and M are the molar concentrations of reaction solution at $t=0$ and any reaction point, respectively, and β is the mode of termination defined by $k_{tc}/(k_{tc}+k_{td})$.

If the steady-state hypothesis is assumed, equations (3) to (9) become

$$\mu_0 = \left[\left(2\sum_{\alpha} f_\alpha k_{d\alpha} I_{\alpha 0}\exp(-k_{d\alpha}t)\right)\Big/ k_t\right]^{1/2} \quad (10)$$

$$\mu_1 = \mu_0 + (k_p/k_t)M_0(1-m) \quad (11)$$

$$\mu_2 = \mu_0 + 3(k_p/k_t)M_0(1-m) + 2(k_p^2 M_0^2/k_t^2\mu_0)(1-m)^2 \quad (12)$$

$$dm/dt = d\sigma_1/dt$$

$$= k_p M_0(1-m)\left[\left(2\sum_{\alpha} f_\alpha k_{d\alpha} I_{\alpha 0}\exp(-k_{d\alpha}t)\right)\Big/ k_t\right]^{1/2} \quad (13)$$

$$d\sigma_0/dt = (2-\beta)\sum_{\alpha} f_\alpha k_{d\alpha} I_{\alpha 0}\exp(-k_{d\alpha}t) \quad (14)$$

$$d\sigma_2/dt = 2(1+\beta)\sum_{\alpha} f_\alpha k_{d\alpha} I_{\alpha 0}\exp(-k_{d\alpha}t) + (3+2\beta)k_p M_0(1-m) \times \left[\left(2\sum_{\alpha} f_\alpha k_{d\alpha} I_{\alpha 0}\exp(-k_{d\alpha}t)\right)\Big/ k_t\right]^{1/2} + (2+\beta)(k_p^2 M_0^2/k_t)(1-m)^2 \quad (15)$$

Correlation of the auto-acceleration function

It has been shown[6,7] that auto-acceleration in polymerization rate is a consequence of a decrease in the rate constant of termination. Studies on the diffusion-controlled termination reaction have been done extensively and are well documented[4,5,8]. According to North's description[4,9-11], translational diffusion or segmental diffusion is the rate-determining step in the diffusion-controlled termination processes. Segmental diffusion can be the rate-controlling step only in the early stages of polymerization[4,12,13]. Translational diffusion is profoundly affected by the viscosity of the reaction medium. Increase in viscosity will increase the retardation of translational diffusion and thus decrease the termination rate. The viscosity of the reaction medium increases with increase in polymer molecular weights and conversion. It is well known that polymer molecular weights and polymer concentration in the reaction medium as well as polymerization rate can be controlled by the kind and concentration of initiators used.

In reactor calculations, Hamielec[3,20] suggests a useful empirical correlation, which is called the auto-acceleration function or gel function, for the rate constants for termination of polymerizations. The auto-acceleration function is defined by $g(m,T) = k_t/k_{t0}$, where k_{t0} refers to the termination rate constant at zero conversion, and k_t to the rate constant of diffusion-controlled termination. Obviously, the auto-acceleration function has been assumed to be independent of conversion (m) and reaction temperature (T).

In this study, following the discussion mentioned above, we assume that the auto-acceleration function may be correleated with the kind and concentration of initiators by the following relationship:

$$\frac{g^2(m,T)}{(1-m)^2} = \sum_{\alpha} A_\alpha \exp(-a_\alpha m) \quad (16)$$

where A_α and a_α, functions of concentration and kind of mixed initiators, respectively, are adjustable parameters and can be determined by the iterative curve-fitting technique.

Equations for determination of kind and concentration of initiators for constant-rate polymerization

If the rate of polymerization is set to be C, where $C = dm/dt = M_0^{-1}dM/dt$, equation (13) may then be rearranged to

$$\frac{C^2 k_{t0}}{2k_p^2}\frac{g^2(m,T)}{(1-m)^2} = \sum_{\alpha} f_\alpha k_{d\alpha} I_{\alpha 0}\exp(-k_{d\alpha}m/C) \quad (17)$$

where $t = m/C$ is obtained by integration of $dm/dt = C$ with the initial condition $m=0$ at $t=0$. Substitution of (16) into (17) gives

$$\frac{C^2 k_{t0}}{2k_p^2}\sum_{\alpha} A_\alpha \exp(-a_\alpha m) = \sum_{\alpha} f_\alpha k_{d\alpha} I_{\alpha 0}\exp(-k_{d\alpha}m/C) \quad (18)$$

Each term in the series of equation (18) is for a different kind of initiator, and they are independent of one another. Hence, comparing the appropriate terms on both sides of (18), we obtain

$$a_\alpha = k_{d\alpha}/C \quad \text{or} \quad k_{d\alpha} = a_\alpha C \quad (19)$$

$$\frac{C^2 k_{t0}}{2k_p^2}A_\alpha = f_\alpha k_{d\alpha} I_{\alpha 0} \quad \text{or} \quad I_{\alpha 0} = \frac{C^2 k_{t0}}{2k_p^2 f_\alpha k_{d\alpha}}A_\alpha \quad (20)$$

Utilizing both (19) and (20), the kind $k_{d\alpha}$ and concentration $I_{\alpha 0}$ of the initiators for polymerization to take place at a given rate C may be obtained.

RESULTS

Bulk polymerization of methyl methacrylate (MMA) has been studied extensively and is well documented[4,5,15-17].

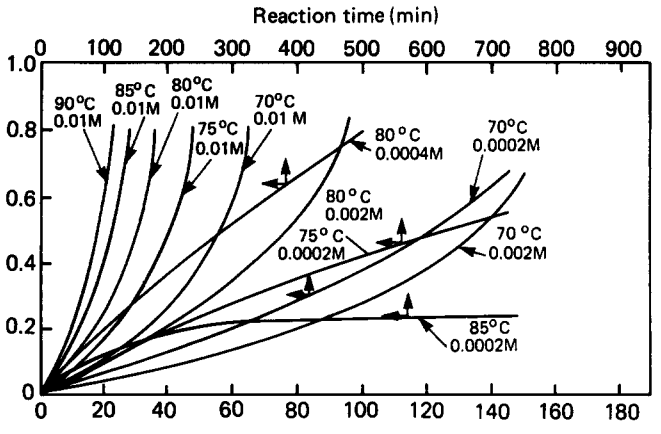

Figure 1 Effects of initial initiator concentrations and reaction temperatures on the course of methyl methacrylate polymerization initiated by t-butyl perpivalate

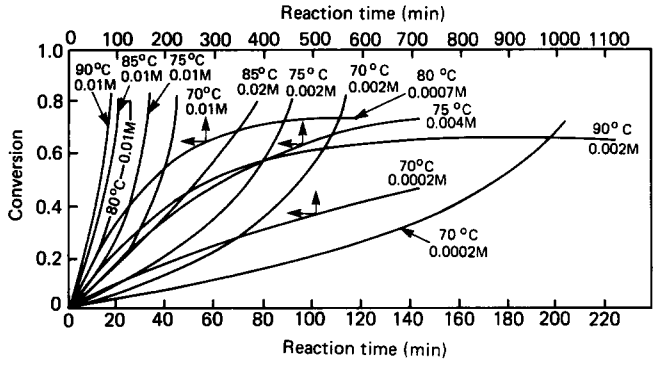

Figure 2 Effects of initial initiator concentrations and reaction temperatures on the course of methyl methacrylate polymerization initiated by decanoyl peroxide

Meanwhile this system is known to have serious auto-acceleration. Hence, bulk polymerization of MMA was chosen for the present study.

Effects of using a single initiator on the course of polymerization

In this study it was assumed that the auto-acceleration function may be correlated with the kind and concentration of initiators in the form of equation (16). The courses of polymerization for bulk polymerizations of MMA initiated by decanoyl peroxide (DPO) or t-butyl perpivalate (TBP) of various concentrations at different temperature were calculated to see how the course of polymerization varied with kind and concentration of initiators. The Runge–Kutta–Gill (RKG) method was used for the calculation. The kinetic parameters of bulk polymerization of MMA used are given as follows.

The rate constants of initiation of DPO and TBP are given respectively as[18]

$$k_{d,DPO} = 1.526 \times 10^{15} \exp(-30518/RT)$$

$$k_{d,TBP} = 1.507 \times 10^{14} \exp(-23394/RT)$$

The activation energy and the frequency factor of propagation and termination for the chemical controlling process [4,18] are given respectively as

$$E_{p0} = 6.3 \text{ kcal mol}^{-1} \qquad A_{p0} = 5.1 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$$

$$E_{t0} = 2.8 \text{ kcal mol}^{-1} \qquad A_{t0} = 7.8 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$$

The gel function obtained by Friis and Nyhagen[15] is adopted here

$$g^2(m,T) = \frac{k_{td}}{k_{td0}} = \frac{1}{(1-m)^2} \exp\{2[(0.1082T - 11.97)m + (-0.0785T + 2.01)m^2]\} \qquad (21)$$

where k_{td0} denotes the rate constant of disproportionation at zero conversion and k_{td} the rate constant of disproportionation of the diffusion-controlled process, and T refers to the reaction temperature in Kelvin. For equation (21), they assumed that termination in MMA polymerization occurs exclusively by disproportionation.

Figure 1 and *2* show the results obtained for plots of conversion vs. reaction time. The courses of polymerization of MMA initiated by DPO and TBP are quite different. Conversion–time curves varying with the concentration of initiator and reaction temperature were observed. As shown in the figures auto-acceleration obviously takes place in most cases of single initiators studied, but if the concentration of initiators is reduced below a critical value, auto-acceleration is no longer observed.

Determination of the kind and concentration of mixed initiators for constant-rate polymerization

In this work we used equations (18) to (20) to determine suitable binary-component initiator systems for the bulk polymerization of MMA at prescribed rates of 0.1 and 0.2 h^{-1}. When (16) is used to determine both parameters A_α and a_α, a two-term expression for $\sum_\alpha A_\alpha \exp(-a_\alpha m)$ was assumed, and Friis' auto-acceleration function (21) was employed. Also Moore's iterative technique[19] was used. The values of A_α and a_α thus obtained (*Table 1*) were further substituted into (19) and (20) to obtain the dissociation rate constants $k_{d\alpha}$ and concentrations $I_{\alpha 0}$ of the initiators for polymerization at the prescribed rate. Many sets of initiator pairs might be obtained. Among them those of commercially available initiators were adopted and these are given in *Tables 2* and *3*. It can be seen in the tables that for each initiator pair the initiator of higher dissociation rate constant is used in higher concentration, and for the initiator of lower dissociation rate constant, a lower concentration is used.

Substituting $k_{d\alpha}$ and $I_{\alpha 0}$ obtained from *Tables 2* and *3* equation (21) into equation (13), and using the RKG method for numerical integration, we calculated the conversion–time curves of the MMA polymerizations. The results are shown as the full lines in *Figures 3* to *6*. All the lines are linear and have slopes of 0.1 and 0.2 of the prescribed rate. For comparison, conversion–time curves of the polymerizations initiated by one of the single initiators in the given initiator pair (whose concentration

Table 1 Parameters A_α and a_α in equation (17) obtained for polymerization of methyl methacrylate at 70, 75 and 80°C

Temperature (°C)	A_α		a_α	
	$\alpha=1$	$\alpha=2$	$\alpha=1$	$\alpha=2$
70	1.200	0.070	1.98×10^{-3}	3.70×10^{-4}
75	1.656	0.0173	2.24×10^{-3}	4.473×10^{-4}
80	0.880	0.500	1.96×10^{-3}	13.40×10^{-4}

Table 2 Binary initiators and their concentrations for obtaining a constant rate of $0.1\ h^{-1}$

Temp. (°C)	Initiators		$I_{\alpha 0}$	
	$\alpha=1$	$\alpha=2$	$\alpha=1$	$\alpha=2$
70	2,2-Azobis-2,4-dimethylvaleronitrile[a]	Azobisisobutyronitrile[b]	2.000×10^{-4}	6.243×10^{-6}
75	t-Butyl perpivalate[c]	Benzoyl peroxide[d]	2.031×10^{-4}	1.066×10^{-5}
80	Decanoyl peroxide[e]	Azobisisobutyronitrile[b]	1.006×10^{-4}	8.256×10^{-5}

[a] $k_d=6.2\times10^{14}\exp(-26630/RT)$
[b] $k_d=1.58\times10^{15}\exp(-30800/RT)$
[c] $k_d=1.507\times10^{14}\exp(-23394/RT)$
[d] $k_d=2.34\times10^{12}\exp(-26630/RT)$
[e] $k_d=1.526\times10^{15}\exp(-30518/RT)$

Table 3 Binary initiators and their concentrations for obtaining a constant rate of $0.2\ h^{-1}$

Temp. (°C)	Initiators		$I_{\alpha 0}$	
	$\alpha=1$	$\alpha=2$	$\alpha=1$	$\alpha=2$
70	4-Nitrophenylazotriphenylmethane[f]	Cumyl perpropionate[g]	4.064×10^{-4}	7.842×10^{-5}
75	2,2-Azobis-2,4-dimethylvaleronitrile[a]	Azobisisobutyronitrile[b]	3.776×10^{-4}	1.502×10^{-5}
80	t-Butyl perpivalate[c]	Benzoyl peroxide[d]	3.489×10^{-4}	4.147×10^{-5}

[a-e] As in *Table 2*
[f] $k_d=4.619\times10^{15}\exp(-29932/RT)$
[g] $k_d=4.11\times10^{7}\exp(-20713/RT)$

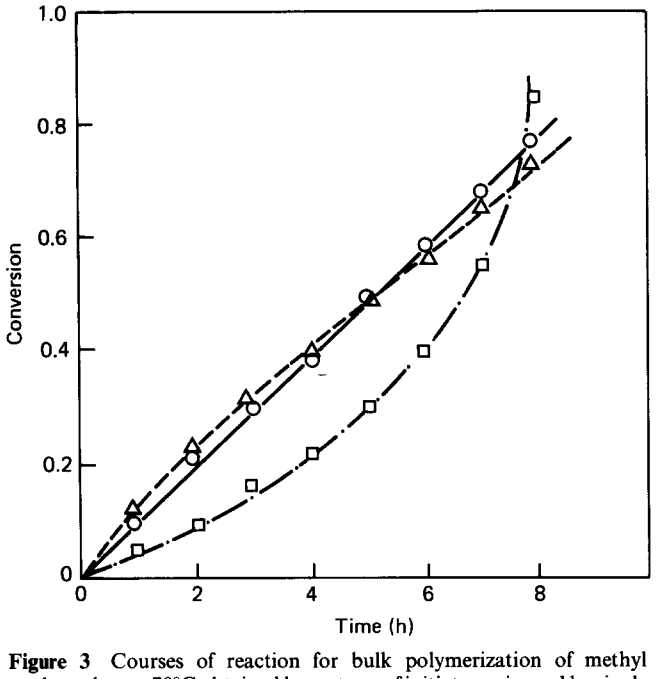

Figure 3 Courses of reaction for bulk polymerization of methyl methacrylate at 70°C obtained by systems of initiator pairs and by single initiators: —○—, 2.00×10^{-4} M 2,2-azobis-2,4-dimethylvaleronitrile and 6.243×10^{-6} M azobisisobutyronitrile; – – –△– – –, 2.06×10^{-4} M 2,2-azobis-2,4-dimethylvaleronitrile; –·–□–·–, 2.06×10^{-4} M azobisisobutyronitrile

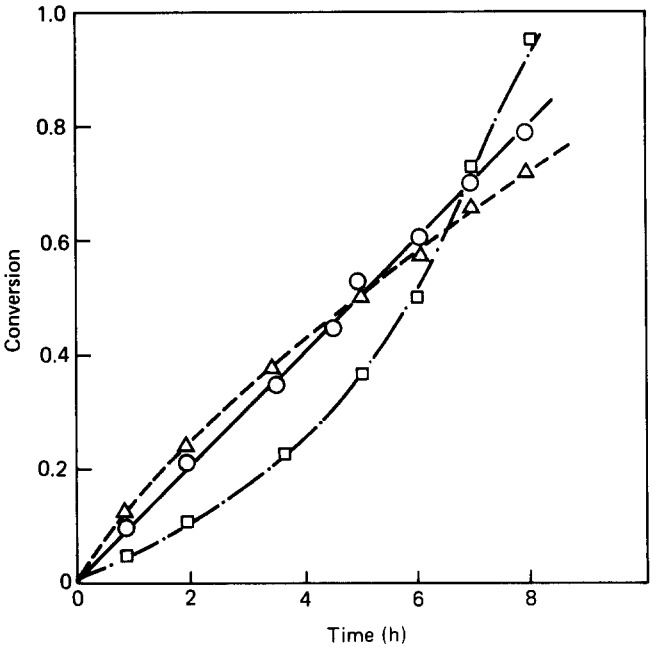

Figure 4 Courses of reaction for bulk polymerization of methyl methacrylate at 75°C obtained by systems of initiator pairs and by single initiators: —○—, 2.031×10^{-4} M t-butyl perpivalate and 1.066×10^{-5} M benzoyl peroxide; – – –△– – –, 2.138×10^{-4} M t-butyl perpivalate; –·–□–·–, 2.138×10^{-4} M benzoyl peroxide

was the same as that used for its initiator pair system) are also calculated. The broken and chain curves in *Figures 3* to *6* show the conversion curves obtained. These curves do not show constant-rate polymerization. It is interesting to see that the initiators of higher dissociation rate constant exhibit a concave-downward conversion curve while those of lower dissociation rate constant show a concave-upward curve. In other words, the latter kind of initiator shows auto-acceleration phenomena. The conversion curves obtained with the given initiator pairs lie between the conversion curves of the two single initiator systems. Thus the initiator pairs determined by the method suggested do induce polymerization of MMA at a prescribed rate.

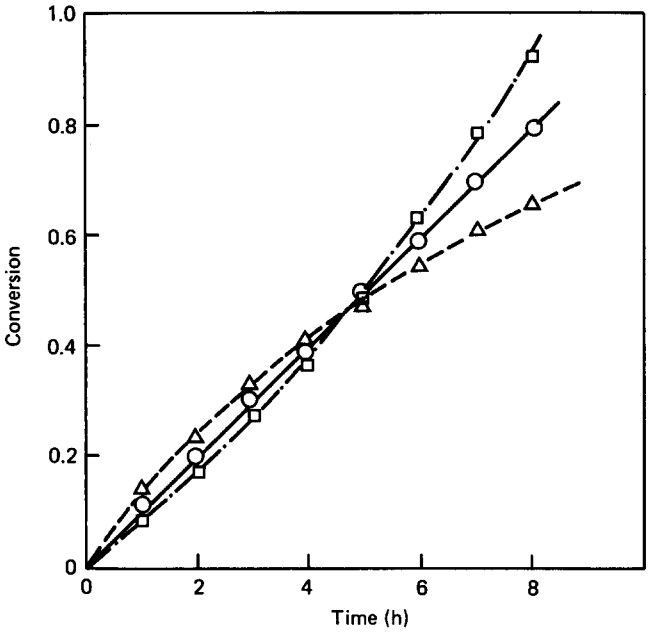

Figure 5 Courses of reaction for bulk polymerization of methyl methacrylate at 80°C obtained by systems of initiator pairs and by single initiators: —○—, 1.006×10^{-4} M decanoyl peroxide and 8.256×10^{-5} M azobisisobutyronitrile; ---△---, 1.83×10^{-4} M decanoyl peroxide; -·-□-·-, 1.83×10^{-4} M azobisisobutyronitrile

Molecular weights and distributions of polymer obtained

The cumulative number- and weight-average molecular weights of the polymers produced have been defined as

$$\bar{M}_n = \frac{\mu_1 + \sigma_1}{\mu_0 + \sigma_0} M_A \sim \frac{\sigma_1}{\sigma_0} M_A = \frac{M_0 m}{\sigma_0} M_A \tag{22}$$

$$\bar{M}_w = \frac{\mu_2 + \sigma_2}{\mu_1 + \sigma_1} M_A \sim \frac{\sigma_2}{\sigma_1} M_A = \frac{\sigma_2}{M_0 m} M_A \tag{23}$$

where M_A denotes the molecular weight of monomer. The polydispersity may be measured by the ratio $\bar{M}_w/\bar{M}_n$.

The zeroth and second moments σ_0 and σ_2 in (22) and (23) may be related to conversion m and prescribed rate C by

$$\frac{d\sigma_0}{dm} = \frac{d\sigma_0}{dt}\frac{dt}{dm} = \frac{1}{C}\frac{d\sigma_0}{dt}$$

giving

$$\sigma_0 = \frac{1}{C}\int_0^m \frac{d\sigma_0}{dt} dm \tag{24}$$

and by

$$\frac{d\sigma_2}{dm} = \frac{d\sigma_2}{dt}\frac{dt}{dm} = \frac{1}{C}\frac{d\sigma_2}{dt}$$

giving

$$\sigma_2 = \frac{1}{C}\int_0^m \frac{d\sigma_2}{dt} dm \tag{25}$$

Substituting (14) into (24) and (15) into (25) and further combining (17) leads to

$$\sigma_0 = \frac{(2-\beta)}{2}\frac{Ck_{t0}}{k_p^2}\int_0^m \frac{g^2(m,T)}{(1-m)^2} dm \tag{26}$$

$$\sigma_2 = (1+\beta)\frac{Ck_{t0}}{k_p^2}\int_0^m \frac{g^2(m,T)}{(1-m)^2} + (3+2\beta)M_0 m + (2+\beta)\frac{k_p^2 M_0^2}{Ck_{t0}}\int_0^m \frac{(1-m)^2}{g^2(m,T)} dm \tag{27}$$

If the long-chain approximation is assumed, the first term of the right-hand side of (27) may be neglected, and the equation becomes

$$\sigma_2 = (3+2\beta)M_0 m + (2+\beta)\frac{k_p^2 M_0^2}{Ck_{t0}}\int_0^m \frac{(1-m)^2}{g^2(m,T)} dm \tag{28}$$

Utilizing (26) and (28) or (27), we obtain the number- and weight-average molecular weights and polydispersity index of polymer obtained by the multiple initiator method, and these are given in *Tables 4* and *5*.

EXPERIMENTAL

Methods and materials

Commercially available methyl methacrylate monomer was purified by the conventional method. The fractions of 39.8–40.5°C at 81 mmHg vacuum were collected for use. The initiators, azobisisobutyronitrile, azobis-2,4-dimethylvaleronitrile, decanoyl peroxide, and t-butyl perpivalate, were recrystallized in absolute alcohol three times.

Purified MMA monomer was purged with nitrogen to remove the dissolved oxygen before use. The prescribed

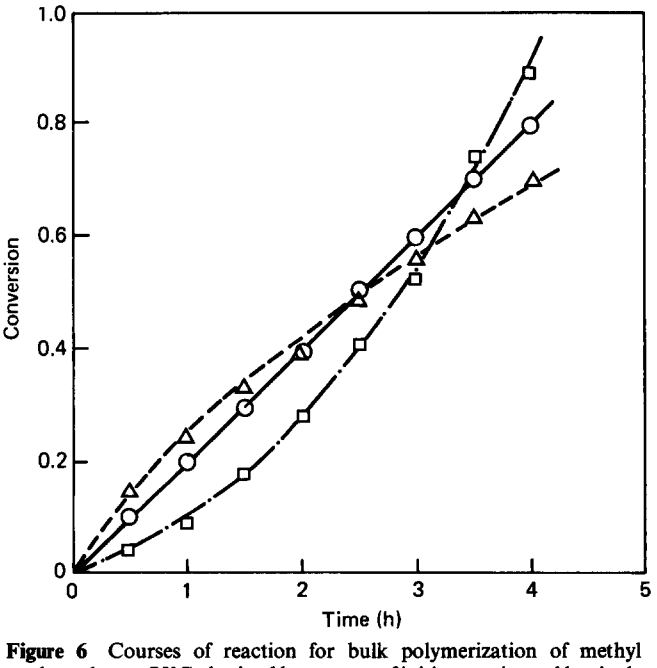

Figure 6 Courses of reaction for bulk polymerization of methyl methacrylate at 75°C obtained by systems of initiator pairs and by single initiators: —○—, 3.776×10^{-4} M 2,2-azobis-2,4-dimethylvaleronitrile and 1.502×10^{-5} M azobisisobutyronitrile; ---△---, 3.926×10^{-4} M 2,2-azobis-2,4-dimethylvaleronitrile; -·-□-·-, 3.926×10^{-4} M azobisisobutyronitrile

Table 4 Molecular weights and polydispersity obtained by the multiple initiator technique for the polymerizations of methyl methacrylate of 0.1 h^{-1} rate at 70, 75 and 80°C

(a) Temperature 70°C

Conversion (%)	$\bar{M}_n \times 10^{-6}$		$\bar{M}_w \times 10^{-7}$		Polydispersity	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
10	0.82	0.85	0.17	0.18	2.05	2.10
20	1.05	1.05	0.23	0.24	2.23	2.28
30	1.32	1.42	0.35	0.39	2.64	2.71
40	1.64	1.57	0.56	0.55	3.43	3.50
50	1.98	2.09	0.97	1.00	4.88	4.81
60	3.34	2.46	1.74	1.62	7.41	6.59

(b) Temperature 75°C

Conversion (%)	$\bar{M}_n \times 10^{-6}$		$\bar{M}_w \times 10^{-7}$		Polydispersity	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
10	0.96	0.98	0.19	0.20	2.03	2.04
20	1.19	1.10	0.26	0.24	2.16	2.20
30	1.47	1.42	0.36	0.37	2.46	2.60
40	1.79	1.72	0.55	0.56	3.06	3.24
50	2.15	2.07	0.89	0.84	4.17	4.07
60	2.53	2.71	1.55	1.69	6.11	6.24

(c) Temperature 80°C

Conversion (%)	$\bar{M}_n \times 10^{-6}$		$\bar{M}_w \times 10^{-7}$		Polydispersity	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
10	1.12	1.20	0.23	0.25	2.02	2.08
20	1.33	1.39	0.28	0.35	2.10	2.55
30	1.61	1.71	0.37	0.41	2.32	2.40
40	1.93	1.89	0.53	0.53	2.77	2.81
50	2.30	2.24	0.83	0.86	3.61	3.82
60	2.69	2.52	1.37	1.29	5.10	5.13

Table 5 Molecular weights and polydispersity obtained by the multiple initiator technique for the polymerizations of methyl methacrylate of 0.2 h^{-1} rate at 75°C

Conversion (%)	$\bar{M}_n \times 10^{-7}$		$\bar{M}_w \times 10^{-7}$		Polydispersity	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
10	0.46	0.48	0.94	0.96	2.03	2.00
20	0.57	0.55	1.23	1.25	2.16	2.27
30	0.71	0.70	1.67	1.68	2.35	2.40
40	0.87	0.90	2.49	2.40	2.86	2.67
50	1.05	1.07	4.03	4.01	3.85	3.75
60	1.24	1.25	6.92	7.01	5.60	5.61

amounts of MMA monomer and initiators were filled into a one-litre four-necked Pyrex kettle which had been purged sufficiently with nitrogen. The kettle was equipped into a well thermostated water bath. The temperature was controlled at the desired temperature 70, 75 or 80±0.5°C). Three samples of 20 ml each were taken at a suitable time period for determinations of monomer conversion and molecular weights. The average value of them was reported. The monomer conversion was determined gravimetrically.

The average molecular weights of polymers obtained were measured by a gel permeation chromatograph (Waters Associates HPLC/GPC model). A train of five μ-styragel packed columns of 10^6, 10^5, 10^4, 10^3 and 500 Å were used. Tetrahydrofuran was used as solvent and at a flow rate of 0.8 ml min^{-1}.

The universal calibration principle suggested by Benoit and coworkers[20] was used for determining molecular weights, that is

$$\{[\eta]M\}_{ui} = \{[\eta]M\}_{si}$$

or

$$k_u M_{ui}^{a_u+1} = k_s M_{si}^{a_s+1}$$

for an elution volume i, where M_{ui} and M_{si} denote molecular weights of polymer sample and polymer standard, respectively. Here k_u and a_u are the Mark–Houwink constants of the unknown polymer sample, and k_s and a_s those of the polymer standard. In this work, the polymer standard is polystyrene (PSt) which was purchased from Waters Associates. The Mark–Houwink constants of PSt and PMMA in tetrahydrofuran at 25°C[21,22] are as follows:

PSt	$k_s = 1.60 \times 10^{-4}$	$a_s = 0.706$
PMMA	$k_u = 1.28 \times 10^{-4}$	$a_u = 0.690$

Results

By utilizing the initiator pairs and concentrations given in *Tables 2* and *3*, polymerizations for the rate of 0.1 h^{-1} at 70, 75 and 80°C and for the rate of 0.2 h^{-1} at 75°C were studied. The results are shown in *Figure 3* to *6*. As can obviously be seen, all the experimental points lie well on the predicted conversion–time curves. This indicates that the bulk polymerization induced by the given initiator pairs can take place at the prescribed rate.

Tables 4 and *5* also give the molecular weights $\bar{M}_n$ and $\bar{M}_w$ obtained experimentally. The agreement between experiment and the predictions are pretty good. It can also be observed that the molecular weights and dispersity obtained by these initiator pair systems are quite appropriate: below 40% conversion, the polydispersity is about 2, whereas when the conversion becomes larger than 40%, the polydispersity gets larger. The broader molecular weight distribution of polymers obtained at high conversion may be attributed to the nature of diffusion-controlled polymerization rather than to the multiple initiators used.

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