

On the Gel Effect in the Presence of a Chain Transfer Agent in Methyl Methacrylate Polymerization and Its Copolymerization with Various Acrylates

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SYNOPSIS

The kinetics of methyl methacrylate (MMA) polymerization, and of its copolymerization with various acrylates, at high conversions in the presence of a chain transfer agent, are investigated with a dilatometer over the entire course of reaction. The displacement to higher conversions of the onset of the gel effect in the MMA homopolymerization, in the presence of a chain transfer agent, was determined. Similar information is also provided for the MMA-acrylate copolymerization systems. An increase in polymerization temperature slightly delays the onset of the gel effect in the MMA-acrylate copolymerization, but considerably increases the final conversion. The final conversion in copolymerization for a constant concentration of the chain transfer agent is independent of the initiator concentration, but is a function of the polymerization temperature. The reaction time for reaching the limiting conversion in copolymerization is increased with an increasing amount of the second monomer, as well as with an increasing number of carbon atoms in the acrylate used as the second monomer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Both the methyl methacrylate (MMA) homopolymer and its copolymers, with any of the acrylates, have good optical transmittancy and mechanical properties and are, therefore, used as optical materials.¹ The copolymerization of methyl methacrylate with any of the acrylates can improve the properties of these materials, such as flexibility and heat resistance. The polymerization evolution, particularly at high conversions, affects the transparency and other properties of the polymerization product.² While the kinetics of homopolymerization were already investigated,³⁻²⁸ the copolymerization kinetics of methyl methacrylate with various acrylates, at high conversions and in the presence of chain transfer agents, appears not to have been investigated. The goal of the research presented in this article is to perform such experiments. The emphasis of the article is on the gel effect and the crit-

ical conversion at which the gel effect starts, as well as on the final conversion.

The polymerization of MMA, initiated by benzoyl peroxide, was studied by Schulz and Trommsdorff^{30,31} for high conversions; these authors confirmed and extended earlier results obtained by Norrish and Brookman.³² The surprising feature of this reaction is the rapid increase in the rate after about 15% conversion up to a maximum value at 70% conversion, followed by a decrease in the polymerization rate. Depending upon the experimental conditions, polymerization can, in fact, cease before the complete conversion of the monomer. The rapid increase in rate is accompanied by a parallel, though not as marked, increase in molecular weight.³³ This is called the gel effect because it can be related to the formation of a fluctuating network of macromolecules (polymer entanglements). These entanglements increase the viscosity of the system and cause considerable retardation of the macro radicals mutual diffusion, resulting in a decreased termination rate.^{7-9,20,21} A similar mechanism was proposed by Lachinov et al.^{34,35} on the basis of light-scattering studies of the structures generated during the MMA

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radical polymerization. The onset of the gel effect, in the case of the polymerization of methyl methacrylate, was correlated with the extent of polymer entanglement in the reaction medium in Refs. 13 and 26. Li et al.²⁷ studied the bulk polymerization of MMA over the complete course of reaction by employing a dilatometer and differential scanning calorimetry (DSC). They attempted to quantitatively relate the onset of the gel effect and the final conversion to the polymerization conditions, such as temperature, nature, and concentration of the initiator.

EXPERIMENTAL

Reagents

Methyl methacrylate (MMA, 99%, Aldrich), methyl acrylate (MA, 99%, Aldrich), ethyl acrylate (EA, 99%, Aldrich), and butyl acrylate (BA, 99%, Aldrich) were distilled to remove the inhibitor. The initiator Azobisisobutyronitrile (AIBN, Alfa) was recrystallized from methanol. *N*-butyl mercaptan (BuSH, > 97%, Fluka) was employed as a chain transfer agent. The solvents acetone (99.5%, Aldrich) and methanol (99.9%, Aldrich) were used as received.

The amounts of the components employed in the polymerization systems are listed in Table I.

Experimental Equipment and Procedure

The polymerization of methyl methacrylate and its copolymerization with various acrylates was carried out in a dilatometer. The sketch of the dilatometer is given in Figure 1. The monomer, or the mixture of monomers, containing the initiator and the chain transfer agent was placed in a dilatometer immersed in a constant temperature water bath. Prior to polymerization, the oxygen was removed from the reaction system by bubbling with nitrogen for 20 min. The polymerization was carried out at 80°C. The polymerization evolution was followed by recording the drop in the liquid level in the glass capillary of the dilatometer. The following equation^{27,29} was employed to calculate the percent conversion X

$$X\% = \frac{H_0 - H_t}{H_0 - H_f} \times X_f, \quad (1)$$

where H_0 is the initial liquid level height of the polymerization system at thermal equilibrium, H_f is the final liquid level height, H_t is the liquid level height at time t , and X_f is the final percent conversion of the polymerization system.

When the dilatometer is immersed in a constant temperature water bath, the liquid level height is affected by both the thermal expansion of the monomers and the volume contraction caused by polymerization. Because the temperature of the

Table I Amounts of Components Used in the Polymerization Systems

Polymerization System	MMA (mL)	Second Monomer ^a (Mol Ratio × 100)	AIBN ^b	BuSH ^c (μL)	
I MMA	50	—	0.025	200	
	50	—	0.050	200	
	50	—	0.075	200	
	50	—	0.100	200	
II MMA—MA	50	15	0.075	225.3	
	MMA—EA	50	15	0.075	230.4
	MMA—BA	50	15	0.075	240.2
III MMA—MA	50	5	0.075	208.4	
	50	10	0.075	216.8	
	50	15	0.075	225.3	
	50	20	0.075	233.7	
	50	25	0.075	242.1	

^a Mole ratio of the second monomer with respect to MMA × 100.

^b Mole ratio of AIBN with respect to both MMA and the second monomer × 100.

^c The amounts of the chain transfer agent BuSH are 0.4 V% of the monomers.

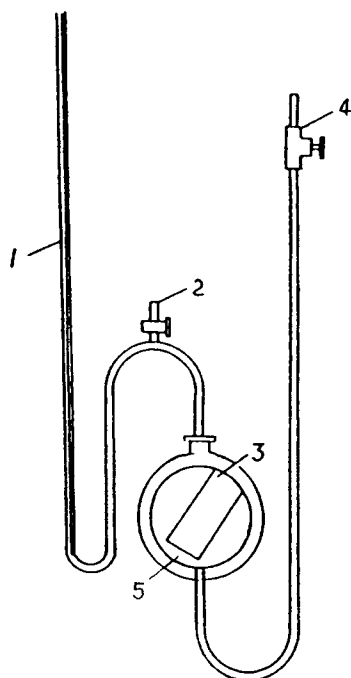


Figure 1 Sketch of the dilatometer. (1) Glass capillary, (2) exhaust valve, (3) polyester reaction bag, (4) needle-shaped valve, and (5) water.

monomers and dilatometer is 25°C and some time is needed for them to acquire the polymerization temperature of 80°C, the initial liquid level height was determined by introducing monomers that contain an inhibitor. About 20 min were needed to achieve thermal equilibrium. The obtained polymer was dissolved in acetone and was finally precipitated with methanol. The final conversion was calculated after the polymer was dried in vacuum for about 5 h.

RESULTS AND DISCUSSION

The conversions for the systems I, II, and III of Table I, as a function of time, are presented in Figures 2–4, respectively. The curves conversion vs. time exhibit an *S*-shape. The polymerization rate is slow in the initial stage of reaction, to which the conventional stationary state kinetics are applicable, but the rate accelerates with an increasing extent of polymerization.⁴ This auto-acceleration was attributed to the increase in the viscosity of the reaction medium as the polymer is formed, and to its effect on the termination rate constant k_t . The chain termination involves the rate of collision between two active chain molecules at the growing ends of the chains, which is retarded by the increased viscosity.

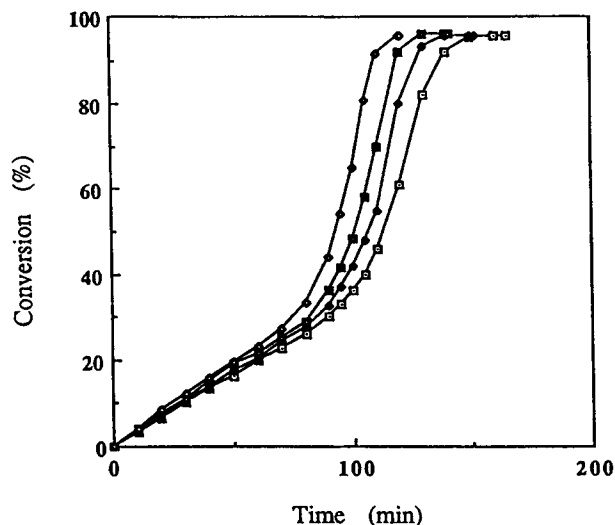


Figure 2 Relationship between percent conversion and reaction time in MMA homopolymerization for 0.4 V% (of the volume of the monomer) of BuSH chain transfer agent, and various concentrations of AIBN at 80°C. (◆) AIBN, 0.10 mol % of the monomers, (■) AIBN, 0.075 mol % of the monomers, (●) AIBN, 0.05 mol % of the monomers, (□) AIBN, 0.025 mol % of the monomers.

However, the chain continues to grow, because the monomer still retains sufficient mobility. The overall result is an acceleration in rate and an increase in molecular weight. The sharp fall-off of the rate in

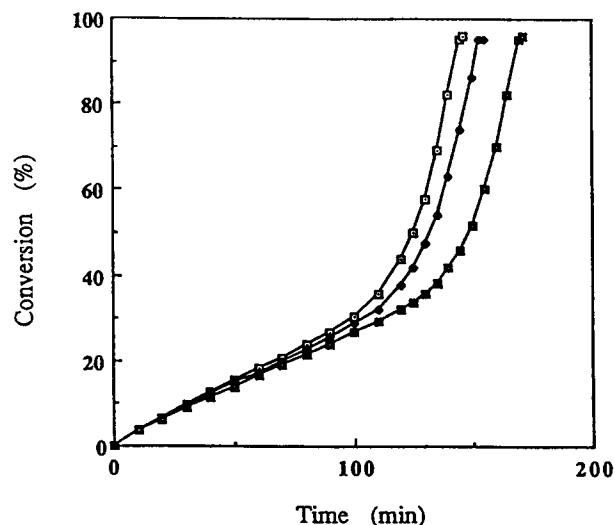


Figure 3 Relationship between percent conversion and reaction time in the copolymerization of MMA with various acrylates (100 : 15 mol ratio). (AIBN) 0.075 mol % of the monomers, (BuSH) 0.4 V% of the volume of the monomers, 80°C. (□) MMA—MA, (◆) MMA—EA, and (■) MMA—BA.

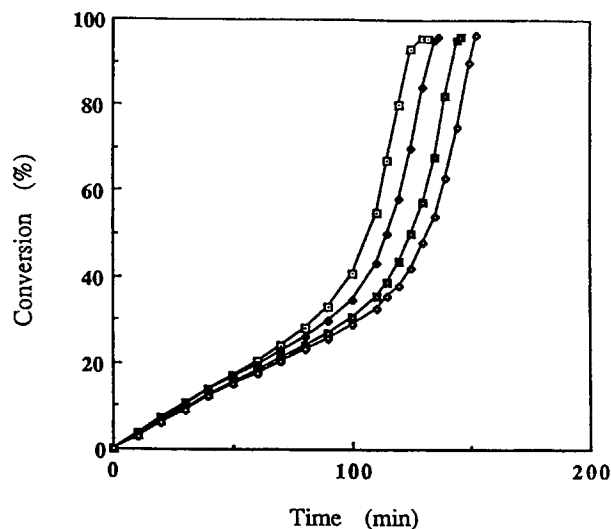


Figure 4 Relationship between percent conversion and reaction time in the copolymerization of MMA for various concentrations of MA at 80°C. (AIBN) 0.075 mol % of the monomers, (BuSH) 0.4 V% of the volume of the monomers. (□) MMA : MA = 100 : 5 mol ratio, (◆) MMA : MA = 100 : 10 mol ratio, (■) MMA : MA = 100 : 15 mol ratio, and (◈) MMA : MA = 100 : 20 mol ratio.

the later stages of polymerization is brought about by the immobilization of the growing polymer radicals in a network of polymer molecules. When the polymer network reaches a high degree of entanglement, the active radicals become completely buried, and the monomers no longer have access to them. At sufficiently high conversions, there is a change in the structure of the entangled polymers from a rubbery to a glassy state, in which the diffusion of the monomers is greatly hindered and the polymerization is almost stopped. The existence of radicals, trapped in the polymerization system after the final conversion was achieved, was confirmed by Burnett and Duncan,⁴ and a quantitative estimation of the trapped radicals in such systems was made by Bresler et al.,³⁷ on the basis of electron-spin resonance investigations.

Effect of the Chain Transfer Agent on the Onset of the Gel Effect in MMA Homopolymerization

The gel effect results in the accumulation of macro radicals in the system because the high viscosity decreases the probability of collisions between them. The overall rate of polymerization increases because of the decrease in the termination rate, combined with the continuous addition of monomers to the macro radicals. Burnett and Duncan⁴ proposed the following equation for the rate of conversion

$$[(R_x/R_0) - 1]^{1/2} = K_1^{1/2}(X - X_1), \quad (2)$$

where R_x is the rate at conversion X , R_0 is the initial rate of polymerization, and X_1 is the "threshold" or critical conversion for the onset of the gel effect, which is dependent on the molecular weight of the polymer produced in the earlier stages.^{4,13,23,26} The reaction rate constant, K_1 , is given by the expression

$$K_1 = (1/2)k_1(k_t/R_i)^{1/2},$$

where k_1 is a constant, R_i is the rate of initiation, and k_t is the termination rate constant.

Equation (2) indicates that the plot of $[(R_x/R_0) - 1]^{1/2}$ against X , over the accelerated domain of the reaction, should be linear, with the intercept on the conversion axis equal to X_1 and the slope $K_1^{1/2}$.

Li et al.²⁷ have modified the Burnett and Duncan eq. (2) as follows, to calculate the critical conversion X_1' for the onset of the gel effect:

$$[(R_x/R_0)(1 - X) - 1]^{1/2} = K_1^{1/2}(X - X_1'). \quad (3)$$

The critical conversions for the onset of the gel effect in MMA homopolymerization for a constant concentration of the chain transfer agent (BuSH, 0.4 V% of the volume of the monomers), and for various initiator concentrations, calculated according to eq. (3), are listed in Table II. To discuss the effect of the chain transfer agent on the critical conversion in the MMA homopolymerization, Table III lists the critical conversions in the absence of the chain transfer agent. Comparing the data of Tables II and III, one can observe that, in the absence of the chain transfer agent (BuSH), the critical conversion increases markedly with increasing initiator concentration. The larger the initiator concentration, the higher the critical conversion at which the

Table II Critical Conversion at the Onset of the Gel Effect in the MMA Homopolymerization for a Constant Concentration of the Chain Transfer Agent (BuSH, 0.4 V% of the Monomers) and Various Contents of Initiator at 80°C

Initiator Content $\times 10^4$ (Mol/Mol Monomer)	Critical Conversion X_1' (%)
10	26
7.5	25.4
5	25
2.5	24.2

Table III Critical Conversion at 80°C at the Onset of the Gel Effect in the MMA Homopolymerization for Various Initiator Concentrations Without the Chain Transfer Agent

Initiator Content $\times 10^4$ (Mol/Mol Monomer)	Critical Conversion X'_1 (%)
10	22.6
7.5	20.1
5	18.5
2.5	16.7

gel effect starts, because a higher conversion is needed to achieve a higher molecular weight of the polymer and, hence, a sufficiently high viscosity of the system. In the presence of the chain transfer agent, the effect of the initiator concentration on the molecular weight of the polymer and on the critical conversion is greatly weakened because of the transfer of the active center to the chain transfer agent. As a result, there is only a weak increase of the critical conversion with increasing initiator concentration. The most striking feature of the reaction in the presence of a chain transfer agent is, however, the postponement to higher conversions of the onset of the gel effect. This happens because the molecular weight of the polymer, formed at a given conversion, in the presence of a chain transfer agent, is lower than in its absence.

In parallel experiments, the reaction was stopped at conversions corresponding to the onset of the gel effect, and the polymers were separated from the polymerization system by the dropwise addition with stirring of the system, to a large excess of precipitant (methanol); further, the precipitated polymer was dried in vacuum at 110°C. The viscosity average molecular weights of the polymers were calculated from the intrinsic viscosities $[\eta]$ (in dL/g) at 30°C in benzene, using the following equation³⁶

$$\log \bar{M}_v = (\log [\eta] + 4.28) / 0.76. \quad (4)$$

Table IV The Viscosity Average Molecular Weights of Polymers at the Onset of the Gel Effect for MMA Polymerization with and Without the Chain Transfer Agent at 80°C

Polymerization System	AIBN Concentration Mol Ratio to Monomer	BuSH Concentration V% of the Monomer	Critical Conversion X'_1 (%)	\bar{M}_v
MMA	7.5×10^{-4}	0	20.1	260200
MMA	7.5×10^{-4}	0.4	25.4	256500

The viscosity average molecular weights of the polymers at the critical point are presented in Table IV. The determination of the molecular weight of the polymers at the onset of the gel effect for two polymerization systems, one with and another without the chain transfer agent, indicates that the molecular weight is almost the same at the critical conversion points. This suggests that the molecular weight constitutes an important factor for the critical conversion. Consequently, the critical conversion for the onset of the gel effect can be controlled with the help of a chain transfer agent.

Effect of the Concentration of the Chain Transfer Agent on the Onset of the Gel Effect and on the Final Conversion in Copolymerization

The effect of the chain transfer agent concentration on both the onset of the gel effect and the final conversion in the MMA—MA copolymerization system is presented in Figure 5. The curves of polymerization rate vs. conversion show that the initial rate increases moderately with increasing concentration of the chain transfer agent for a fixed amount of monomer. As expected, the accelerated domain is displaced to higher conversions and the strength of the gel effect decreases with increasing concentration of the chain transfer agent. The gel effect is expected to disappear completely for a large concentration of the chain transfer agent, and complete conversion of the monomer is expected to be attained under such conditions. It is worth noting that both the critical conversion for the onset of the gel effect and the final conversion are higher as the concentration of the chain transfer agent increases (see below an explanation of this fact).

Effect of the Polymerization Temperature on the Onset of the Gel Effect and on the Final Conversion in Copolymerization

A plot of the polymerization rate against percent conversion in MMA—MA (100 : 15 mol ratio) co-

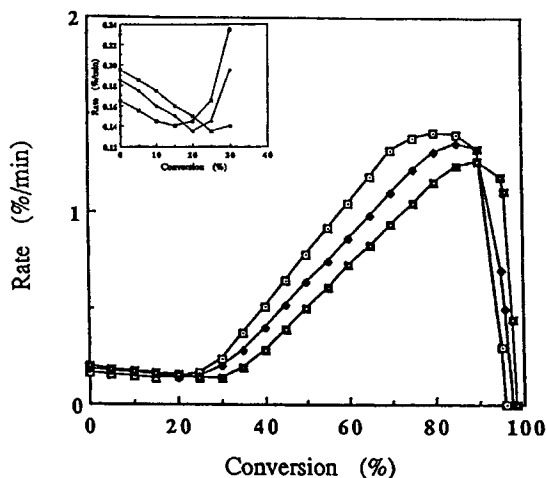


Figure 5 The curves of polymerization rate vs. percent conversion in the MMA—MA (100 : 15 mol ratio) copolymerization for various concentrations of the chain transfer agent (BuSH) and a constant concentration of initiator (AIBN, 0.075 mol % of the monomers) at 80°C. (□) BuSH, 0.4 V% of the volume of the monomers, (◆) BuSH, 2 V% of the volume of the monomers, and (■) BuSH, 4 V% of the volume of the monomers.

polymerization, for a constant concentration of the chain transfer agent and various polymerization temperatures, is presented in Figure 6. This figure shows that over the range of 30–70% conversion, the rate is approximately a linear function of the

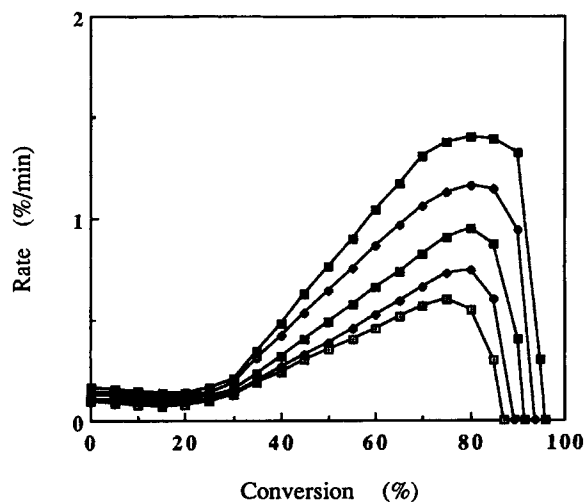


Figure 6 The curves of polymerization rate vs. percent conversion in the MMA—MA (100 : 15 mol ratio) copolymerization for a constant concentration of BuSH (0.4 V% of the volume of the monomers), a constant concentration of initiator (AIBN, 0.075 mol % with respect to the monomers), and various temperatures. (■) 80°C, (◆) 70°C, (●) 60°C, (◇) 50°C, and (□) 40°C. The temperature decreases from the upper to the lower curve.

extent of the reaction. Thereafter, the rate passes through a maximum before falling rapidly to a zero value.

The onset of the gel effect and the sharp fall-off in the polymerization rate are both dependent on the initiation rate and on the reaction temperature. The lower their values, the lower is the critical conversion at which the auto-acceleration begins. An increase in temperature slightly displaces the critical conversion to higher values, but appreciably increases the final conversion. It was, in fact, found that the relationship between the final conversion and temperature is nearly linear¹⁵; the final conversion attained over the temperature range studied for the MMA—MA copolymerization system, for a constant concentration of the chain transfer agent, is given in Table V, and the graph in Figure 7 predicts complete polymerization at around 98°C under the given conditions. The final conversion in the MMA—MA copolymerization for various initiator concentrations and a constant concentration of the chain transfer agent is presented in Table VI. Tables V and VI show that the final conversion for a constant concentration of the chain transfer agent is independent of the initiator concentration, but depends on the polymerization temperature.

The effect of the polymerization temperature on the final conversion can be explained on the basis of the glass transition temperature (T_g) of the system.³⁸ The final conversion is at completion only at relatively high temperatures, namely at polymerization temperatures higher than the glass transition temperature of the polymer (or copolymer). At lower polymerization temperatures, the transition to the glassy state occurs before the polymerization is

Table V The Final Conversion in the MMA—MA Copolymerization for Various Temperatures^a

Temperature (°C)	Final Conversion X_f (%) Precipitation Method
40	87.31
45	88.40
50	89.51
55	90.59
60	91.60
65	92.75
70	93.79
75	94.85
80	96.00

^a Initiator concentration $[I] = 0.00075$ mol/mol monomers; MMA—MA = 100 : 15 (mol ratio); chain transfer agent (BuSH) concentration: 0.4 V% of the monomers.

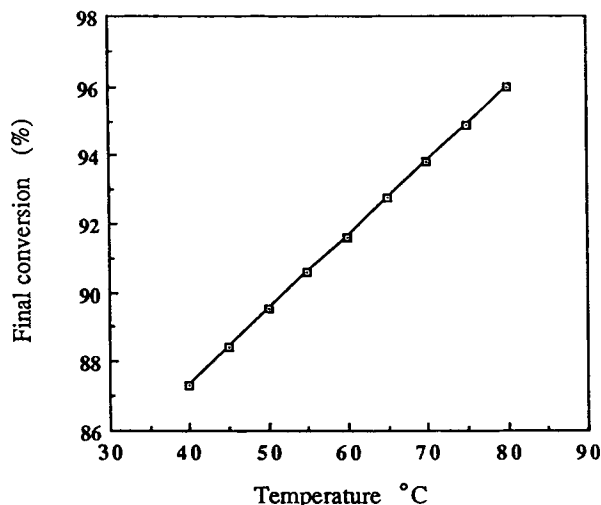


Figure 7 Relationship between the final conversion and temperature for the MMA—MA copolymerization. MMA : MA = 100 : 15 (mol ratio), (AIBN) 0.075 mol % with respect to the monomers, (BuSH) 0.4 V% of the monomers.

completed. In the glassy state, the translational diffusion of the monomer and the segmental diffusion of the polymeric chain ends are almost suppressed, and the rate of polymerization is reduced to zero. As the polymerization temperature increases, the final conversion becomes higher, because the volume fraction of the polymer, at which the glass transition temperature of the system becomes equal to the polymerization temperature, increases. Indeed, following the suggestion of Kelly and Bueche,¹⁶ the glass transition temperature T_g of the copolymer monomers mixture can be evaluated, assuming the additivity of the free volumes of the constituents

$$T_g = \{ \alpha_{cp} \phi_{cp} T_{gcp} + \alpha_{m_1} \phi_{m_1} T_{gm_1} + \alpha_{m_2} \phi_{m_2} T_{gm_2} \} / (\alpha_{cp} \phi_{cp} + \alpha_{m_1} \phi_{m_1} + \alpha_{m_2} \phi_{m_2}) \quad (5)$$

In eq. (5), ϕ_{cp} , ϕ_{m_1} , and ϕ_{m_2} are the volume fractions of the copolymer and of the two monomers, respectively, and α_{cp} , α_{m_1} , and α_{m_2} are the corresponding volume expansion coefficients. It is obvious that $\phi_{cp} + \phi_{m_1} + \phi_{m_2} = 1$. Equation (5) clearly shows that complete conversion, $\phi_{cp} = 1$, can be achieved when the polymerization temperature is higher or at least equal to T_{gcp} .

The effect of the polymerization temperature on the critical conversion for the onset of the gel effect can be explained by the decreased viscosity of the system because of the mild weakening of the entanglement as the temperature is increased. As a result,

the critical conversion is slightly displaced to higher values.

It is worth noting that both the critical and the final conversion are increased as the temperature is increased. Their similar behavior is a result of the fact that both are associated with the entanglements of the polymer chains, a more fluctuating one at the critical conversion and a less fluctuating one in the vicinity of the final conversion.

Table VII lists the final conversions for the three types of polymerizations at 80°C that are listed in Table I, and shows that homopolymerization and copolymerization have almost identical final conversions.

Li et al.²⁷ have studied the homopolymerization of MMA and have concluded that the final conversion is a function of the polymerization temperature, but is independent of the initiator concentration. The relationship between the final conversion and temperature proposed by them has the form:

$$X_f \% = 0.225 T (^\circ\text{C}) + 78.25 \quad (6)$$

For $T = 80^\circ\text{C}$, $X_f \% = 96.25$, which is near the values listed in Table VII. This further confirms that both homopolymerization and copolymerization provide similar final conversions.

Effect of Various Acrylates as the Second Monomer on the Gel Effect

The plot of the polymerization rate vs. percent conversion for the copolymerization of MMA and various acrylates as the second monomer (MA, EA, or BA, 100 : 15 mol ratio) for a given concentration of initiator (AIBN, 0.075 mol % of the monomers) and a constant concentration of chain transfer agent (BuSH, 0.4 V% of the monomers), at 80°C, is pre-

Table VI The Final Conversion in the MMA—MA Copolymerization for Various Initiator Concentrations^a

Initiator Content $\times 10^4$ (Mol/Mol Monomer)	Final Conversion X_f (%) Precipitation Method
10	95.6
7.5	96.0
5	95.9
2.5	96.2

^a Polymerization temperature: 80°C; MMA—MA = 100 : 15 (mol ratio); chain transfer agent (BuSH) concentration: 0.4 V% of the monomers.

Table VII The Final Conversions in Various Types of Polymerization at 80°C Listed in Table 1

Polymerization Systems	Initiator Concentration $\times 10^4$ Mol/Mol Monomer	Second Monomer Ratio Mol/Mol MMA $\times 100$	Final Conversion X_f (%)
MMA	2.5	—	94.45
	5	—	95.59
	7.5	—	95.99
	10	—	95.67
MMA—MA	7.5	15	96.00
MMA—EA	7.5	15	95.32
MMA—BA	7.5	15	95.79
MMA—MA	7.5	5	95.73
	7.5	10	96.05
	7.5	15	96.00
	7.5	20	96.26
	7.5	25	96.18

sented in Figure 8. From Figures 3 and 8, it is evident that the accelerated domain is slightly displaced to higher conversions and that the reaction time for reaching the final conversion becomes larger with an increasing number of carbon atoms in the second monomer. The final conversions for the copolymerization with various acrylates are almost identical.

The effect of the various acrylates as the second monomer on the final conversion can be explained

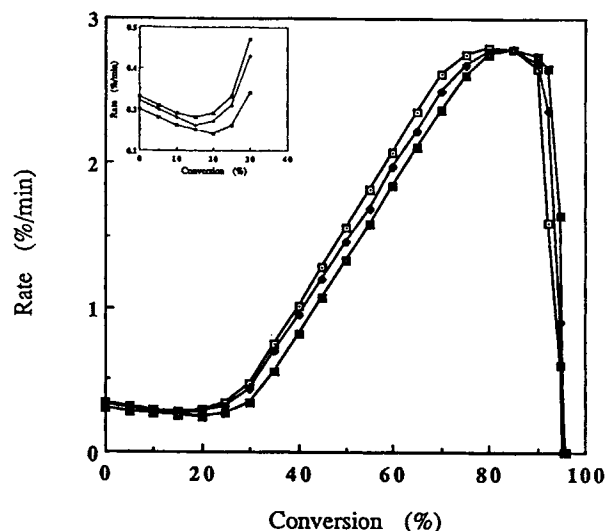


Figure 8 The curves of polymerization rate vs. percent conversion in the copolymerization of MMA with various acrylates (100 : 15 mol ratio). (AIBN) 0.075 mol % with respect to the monomers; (BuSH) 0.4 V% of the monomers, 80°C. (\square) MMA—MA, (\blacklozenge) MMA—EA, and (\blacksquare) MMA—BA.

by comparing the polymerization temperature with the glass transition temperature. The polymers of various acrylates have lower glass transition temperatures than polymethyl methacrylate (PMMA). The glass transition temperature of PMMA is 114°C,¹¹ of polymethyl acrylate (PMA) is about 0°C³⁹ or 10°C,⁴⁰ and those of polyethyl acrylate (PEA) and polybutyl acrylate (PBA) are -24°C and -54°C, respectively.⁴⁰ One can therefore conclude that the copolymers of methyl methacrylate, with any one of the above acrylates, will have lower glass transition temperatures than polymethyl methacrylate. The polymerization temperature of 80°C, employed in the present experiments, is greater than the glass transition temperatures of the polymers of various acrylates. As a result, for the present copolymerization systems, the propagation reaction will be less seriously affected as compared to methyl methacrylate, and the final conversion will be higher. The slight displacement of the acceleration domain to higher conversions, with increasing size of the alkyl group, may be explained by the higher plasticizing effect of the longer side chains. Their presence increases the free volume associated with the polymer molecules and this increases their mobility. A higher conversion is needed before their mobility is reduced.

Effect of the MA Concentration on the Gel Effect

Figures 4 and 9 present, respectively, the relationship between the percent conversion and reaction time and the polymerization rate vs. percent con-

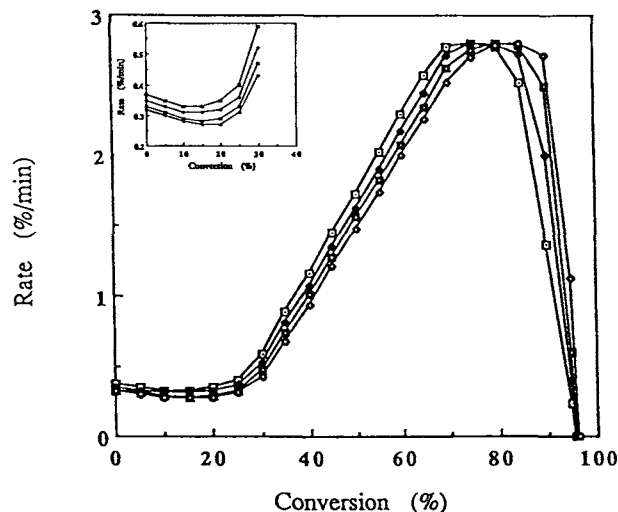


Figure 9 The curves of polymerization rate vs. percent conversion in the copolymerization system of MMA for various concentrations of MA at 80°C. (AIBN) 0.075 mol % with respect to the monomers; (BuSH) 0.4 V% of the monomers. (□) MMA : MA = 100 : 5 mol ratio, (◇) MMA : MA = 100 : 10 mol ratio, (■) MMA : MA = 100 : 15 mol ratio, and (◆) MMA : MA = 100 : 20 mol ratio.

version for MMA—MA copolymerization for various MA concentrations. They show that with increasing MA concentration, the onset of the gel effect is displaced to higher conversions and the reaction time for reaching the final conversion is increased. The values of the final conversions for various concentrations of MA are almost identical. The copolymerization of methyl methacrylate with methyl acrylate decreases the glass transition temperature of the copolymer as compared to polymethyl methacrylate, because the glass transition temperature of polymethyl acrylate is about 0°C, while that of polymethyl methacrylate is about 114°C. The higher the methyl acrylate concentration in the copolymerization system, the lower will be the glass transition temperature of the copolymer. For the same polymerization temperature of 80°C, the lower the glass transition temperature, the higher will be the final conversion and the longer the reaction time for reaching the final conversion. This happens because the transition of the polymer monomer system to a glassy state is displaced to higher conversions. The fact that the final conversions are the same for the four cases considered is perhaps due to the relatively small amounts of methyl acrylate. The acceleration domain is displaced to higher values because of the higher mobility of the copolymer molecules, due to the greater free volume available to them.

CONCLUSIONS

The critical conversions at which the gel effect sets up have been determined experimentally for the methyl methacrylate polymerization and its copolymerization with various acrylates at high conversions in the presence of a chain transfer agent.

1. The main characteristics of the MMA—MA copolymerization for various concentrations of the chain transfer agent are the marked displacement of the acceleration domain to higher conversions and the decrease of the gel effect with increasing concentrations of the chain transfer agent.
2. The increase in polymerization temperature slightly delays the onset of the gel effect in the MMA—MA copolymerization, but increases appreciably the final conversion. The final conversion in copolymerization, for a constant concentration of the chain transfer agent, is independent upon the initiator concentration, but is a function of temperature.
3. In copolymerization, the acceleration domain is slightly displaced to higher conversions and the reaction time for reaching the final conversion is increased with increasing concentrations of MA as the second monomer, as well as with increasing the number of carbon atoms of the acrylate from MA to BA as the second monomer.

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