

High Conversion Polymerization of Methyl Methacrylate in the Presence of *n*-Dodecylmercaptan

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Synopsis

The kinetics of free-radical homopolymerization of methyl methacrylate in the presence of different amounts of *n*-dodecylmercaptan has been studied at 70°C. The introduction of *n*-dodecylmercaptan in the reaction mixture modifies not only the onset and magnitude of the gel effect but also the limiting conversion with respect to the corresponding parameters for the homopolymerization of pure methyl methacrylate. The results obtained are qualitatively correlated with the current theories on the free radical polymerization at high conversion degrees.

INTRODUCTION

It is well known that the bulk polymerization of methyl methacrylate exhibits a large autoacceleration of the overall rate of polymerization, referred to as the Trommsdorff or gel effect, which is associated with a drastic increase of the molecular weight of the polymer produced.¹

Recently, several kinetic models for the bulk polymerization have been suggested in order to predict both the conversion and the molecular weight averages during the free-radical polymerization.²⁻⁶ It has also been predicted that the onset of the gel effect is a consequence of changes in the nature of the diffusion processes of macroradicals controlling the termination step. Although the exact mechanism is still unknown it becomes clear that the onset of the gel effect must be related to both the concentration and the molecular weight of the polymer obtained in the sense that when the molecular weight is lowered more concentrated solutions are required to cause the onset of the gel effect.

The presence of a chain transfer agent in the reaction medium leads to a decrease in the molecular weight of polymer produced and although at low conversion the chain transfer reaction does not have a significant effect on the overall rate of polymerization, at high conversion the chain transfer reaction affects both the onset of the gel effect and the increase of the polymerization rate in the autoaccelerated region.⁷⁻⁹

Kinetic studies on suspension polymerization of methyl methacrylate in the presence of alkyl mercaptans indicate that the onset of the gel effect is shifted to higher conversions and its magnitude is reduced as the alkyl mercaptan concentration increases.^{10,11} On the other hand, experimental studies^{11,12} are in fairly good agreement with theoretical predictions⁷ which pointed out that when the chain transfer plays a more prominent role, molecular weight distri-

bution is shifted to lower values of molecular weights and a satisfactory control of the molecular weight distribution in the whole conversion range is attained.

Furthermore, at high conversion the reaction mixture becomes so viscous that not only the termination but also the propagation steps are diffusion controlled. Therefore, when bulk polymerization is carried out at temperatures below T_{gp} , the glass transition temperature of the corresponding pure polymer, a limiting conversion occurs, being the residual monomer concentration dependent on the reaction conditions.¹³

The bulk polymerization of methyl methacrylate initiated by 2-2'-azobisisobutyronitrile, at 70°C, in the presence of *n*-dodecylmercaptan, is reported in the present paper and the effect of chain transfer reaction on the onset and magnitude of the autoacceleration as well as the effect on limiting conversion are considered.

EXPERIMENTAL

2-2'-Azobisisobutyronitrile (AIBN) was purified using a method previously described.¹⁴ Methyl methacrylate (MMA) was purified by conventional methods and *n*-dodecylmercaptan (DDM) was used without further purification.

Homopolymerization reactions were conducted at $70 \pm 0.05^\circ\text{C}$ in pyrex glass ampoules sealed under high vacuum ($> 10^{-3}$ mm Hg). AIBN (0.5 wt %) with respect to the weight of monomer and concentrations of DDM ranging between zero and 15.6×10^{-2} mol/L were used as initiator and chain transfer agent, respectively. After the desired time, the reaction was quenched by placing the ampoule in ice. Monomer conversion was measured gravimetrically, by dissolving the reaction mixture in chloroform adding hydroquinone as inhibitor, later precipitating the polymer in a 20-fold excess of methanol. Finally the precipitated material was filtered and dried under vacuum until constant weight was attained.

The intrinsic viscosities were determined at $30 \pm 0.05^\circ\text{C}$ by viscosity measurements on benzene solution. The average molecular weights were determined by using the relationship¹⁵

$$[\eta] = 8.69 \times 10^{-3} \bar{M}^{0.76} \text{ mL/g} \quad (1)$$

RESULTS AND DISCUSSION

The bulk polymerization of MMA in the presence of DDM, has been studied at 70°C. Experimental conversion-time plots and variation of the molecular weight with conversion for the homopolymerization of MMA in the presence and absence of DDM are shown in Figures 1 and 2 respectively. The introduction of DDM in the reaction medium modifies the overall rate of polymerization as well as the molecular weight of polymers, compared with the homopolymerization of MMA in absence of DDM. Similar results have been obtained by Gianetti et al.¹¹ in the nonisothermal suspension polymerization of MMA in the presence of *n*-butyl and *n*-dodecyl mercaptans.

Dionisio et al.¹⁶ proposed that the onset of the gel effect occurred at conversions at which the rate of segmental diffusion of polymer radicals equals the

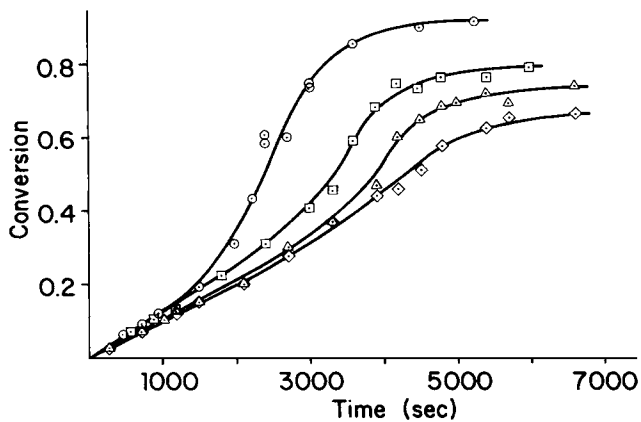


Fig. 1. Conversion-time plots for the free-radical polymerization of MMA with 0.5% AIBN at 70°C in the presence of DDM. $[\text{DDM}] \times 10^{-2}$ mol/L: (○) zero; (□) 5.6; (△) 10.8; (◇) 15.6.

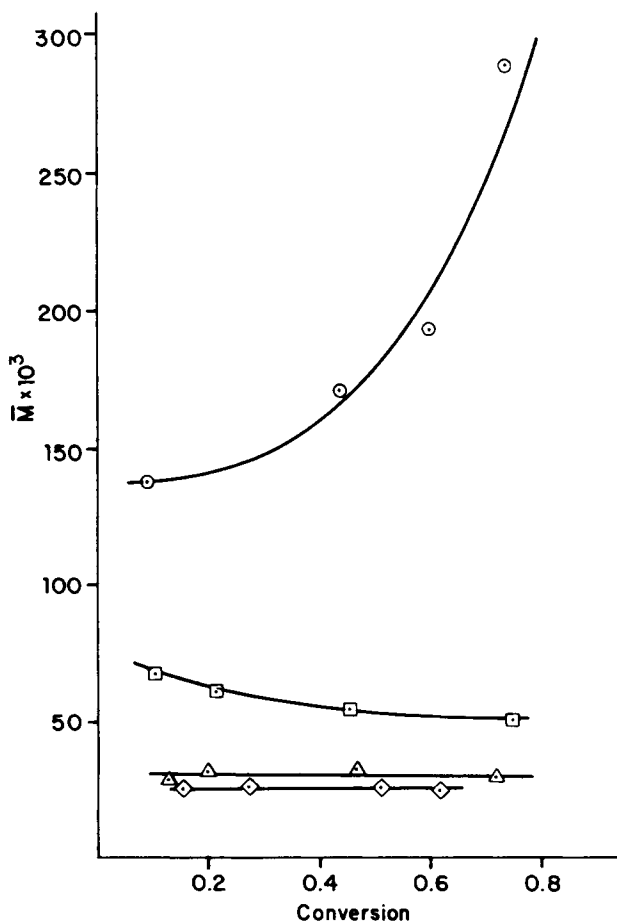


Fig. 2. Plot of molecular weight vs. conversion (see Fig. 1 for key of symbols).

rate of their translational diffusion given rise to a minimum in the polymerization rate. The minimum is correlated with the molecular weight of polymer obtained, since as Dionisio et al.¹⁶ have pointed out, the variation of the net constant of segmental and the net constant of translational diffusion with the conversion, decreases when a lower molecular weight is obtained. Thus the onset of the gel effect is delayed to higher conversion. Figure 3 shows the reduced rate of polymerization ($R_p/[M]$) vs. conversion. When the polymerization of MMA is carried out in the presence of DDM the minimum is shifted to higher conversions as the concentration of chain transfer agent increases in agreement with the Dionisio et al.¹⁶ theory, at least qualitatively. However no correlation exists between the minimum of the reduced rate of polymerization of MMA in absence of DDM compared with the minimum obtained in the presence of a chain transfer agent.

Tulig and Tirrell⁴ have proposed that the termination rate constant is controlled in the early stages, by segmental diffusion with translational diffusion exerting control in the later stages, the termination rate constant being a decreasing function of the concentration. When the concentration of the semidilute regime reaches values above which entanglements occur, the rate constant for the termination step is governed by reptation. However, Tulig and Tirrell¹⁷ have defined a new time scaling procedure which allows presentation of the low conversion kinetic data at different temperatures and initiator concentrations in a single "master curve." They have pointed out that deviation of the superposed dilute solution data, shows the dependence of the critical concentration on the degree of polymerization at which the reptative behavior becomes

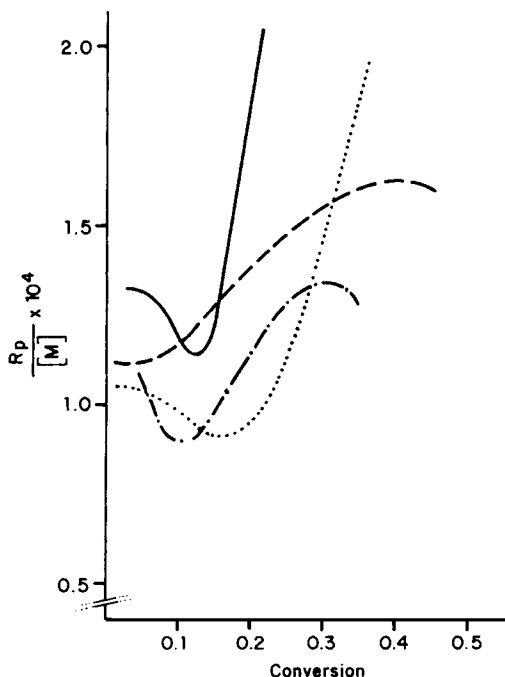


Fig. 3. Plot of reduced rates of polymerization vs. conversion. $[DDM] \times 10^{-2}$ mol/L: (—) zero; (---) 5.6; (- · - ·) 10.8; (· · · ·) 15.6.

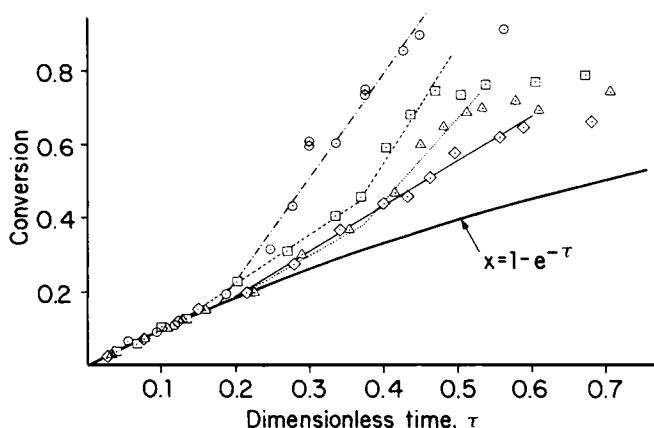


Fig. 4. Plot of conversion vs. Tulig and Tirrell scaled time values (see Fig. 1 for key of symbols).

dominant. The sharpness of the transition from the classical to accelerating kinetic models is more pronounced for the experimental condition that produce the highest molecular weight.

The “master curve” plots for the homopolymerization of MMA in absence and in presence of DDM are shown in Figure 4. The sharpness in the accelerated region has been measured tentatively by the linear-square analysis of experimental points which deviate from superposed dilute solution data. Two trends could be distinguished in the “master curve” plots: For the homopolymerization of MMA in absence of DDM and for the homopolymerization of MMA in the presence of 15.6×10^{-2} mol/L of DDM only one slope is observed in the accelerated region, whereas for the homopolymerization of MMA in the presence of 5.6 and 10.8×10^{-2} mol/L of DDM two slopes could be considered, the first from, approximately, 0.1 to 0.4 fractional conversion and the second from, approximately, 0.4 to 0.7 fractional conversion. Considering that the magnitude of the gel effect may be related with the higher slope, it is clear from Table I that the magnitude of the gel effect is a function of the molecular weight of the polymer produced. However, the trend observed for the homopolymerization of MMA in the presence of 5.6 and 10.8×10^{-2} mol/L of DDM with an initially relatively smooth slope could be related with the minimum of reduced rate of polymerization which appears at conversion lower than that obtained for ho-

TABLE I
Magnitude of the Gel Effect (Sharpness) for the Systems Studied

[DDM] $\times 10^2$ (mol/L)	Range of conversion	Slope	Correlation coefficient
0	0.20–0.90	2.87	0.976
5.6	0.07–0.41	1.25	0.998
5.6	0.41–0.75	2.71	0.990
10.8	0.07–0.37	1.05	0.998
10.8	0.37–0.70	1.96	0.978
15.6	0.10–0.65	1.18	0.997

mopolymerization of MMA in absence of DDM (Fig. 3). Therefore, the presence of DDM in the reaction medium not only influences the molecular weight of the polymer with the consequences that this fact has on the accelerated region, but also it seems that the chain transfer agent has another kind of influence on the free-radical polymerization.

In this sense it is remarkable the relatively low limiting conversion, shown in Figure 1, obtained for the polymerization of MMA in the presence of DDM. A classical interpretation of this fact is connected with the so-called "dead-end polymerization" or with the cessation of the propagation step when the reaction mixture approaches its glass transition temperature.

The decay of initiator concentration was calculated according to

$$[I] = [I_0] \exp(-k_d \times t) \quad (2)$$

where $[I_0]$ is the initial concentration of initiator, t the reaction time and k_d the rate constant for the initiator decomposition. Taking into consideration the k_d values obtained by Tobolsky et al.,¹⁸ the initiator concentration after 110 min of polymerization is higher than the half of the initial concentration so that the relatively low limiting conversion obtained can not be ascribed to "dead-end polymerization."

In order to test if the reaction temperature is the parameter responsible of the relatively low limiting conversion, after 100 and 110 min of polymerization at 70°C, the reaction mixture was quickly raised up to 80°C. This temperature jump, as it is indicated in the Figure 5, produces an increasing of the conversion degree of about 5%. A more quantitative approach of the effect of polymerization temperature on the limiting conversion was reported by Horrie et al.¹³ who suggested that the relation between the final or limiting conversion and temperature may be deduced from eq. (3) derived by Kelley and Bueche,¹⁸ assuming the additivity of the free volume of each constituent

$$T_g = \{ \alpha_p \phi_p T_{gp} + \alpha_m (1 - \phi_p) T_{gm} \} / \{ \alpha_m \phi_p + \alpha_m (1 - \phi_p) \} \quad (3)$$

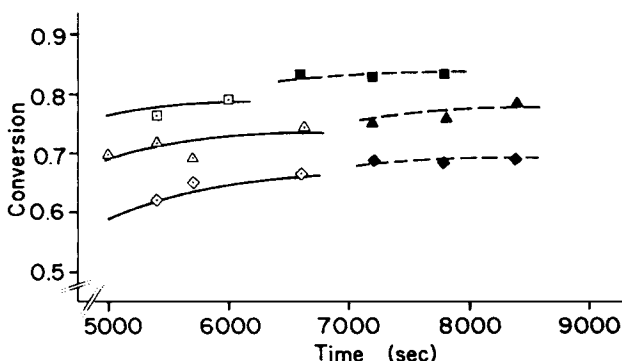


Fig. 5. Time-conversion plot for the isothermal polymerization of MMA at 70°C, followed by a temperature jump to 80°C. Open symbols: 70°C. Closed symbols: 80°C. (see Fig. 1 for key of symbols).

where ϕ is the volume fraction of the system, α the differences between the volume expansion coefficients in the melt and in a glassy state, and subscripts p and m represent polymer and monomer respectively. T_g and T_{gp} are the glass-transition temperature of the polymer–monomer mixtures and the pure polymer, respectively. T_{gp} was obtained considering the molecular weight (M), calculated from the viscosity data of the sample of polymer obtained at 70°C with the highest conversion, from the Fox and Flory²⁰ equation

$$T_{gp} = T_{g\infty} - 2\rho N\theta / (\alpha_p M) \quad (4)$$

where $T_{g\infty}$ is the glass transition temperature of the polymer with infinite molecular weight, ρ is the density of the polymer, N is Avogadro's number and θ is the contribution of the chain end to the free volume.

In this work we have used¹³ the following set of values: $\alpha_m = 10^{-3} K^{-1}$, $\alpha_p = 4.8 \times 10^{-4} K^{-1}$, $T_{gm} = -106^\circ\text{C}$, $T_{g\infty} = 114^\circ\text{C}$, $\rho = 1.1 \text{ g/cm}^3$, and $\theta = 80 \text{ \AA}^3$, and on setting T_g equals to the polymerization temperature we obtained the values quoted in Table II, which indicate that the concentration of chain transfer agent slightly influences the limiting conversion. So that an explanation of the differences in the limiting conversion reached in the presence of different amounts of DDM (Fig. 1), based exclusively on the T_g of the reaction mixture, it is not reliable. On the other hand, experimental evidence shows that in the bulk polymerization of MMA at 80°C the limiting conversion is a moderately strong function of the initiator concentration.²¹ This fact has been explained^{21,22} considering that when the polymer concentration is high, the macroradicals have so reduced mobility that they may be considered truly immobile. In this case ordinary bimolecular reactions can no longer occur, instead, the active end of two propagating chains can move through the space adding monomer, and so come into the same small volume element where they can terminate each other. Thus, at high conversions, rate propagation constant is a function of the free volume fraction of monomer and of the free volume fraction of the polymerizing system. There is also a critical free volume fraction required for migration processes of the monomer. When a free-radical polymerization is conducted in the presence of a strong chain transfer agent, like DDM, and the polymer concentration is so high that macroradicals may be considered immobile, the active end could add monomer or terminate by reaction with the chain transfer agent. At conversion at which the propagation reaction is diffusion controlled, this step could be hindered if the immobilized macroradicals terminate by chain transfer reaction. In this case a lower limiting conversion could be obtained as the chain transfer concentration increases which is in

TABLE II
Glass-Transition Temperature of Polymer–Monomer Systems

[DDM] $\times 10^2$ (mol/L)	$\bar{M} \times 10^{-3}$	T_{gp} ($^\circ\text{C}$)	ϕ_p
5.6	41	108.6	0.919
10.8	30	106.6	0.923
15.6	25	105.2	0.925

fairly good agreement with the experimental results reported in this study. In order to test these assumptions the decay of both monomer and transfer agent with the reaction time are in progress.

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