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Methyl Methacrylate Polymerization at High Conversion. III. Effect of a Chain-Transfer Agent

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ABSTRACT

Bromoform delays the onset of the gel effect of MMA and decreases the acceleration rate in the autoaccelerated region. The first effect can be quantitatively related to the decrease in molecular weight of the produced polymer. The decrease in acceleration shows the dependence of the termination rate constant, in the accelerated region, on the mean size of the growing macroradicals.

The occurrence of a chain transfer reaction decreases the magnitude of the gel effect [1], and Cardenas and O'Driscoll [2] have computed the reaction rate in the autoaccelerated region for different amounts of chain transfer to the monomer. The results obtained show that the chain transfer reaction affects both the onset of the gel effect and the rate increase in the autoaccelerated region. The effect of the chain transfer is then easily rationalized in terms of the sensitivity of the gel effect to the mean size of the polymeric chains [3, 4]. In order to isolate the effect of the chain transfer agent from the change in dead polymer molecular weight that it produces, it is interesting to carry out measurements under conditions such that in the presence and absence of the chain-transfer agent the mean size of the growing radicals, at least to the point where the gel effect appears, are approximately the same. In the present communication we present such data for the bulk polymerization of methyl methacrylate (MMA) at 77° C. The results obtained show that chain-transfer agents do not appreciably alter the conversion at which the gel effect appears, but significantly modify the polymerization rate in the autoaccelerated region.

EXPERIMENTAL

The reaction rates were measured dilatometrically, the experimental set-up being similar to that employed previously [3, 4].

All runs were carried out by employing 1% di-tert-butyl peroxide as initiator. The molecular weight of the polymer produced was modified either by changing the light intensity or by adding bromoform as chain-transfer agent.

The number-average molecular weight of the polymer produced in the thermal reactions was determined viscometrically. A relationship based on osmometric determinations was employed. Since only the relative values of the chain length are relevant to the present work, small differences between $\overline{M}_n$ and $\overline{M}_v$ are not considered to be significant. For the runs initiated photolytically, the mean average molecular weight was obtained from the value of the thermal reaction corrected by the difference in polymerization rate [3].

RESULTS AND DISCUSSION

The effect of bromoform upon the thermal polymerization of bulk MMA initiated by 1% di-tert-butyl peroxide is shown in Fig. 1. The data given in Fig. 1 show that bromoform delays the onset of the gel effect. In order to find if this delay is due completely to the change in molecular weight or due to some specific effect of the chain transfer reaction, these results were related to those obtained in the absence of bromoform but with light added to increase the initiation rate. The relationship between molecular weight and polymer concentration at the critical point (defined as the point where the conversion versus time plot shows a positive second derivative) is shown in Fig. 2. The data of Fig. 2 show that the effect of the bromoform can be completely ascribed to the associated molecular weight change, since the effect is similar to that produced by an equivalent change in initiation rate. This independence of the onset of the gel effect of the process that regulates the molecular weight can be expected when the main termination is macroradical disproportionation. In this case,

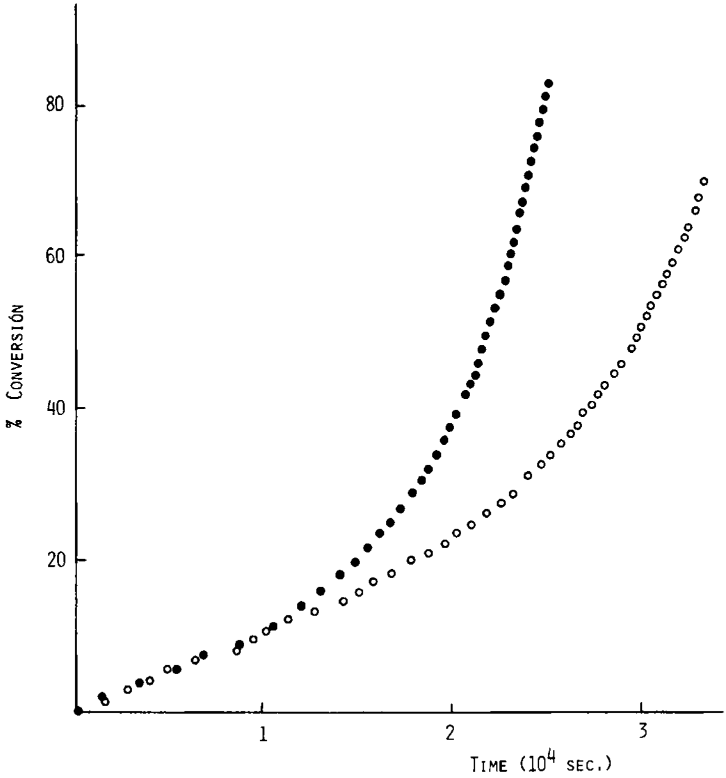

FIG. 1. Effect of bromoform upon the polymerization rate: (●) bulk; (○) 3% bromoform added.

if the change in k_t with macroradical size is disregarded, similar macroradical distributions will be present, irrespective of the chain transfer agent, when the number average molecular weights of the dead polymer are the same.

After the onset of the gel effect, the increase in rate with conversion is mainly due to an increase in the average number of entanglements by macroradical [5], but other factors (i. e., the average time required to disentangle one contact point [6]) can also play a significant role. The polymerization rate will depend then upon the dead polymer concentration (which determines the entanglement density), the average macroradical size (which determines the average number of entanglements by macroradical and the average lifetime of each

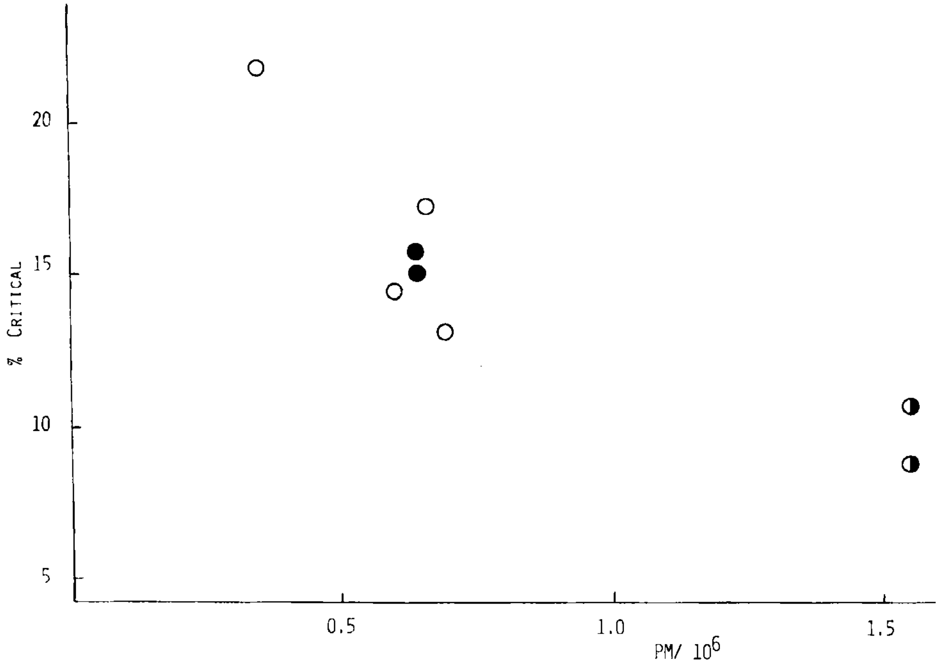

FIG. 2. Dependence of the critical conversion upon the molecular weight of the polymer produced at low conversion: (◑) thermal polymerization; (○) light-induced polymerization; (●) thermal polymerization with added bromoform.

entanglement), and the dead polymer molecular weight (which modifies the disentanglement time). If the chain transfer is small [2, 5, 7, 8], both the size of the average macroradical and the molecular weight of the dead polymer increases when the conversion increases. The value of k_t decreases by the composite effect of an increase in entanglement density, an increase in average number of entanglements by macroradical, and an increase in average lifetime of each contact point. The use of a chain-transfer agent can afford an estimate of the relative importance of these effects. The results obtained for two runs (one with and the other without chain transfer) where chain lengths at zero conversion were approximately 6600 are given in Fig. 3. The chain length (or average size of the terminating macroradicals) is given by

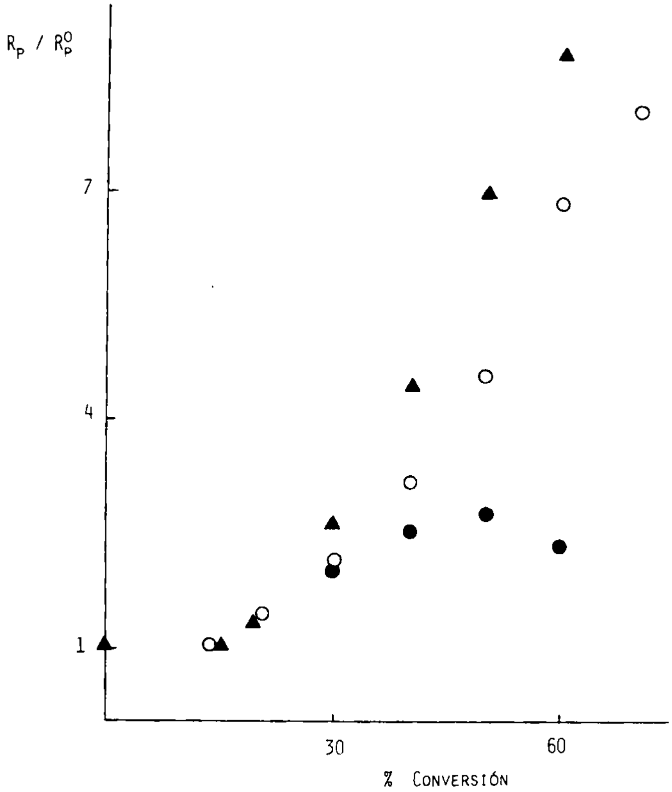

FIG. 3. Dependence of the polymerization rate with the conversion in the accelerated region: (▲) bulk polymerization (photolytically initiated), approximate chain length at low conversion = 6600; (○) polymerization in the presence of bromoform (thermally initiated), approximate chain length at low conversion = 6600; (●) values computed assuming a constant chain length.

$$\frac{1}{\lambda} = \left(\frac{1}{\lambda_t}\right)_0 \frac{(R_p)_0 V_i}{R_p (V_i)_0} + C_T \frac{[T]}{[M]} + C_M \tag{1}$$

where

$$(1/\lambda_t)_0 = (V_i/R_p)_0 \tag{2}$$

$$C_T = k_{tr}/k_p \tag{3}$$

R_p is the polymerization rate, V_i is the initiation rate, [M] is the monomer concentration, [T] is the chain-transfer agent concentration, and C_M is the chain-transfer ratio to the monomer. In these equations the subscript zero indicates initial values.

The value of C_M for methyl methacrylate is small, and a value of 0.27×10^{-4} can be taken at the temperature employed in the present work [9]. The value of $(1/\lambda_t)_0$ can then be obtained from the molecular weight of the polymer produced at low conversion without added T. Determination of the molecular weight in the presence of T gives C_T. A value of 23×10^{-4} was obtained under the conditions employed.

For the present experimental conditions (1% initiator, 3% chain-transfer agent, and $\lambda_0 = 6.6 \times 10^3$), the concentrations of initiator and chain transfer agent can be considered as constant during all the polymerization. If it is assumed [10] that the initiation rate can be expressed by

$$V_i = (V_i)_0 (1 - \phi_p) \tag{4}$$

where ϕ_p is the polymer volume fraction, Eq. (1) allows the estimation of λ as a function of conversion. The results obtained are given in Fig. 4 and show that in the presence of bromoform the chain length slightly decreases when the conversion increases.

Comparison of Figs. 3 and 4 indicates a moderate dependence of R_p in the autoaccelerated region upon the size of the growing macroradicals and, if the values of k_p are assumed to be similar at a given conversion in both runs, provides relative values of the termination rate constant under both conditions as a function of conversion. The values obtained are given in Table 1.

The data of Table 1 show that $(k_t)_{tr}/k_t$ increases when λ/λ_{tr} increases, even when the molecular weight of the dead polymer show only a minor change. Results obtained previously [3] indicate that this change in dead polymer molecular weight cannot account for the observed change in $(k_t)_{tr}/k_t$. The data indicate, then, a clear dependince of k_t upon the mean size of the macroradicals, for a given polymer concentration and dead polymer molecular weight. These results confirmates the preliminary conclusion reached previously [3] regarding the dependence of k_t upon the macroradical size. The dependence of k_t upon λ reflects primarily the larger average number

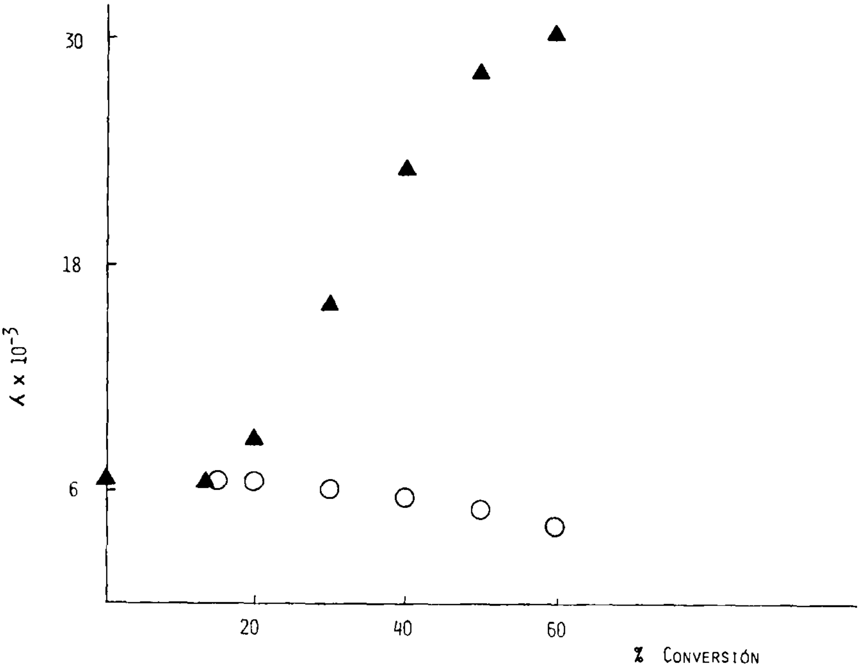

FIG. 4. Computed change in chain length with conversion: (▲) without chain-transfer agent; (○) with bromoform added.

of entanglements by macroradical and the increased lifetime of each entanglement. At a given conversion, the quantitative evaluation of Cardenas and O'Driscoll [5] of the termination rate constant of the entangled radicals k_{te}, leads to

$$(k_{te})_{tr}/k_{te} = (\lambda/\lambda_{tr})^{0.5} \quad (5)$$

The values of $(k_{te})_{tr}/k_{te}$ obtained by employing Eq. (5) have been included in Table 1. The similarity between the experimentally determined value of $(k_t)_{tr}/k_t$ and the evaluated $(k_{te})_{tr}/k_{te}$ values would indicate that most of the termination involves entangled macroradicals. This is a likely conclusion if it is considered [11] that the critical entanglement concentration must be below 15% conversion.

The data obtained in the presence of 3% bromoform can be used

TABLE 1. Experimental Results

Conversion (%)	$(\lambda/\lambda_{tr})^a$	$(PM/PM_{tr})^b$	$(k_t)_{tr}/k_t{}^c$	$[(k_{te})_{tr}/k_{te}]^d$
10	1	1	1.0	1.0
20	1.41	1.1	1.0	1.1
30	2.7	1.4	1.53	1.64
40	3.96	1.85	1.95	2.0
50	5.6	2.4	2.33	2.46
60	7.1	3.0	1.67	2.7

[a] Values obtained from Fig. 4.

[b] P_M is the average molecular weight of the dead polymer accumulated in the solution in the absence of bromoform; PM_{tr} is the value obtained in the presence of bromoform. The PM values were obtained by integration of the data given in Fig. 4.

[c] k_t is the termination rate constant in the absence of bromoform, $(k_t)_{tr}$ is the termination rate constant in the presence of bromoform. The values given were obtained from Fig. 3.

[d] k_{te} is the average termination rate constant of the entangled macroradicals in the absence of bromoform. $(k_{te})_{tr}$ is the value computed in the presence of bromoform. The values given were calculated by using Eq. (5).

to evaluate the influence of the entanglement density over k_t, since both λ and the average molecular weight of the dead polymer show only moderate changes up to 60% conversion. The large increase in R_p observed under these circumstances shows clearly that the entanglement density is the main factor determining the change in k_t and that the increases in λ and PM are only secondary factors.

When 3% bromoform is added to the monomer, chain transfer is the main reaction which determines the average size of the growing macroradicals (60% and 92% of the growing chains terminate by chain transfer for 0 and 50% conversion, respectively). The treatment of Cardenas and O'Driscoll that incorporates the chain transfer reaction [2] allows the evaluation of $R_p/(R_p)_0$ as a function of the polymer concentration. The data obtained employing $K_c = 7.5$ and $\alpha_0 = 0.12$

[5] have been included in Fig. 3. In order to be consistent with the treatment of the data of Cárdenas and O'Driscoll [5] we have assumed that V_i = constant. Even with this assumption, the calculated values underestimate the experimentally determined R_p values. A considerably better fit could be obtained if the rate law is assumed to be proportional to the monomer activity instead of the monomer concentration. Nevertheless, this fitting seems fortuitous since the parameter α_0 employed was obtained by Cárdenas and O'Driscoll from the best fit of experimentally determined data assuming a rate law proportional to the monomer concentration. If the same rate law is considered in the present work, a considerably smaller value of α_0 would be needed to fit our experimental results. The present work qualitatively supports Cárdenas and O'Driscoll's considerations [2, 5], and conclusively shows the dependence of k_t upon the mean macroradical size in the autoaccelerated region, but only a rather poor quantitative fit is obtained between experimental results and predicted values of $R_p/(R_p)_0$ in the autoaccelerated region when chain transfer is dominant in determining the macroradical size.

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