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Effect of 1-n-Dodecanethiol on the Molecular Weight Distribution of Poly(methyl Methacrylate) Synthesized by Suspension Polymerization

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ABSTRACT

Fractionation data of two poly(methyl methacrylate) samples prepared by suspension polymerization up to limiting conversion, in the presence of different amounts of 1-n-dodecanethiol, indicate that both samples have similar polydispersity factors, although the molecular weight distribution curve for the sample obtained with the highest chain transfer agent concentration is shifted to lower molecular weight values. The results obtained are qualitatively correlated with the high conversion polymerization theory proposed by Cardenas and O'Driscoll.

In the last few years bulk polymerization modeling has been proposed in order to predict both conversion and molecular weight averages during the course of free-radical polymerization.

Balke and Hamielic [1] have proposed that the onset of the gel effect in the bulk polymerization of methyl methacrylate occurs at a characteristic free-volume value, and Cardenas and O'Driscoll [2] have introduced the concept of polymer entanglement to describe quantitatively the main factors of bulk polymerization carried out at

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high conversion, but retained some element of the free-volume theory to characterize the onset of the gel effect. Taking into account that the amount of entanglement at determined conversions depends upon the molecular weight of the polymer whereas the free volume is almost independent of it, Abuin and Lissi [3] have shown that the free volume at the onset of the gel effect depends on both the chain length and temperature, and for high molecular weights the conversion at which the gel effect appears can be related to the critical entanglement.

Kinetic studies on suspension polymerization indicate that bead polymerization normally consists of water-cooled bulk polymerization of monomer droplets, and good agreement exists with bulk polymerization in time-conversion curves when initiators and chain transfer agents are soluble exclusively in the monomer phase. On the other hand, rates of polymerization in suspension polymerization are not markedly influenced by the bead size and type of stabilizing agent [4-8].

As Trommsdorff has shown [5], the progress of the bead polymerization of methyl methacrylate is similar to that of a well-cooled bulk polymerization, and the onset of the gel effect depends upon conversion when different amounts of initiator are used. Recently, Dvornic et al. [9] showed that when methyl methacrylate is polymerized in suspension with benzyl peroxide as the free-radical initiator and in the presence of various 1-n-dodecanethiol concentrations, the onset of autoacceleration is shifted to higher conversions and reduces its magnitude as the 1-n-dodecanethiol concentration increases. Although Trommsdorff [5] and Dvornic [9] explain their results on the basis of an increase of viscosity of the reaction mixture, they are in good agreement with the Cardenas and O'Driscoll theory [2, 10], at least qualitatively, since a decrease in molecular weight of polymers requires higher conversion of monomer to polymer in order to attain a critical volume fraction of polymer to growing radical become entangled.

Theoretical predictions on molecular weight averages and distribution have been proved in bulk [2, 11, 12] and in solution [11]; however, no experimental tests have been applied to polymers obtained by suspension polymerization, so this paper deals with the fractionation of two samples of poly(methyl methacrylate) obtained by suspension in the presence of different amounts of a chain transfer agent.

EXPERIMENTAL

Polymerization

A 2-L three-necked glass reactor with stirrer, reflux condenser, and inlet nitrogen tube was used for polymerization. The reactor was heated with a thermostatic water bath regulated with a precision of ± 1°C. The charge into the reactor consisted of a solution of distilled water (600 mL) containing polyacrylic salt and a solution of methyl methacrylate (MMA) (300 mL) and 1.5 g of lauroyl peroxide (LP) as initiator. 1-n-Dodecanethiol (DDT), 1 mL (Polymer A), or 2.5 mL (Polymer B) was used as a chain transfer agent.

In order to be certain the polymerization ceased, the reaction was stopped after 3 h at 70°C and later 1 h at 80°. The beads obtained were washed with water, filtered and dried to constant weight.

Fractionation

A dilute solution (1% w/v) of poly(methyl methacrylate) (PMMA) in purified benzene was placed in a thermostat at 25°C. After thermal equilibrium, n-hexane was added until the solution became permanently turbid, the temperature was raised to 40°C, and kept until the solution became clear. The temperature was then slowly lowered to 25°C, the stirring stopped, and the polymer-rich phase allowed to settle. After settling overnight, the clear supernatant phase was decanted off and the precipitate redissolved in benzene and reprecipitated with an excess of methanol. The last fraction was obtained by the same method after evaporation of the final solution.

All fractions were dried under vacuum to constant weight. Fractionation results are shown in Tables 1 and 2.

Molecular Weight

The intrinsic viscosities of fractions were determined at 30 ± 0.05°C by viscosity measurements of dilute solutions. The average molecular weights were determined by using the relationship

$$[\eta] = 6.27 \times 10^{-3}\overline{M}_n^{\,0.76}$$

for fractions with $[\eta] > 20$ mL/g [13] and

$$[\eta] = 10.4 \times 10^{-2}\overline{M}_n^{\,0.5}$$

for fractions with $[\eta] < 20$ mL/g [13].

The use of the two relationships mentioned is justified since Fox et al. [13] showed that two straight lines intersecting at $\overline{M}_n = 44{,}000$ are obtained in a log-log plot of $[\eta]$ versus $\overline{M}_n$.

RESULTS AND DISCUSSION

The molecular weight distribution of a polymer can be described by analytical funtctions of two or more parameters. Many molecular

TABLE 1. Fractionation Data for Polymer A ([DDT] = 1.39 × 10^{-2} mol/L)

No.	W_i (g)	W_i × 100	C (M)	[η]	M × 10^{-3}
1	0.2418	0.0263	0.9868	73.5	226
2	0.5122	0.0558	0.9458	64.0	188
3	0.4878	0.0531	0.8914	56.2	158
4	0.6132	0.0668	0.8314	48.0	129
5	0.9831	0.1069	0.7446	42.0	108
6	0.6383	0.0695	0.6564	39.0	98
7	0.4982	0.0543	0.5946	38.5	96
8	0.8392	0.0914	0.5216	35.8	88
9	0.6728	0.0733	0.4393	31.5	74
10	0.4449	0.0485	0.3784	29.0	66
11	0.3393	0.0370	0.3356	27.2	61
12	0.3107	0.0338	0.3002	25.7	57
13	0.5411	0.0589	0.2539	23.7	51
14	0.4920	0.0536	0.1976	21.0	41
15	0.4450	0.0485	0.1466	18.0	30
16	0.3822	0.0416	0.1015	17.2	27
17	0.7406	0.0807	0.0434	12.5	14

weight distribution functions have been proposed, one of which is the empirical function introduced by Tung [14].

$$W(M) = yze^{-yM^z}M^{z-1} \tag{1}$$

to fit the molecular distribution data of polymers where y and z are two adjustable parameters which determine molecular weight distribution. Equation (1) can be integrated analytically to the integral distribution form

$$C(M) = \int_0^M W(M)dM = 1 - e^{-yM^z} \tag{2}$$

TABLE 2. Fractionation Data for Polymer B ($[DDT] = 3.48 \times 10^{-2}$ mol/L)

No.	W_i (g)	$W_i \times 100$	C (M)	$[\eta]$	$M \times 10^{-3}$
1	0.0468	0.0095	0.9952	-	-
2	0.3513	0.0716	0.9546	36.0	88
3	0.4018	0.0817	0.8780	29.7	68
4	0.2367	0.0482	0.8130	27.3	61
5	0.2555	0.0520	0.7629	26.1	58
6	0.2257	0.0460	0.7139	25.8	57
7	0.3976	0.0810	0.6504	23.5	50
8	0.2899	0.0590	0.5804	20.5	39
9	0.3136	0.0639	0.5190	20.5	39
10	0.2875	0.0586	0.4577	18.3	31
11	0.3369	0.0686	0.3941	18.0	30
12	0.2268	0.0462	0.3367	16.8	26
13	0.3332	0.0679	0.2797	15.8	23
14	0.1862	0.0379	0.2268	14.6	20
15	0.2606	0.0531	0.1812	13.6	17
16	0.1283	0.0261	0.1416	12.0	13
17	0.1280	0.0261	0.1156	11.4	12
18	0.1083	0.0221	0.0914	11.2	11
19	0.3949	0.0804	0.0402	7.8	6

which is particularly useful for handling experimental fractionation data.

The integral distribution Eq. (2) can be rewritten

$$\ln \frac{1}{1 - C(M)} = yM^z \tag{3}$$

where C(M) is the cumulative fraction calculated from the data of the Schulz summative method [15]. A plot of log log $\frac{1}{1 - C(M)}$ versus log M gives a straight line, and the y and z parameters can

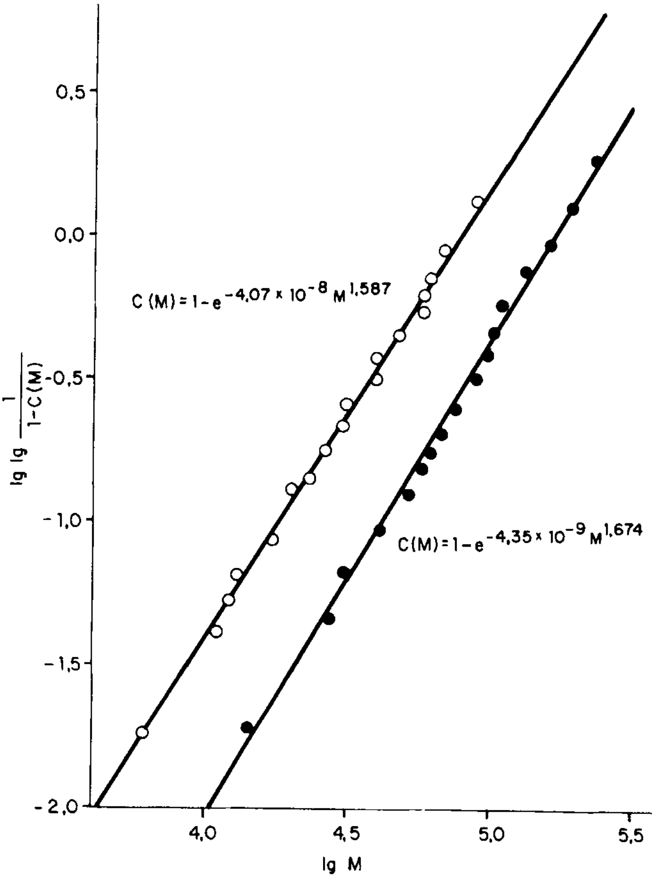

FIG. 1. Double logarithm diagrams of the fractionation data for Polymers A (●) and B (○).

be determined from the slope and intercept. Figure 1 shows such a plot for A and B polymers. The straight lines were adjusted by the least-square method to give correlation coefficients of 0.993 and 0.995, respectively.

Integral and differential distribution curves for Polymer A and Polymer B, calculated from fitted values of y and z, are shown as full lines in Figs. 2 and 3. The open and filled circles in Fig. 2 are the experimental values.

Average degrees of polymerization may be calculated from the y and z parameters by using the following expressions [16]:

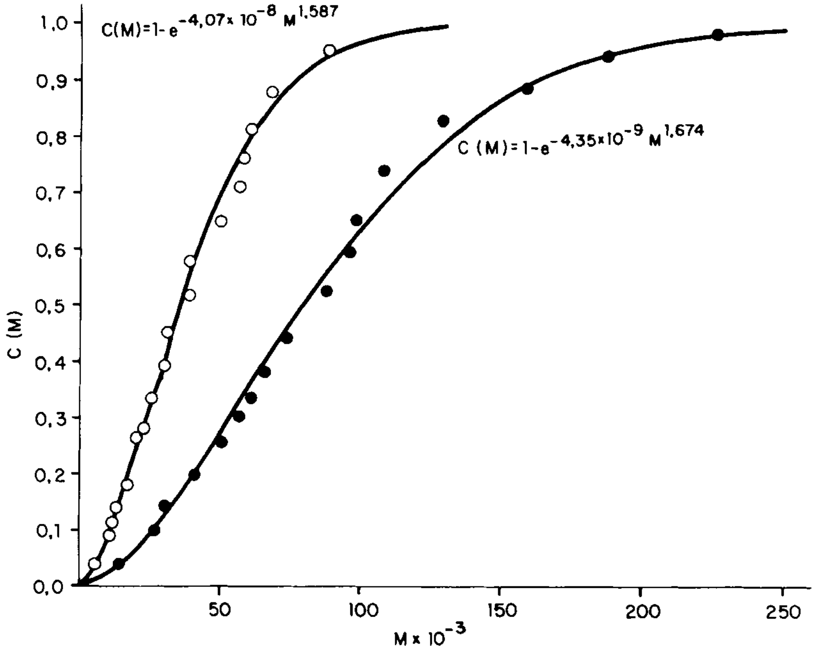

FIG. 2. Integral distribution curves for Polymers A and B. Lines correspond to the application of Tung's treatment; full and open circles are the experimental values.

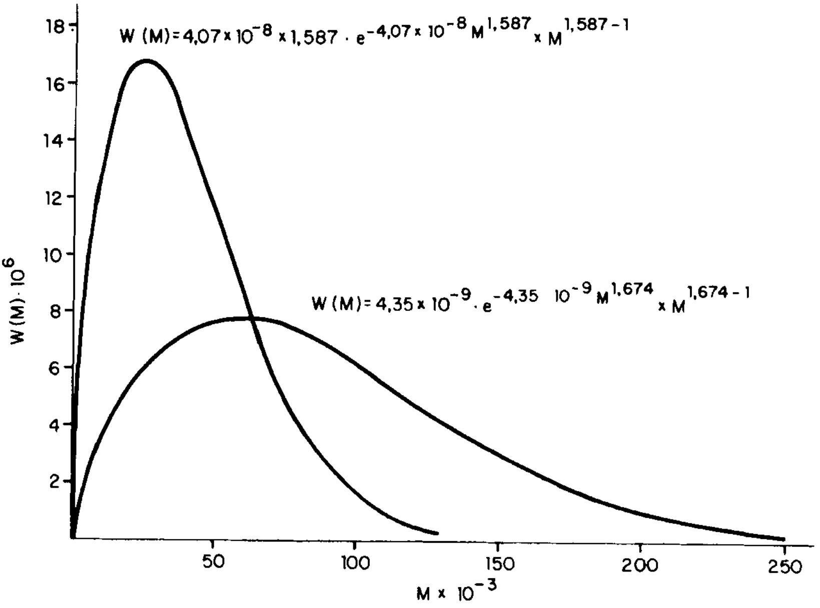

FIG. 3. Differential distribution curves for Polymers A and B according to Tung's treatment.

$$\bar{M}_z = y^{-1/z}\tau(1 + 2/z)/\tau(1 + 1/z) \qquad (4)$$

$$\bar{M}_w = y^{-1/z}\tau(1 + 1/z) \qquad (5)$$

$$\bar{M}_n = |y^{-1/z}\tau(1 - 1/z)|^{-1} \qquad (6)$$

The values obtained, together with those obtained by the direct summation method, are shown in Table 3. As Howard [16] has pointed out, the number-average molecular weights calculated from Eq. (6) are lower than those calculated by direct summation from experimental data, whereas minor errors were obtained in the case of higher averages and the distribution curves are better expressed as the ratio of $\bar{M}_z/\bar{M}_w$ or by the ratio $\bar{M}_w/M_{max}$, where M_{max} is the molecular weight of polymer at the maximum in the differential distribution curve, which is given by [16]

$$M_{max} = y^{-1/z}(1 - 1/z)^{1/z} \qquad (7)$$

Polydispersity factors are shown in Table 3, and the values calculated by the summative method or through the y and z parameters indicate a similar breadth for the distribution curves of the two polymers considered, although the distribution curve obtained for Polymer B is shifted to lower molecular weight compared with that of Polymer A.

As is well known, in free-radical polymerization in which chain transfer is negligible, chain length depends on the initiation, propagation, and termination rate constants as well as on the relationship between monomer concentration and square-root concentration of the initiator. Cardenas and O'Driscoll [2] assume that reactions involving small molecules, such as initiation and propagation, will not be severely affected by the polymer concentration. However, at moderately concentrated solutions, the active polymer chains are either small enough to be regarded as mobile or large enough to be regarded as entangled, and thus of restricted mobility. Cardenas and O'Driscoll [2] analyze the termination step separately for each case. The small chains are regarded as having the same value of rate constant termination (k_t) as in more dilute solution, while the large entangled chains have a rate constant termination (k_{te}) smaller than those of nonentangled radicals, and the cross-termination reaction between large and small chains is regarded as occurring with a rate constant which is the geometric average of k_t and k_{te}. The concentration of entangled radicals will generally increase with monomer conversion, and since the relative termination rate of these radicals is smaller than that of the

TABLE 3. Molecular Weight and Polydispersity Factors for Poly(methyl Methacrylate)s Prepared by Suspension Polymerization in the Presence of 1-n-Dodecanethiol

	DDT × 10^2 (mol/L)	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_z \times 10^{-3}$	$M_{max} \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w/M_{max}$	$\overline{M}_z/\overline{M}_w$
Direct summation method from experimental M of fractions	1.39	53	87	116	-	1.64	-	1.33
	3.48	23	39	53	-	1.70	-	1.36
From Tung's treatment using precipitation data for fractions	1.39	45	88	122	57	1.96	1.54	1.39
	3.48	19	40	57	24	2.11	1.67	1.43

nonentangled radicals, the overall rate of polymerization increases and the molecular weight distribution should shift toward higher molecular weights.

As is well known, there is no dependence between the overall rate of polymerization and the chain transfer constant in any conventional low-conversion kinetics. Cardenas and O'Driscoll [10] proposed an extension of their kinetic treatment for high conversion polymerization in order to include factors associated with the chain transfer reaction and observed some complicated dependence of the rate of polymerization on chain transfer constant at high conversion. This dependence arises from the fact that the relative proportion of entangled to nonentangled radicals will not only depend on the polymer concentration but also on the chain length of the polymer being produced.

When chain transfer is appreciable, chain length is determined by the factor mentioned above and also by the value of the chain transfer constant. As conversion increases, the volume fraction of polymer increases and some polymer chains become entangled; therefore, the relative rate of termination decreases and the chain transfer reaction will become dominant so that the molecular weight of polymer produced is not affected by acceleration of the rate of polymerization [10].

Theoretical predictions show that when chain transfer is not considered, the molecular weight distribution is very broad and the high molecular weight tail is extended considerably [2], but when the chain transfer reaction plays a more prominent role, the distribution is shifted somewhat to a lower molecular weight and the amount of polymer produced with lower molecular weight increases considerably with increasing chain transfer reaction [10-12]. The theoretical predictions mentioned above are in a fairly good agreement with the molecular weight distributions shown in Fig. 3, since the distribution of polymers is shifted toward lower molecular weight when the concentration of DDT increases. On the other hand, the similar polydispersity factors obtained for both polymers could be related to the strong chain transfer effect of DDT since, as Cardenas and O'Driscoll have pointed out [10], for values of chain transfer constant higher than 10^{-3} the response of both number- and weight average molecular weight to changing conversion is almost flat up to limiting conversion.

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