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On the Onset of the Trommsdorff Effect

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ABSTRACT: A new time scaling procedure is applied to data on kinetics of free radical polymerization. Superposition of data at different temperatures and initiator concentrations and from different laboratories is achieved at low conversion with this scaling. Autoacceleration due to the Trommsdorff effect produces deviations from this master curve. The point in scaled time where this deviation occurs depends upon one parameter only: the mean molecular weight of the polymer produced in the reaction mixture up to that point. These scaled kinetic data thus provide the best context for examining the dependence of the onset of autoacceleration on the molecular weight of the polymer. Examination of several sets of data in the literature shows that the transition from normal to accelerating kinetic behavior is sharp when the molecular weight of the polymer being produced is high and more diffuse when the mean molecular weight in the polymerizing medium is lower. Parallels are found between this observation and studies of the concentration dependence of solution viscosity and mutual diffusion coefficient at various molecular weights. From several sets of scaled data we extract the molecular weight dependence of the critical concentration, c^{**}, for the onset of the Trommsdorff effect. We find $c^{**} \sim N^{-0.24}$. This is different from either the molecular weight dependence of the critical concentration for molecular overlap [$c^* \sim N^{-0.5}$ to $c^* \sim N^{-0.8}$] or the molecular weight dependence of the critical concentration for entanglement [$c^{**} \sim N^{-1.0}$]. An explanation for the discrepancy is suggested.

Introduction

Numerous authors[1-10] have attempted to establish the relationship between the onset of autoacceleration of rate in free radical polymerization (the so-called Trommsdorff[11] or "gel" effect) and solution properties of the monomer–polymer system, particularly by association with the onset of "entangled" behavior observed in polymer rheological properties.[12,13] The general conclusion of these studies has been that within the accuracy of current experiments the polymer concentration at which autoacceleration is initiated depends primarily upon the molecular weight of the polymer produced in non-cross-linking systems. Additionally, the "critical" concentration for the onset of acceleration, c_{crit}, is found to fit an equation of a form

$$K_{\text{crit}} = c_{\text{crit}}\bar{M}_{\text{crit}}^{\,b} \tag{1}$$

where $\bar{M}_{\text{crit}}$ is a cumulative molecular weight average. Reported values of the exponent b range from ~0.25 to 1.0, depending on the monomer and the range of conditions investigated.

In a recent publication,[14] kinetic data in the literature have been reexamined, with a strong focus on the relationship between diffusion limitations in free radical kinetics and current theories of macromolecular diffusion. In particular, a kinetic model based on the idea of reptation[15] for polymer diffusion was developed. This model successfully describes the variation of conversion and molecular weight during autoacceleration in bulk methyl methacrylate polymerization to about 70% conversion. In this model a temperature-dependent parameter K_c

$$K_c = c^{**}\bar{N}^{**0.5} \tag{2}$$

was used to describe the onset of reptative diffusion at a critical concentration, c^{**}, in the presence of a dead polymer of number-average degree of polymerization $\bar{N}^{**}$. In the present work we look more closely at the dependence of the *onset* of the gel effect upon the characteristics of the polymerizing medium. By using a new time scaling procedure, we are able to collapse to a single "master curve" low-conversion kinetic data for methyl methacrylate polymerization at different temperatures and initiator concentrations. Deviations of the data from this curve at higher conversions show a systematic dependence of the onset of autoacceleration on a single parameter, the average molecular weight of the polymer generated. The kinetic model of our previous paper[14] is used to quantify this relationship between the critical concentration for onset of reptation during polymerization and the average molecular weight of the polymer produced.

Scheme I[a]
Kinetic Scheme for Free Radical Chain Growth Polymerization in the Presence of an Initiator

initiation $\quad \mathrm{I} \xrightarrow[k_{\mathrm{d}}]{} 2\mathrm{R}\cdot$

$\quad \mathrm{R}\cdot + \mathrm{M} \xrightarrow[k_{\mathrm{i}}]{} \mathrm{P}_1\cdot$

propagation $\quad \mathrm{P}_n\cdot + \mathrm{M} \xrightarrow[k_{\mathrm{p}}]{} \mathrm{P}_{n+1}\cdot$

termination $\quad \mathrm{P}_n\cdot + \mathrm{P}_m\cdot \xrightarrow[k_{\mathrm{t}}]{} \mathrm{D}_n + \mathrm{D}_m$

[a] I = initiator, R = initiated radicals, P_n = growing polymer chain of length n, D_n = dead polymer of length n, and M = monomer.

Theory Development

Given the kinetic scheme in Scheme I (i.e., neglect of chain transfer, termination by disproportionation only), the species balance equations give rise to the following conservation equations for the fractional conversion, x, initiator concentration, I, and the moments of the radical, λ_k, and dead polymer, μ_k, chain length distributions:[14]

$$\frac{\mathrm{d}I}{\mathrm{d}t} = -k_{\mathrm{d}}I + I\epsilon\frac{1-x}{1-\epsilon x}\lambda_0 k_{\mathrm{p}} \tag{3}$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{p}}(1-x)\lambda_0 \tag{4}$$

$$\frac{\mathrm{d}\lambda_0}{\mathrm{d}t} = 2fk_{\mathrm{d}}I - k_{\mathrm{t}}\lambda_0^2 + \lambda_0^2\frac{\epsilon(1-x)}{1-\epsilon x}k_{\mathrm{p}} \tag{5}$$

$$\frac{\mathrm{d}\lambda_1}{\mathrm{d}t} = k_{\mathrm{p}}\frac{M_0}{1-\epsilon x}(1-x)\lambda_0 - k_{\mathrm{t}}\lambda_0\lambda_1 + \lambda_0\lambda_1\frac{\epsilon}{1-\epsilon x}(1-x)k_{\mathrm{p}} \tag{6}$$

$$\frac{\mathrm{d}\lambda_2}{\mathrm{d}t} = k_{\mathrm{p}}\frac{M_0}{1-\epsilon x}(1-x)(2\lambda_1 + \lambda_0) - k_{\mathrm{t}}\lambda_0\lambda_2 + \lambda_2\lambda_0\frac{\epsilon}{1-\epsilon x}(1-x)k_{\mathrm{p}} \tag{7}$$

$$\frac{\mathrm{d}\mu_0}{\mathrm{d}t} = k_{\mathrm{t}}\lambda_0^2 + \mu_0\lambda_0\frac{\epsilon}{1-\epsilon x}(1-x)k_{\mathrm{p}} \tag{8}$$

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$$\frac{d\mu_1}{dt} = k_t\lambda_0\lambda_1 + \mu_1\lambda_0\frac{\epsilon}{1-\epsilon x}(1-x)k_p \qquad (9)$$

$$\frac{d\mu_2}{dt} = k_t\lambda_0\lambda_2 + \mu_2\lambda_0\frac{\epsilon}{1-\epsilon x}(1-x)k_p \qquad (10)$$

The moments λ_k and μ_k are defined as

$$\lambda_k = \sum_{n=0}^{\infty} n^k P_n \qquad (11)$$

$$\mu_k = \sum_{n=0}^{\infty} n^k D_n \qquad (12)$$

where P_n and D_n are the concentrations of radicals and dead polymer chains of length n, respectively. ϵ is the parameter which is included to account for the dependence of reaction volume on fractional conversion $[V = V(x = 0)(1 - \epsilon x)]$.

Under the assumptions of (1) the quasi-steady-state approximation (QSSA), (2) the long-chain hypothesis (zero consumption of monomer by initiation), (3) constant rate constants, (4) no volume change on polymerization, and (5) invariant initiator concentration with time, eq 3–10 simplify considerably and may be combined to yield

$$\frac{dx}{dt} = \left(\frac{2fk_dI_0}{k_{t0}}\right)^{1/2} k_p(1 - x) \qquad (13)$$

This equation suggests a natural dimensionless time for free radical polymerization

$$\tau = \left(\frac{2fk_dI_0}{k_{t0}}\right)^{1/2} k_p t \qquad (14)$$

and corresponding dimensionless concentrations, A^*

$$A^* = A\left(\frac{2fk_dI_0}{k_{t0}}\right)^{-1/2} \qquad (15)$$

where $A = \lambda_0, \lambda_1, \lambda_2, \mu_0, \mu_1$, and μ_2. k_{t0} is the (approximately constant) termination constant prior to the gel effect onset. When the enumerated assumptions are valid, these equations may be solved explicitly:

$$x = 1 - e^{-\tau} \qquad (16)$$

$$\bar{N}' = M_0k_p(1 - x)/(2fk_dI_0k_{t0})^{1/2} \qquad (17)$$

$$\bar{N}_w' = 2\bar{N}' \qquad (18)$$

where $\bar{N}$ and $\bar{N}_w$ are number- and weight-average degrees of polymerization, respectively, and the prime refers to the growing radical distribution. Therefore, when the scaled dimensionless time, τ, is used, plots of x vs. τ should superpose on the curve described by eq 16 for any temperature or initiator concentration. The effects of temperature and initiator concentration are to adjust the instantaneous degree of polymerization of the polymer produced. It should be noted that prior to the obvious manifestations of the gel effect some deviations from eq 16 are to be expected due to possible effects of volume change on polymerization, initiator depletion, or variation of the termination rate constant prior to the onset of marked acceleration as discussed previously.[14] These deviations are typically small, however, as will be seen subsequently.

Manifestations of the Gel Effect

The foregoing discussion has illustrated the superposition of data expected in the absence of large variation in the rate constants governing polymerization. The strong diffusional limitations imposed upon the termination step at the onset of autoacceleration will result in a marked deviation from the classical kinetics exemplified in eq 16. The value of interpreting and studying data in terms of the scaled time τ may be seen in Figures 1 and 2. In both figures three sets of experimental data at different temperatures and initiator concentrations are compared to curves calculated from classical kinetics without the gel effect. In Figure 1, where the fractional conversion is plotted as a function of real time, it is difficult to evaluate the dependence of the onset of acceleration on the characteristics (molecular weight, temperature) of the polymerizing medium. The relative sharpnesses of the transitions to accelerating kinetics are also masked by the intrinsically different rates of polymerization at low conversion in the three experiments, a result of the strong dependence of reaction rate on temperature and initiator concentration at low conversion. In Figure 2, where the same data are plotted as conversion vs. τ, the systematic deviation of the data from the superposed dilute-solution data illustrates the dependence of the critical conversion, x^{**}, on the degree of polymerization of the polymer created. In this scaled time the increasing sharpness of the transition from classical to accelerating kinetics with increasing degree of polymerization of the polymer being formed may be seen clearly. Thus, the reaction conditions which produce the highest molecular weight polymer also produce the sharpest gel effect onset in scaled time. This observation parallels quite closely data on transitions to "entangled" behavior observed in studies of the concentration dependence of solution viscosity[18] and mutual diffusion coefficient[19-20] in polymer–solvent systems. In these experiments the crossover to entangled behavior is found to span a very narrow concentration range at high molecular weight, while for low molecular weight the transition occurs over a much wider range of polymer concentration.

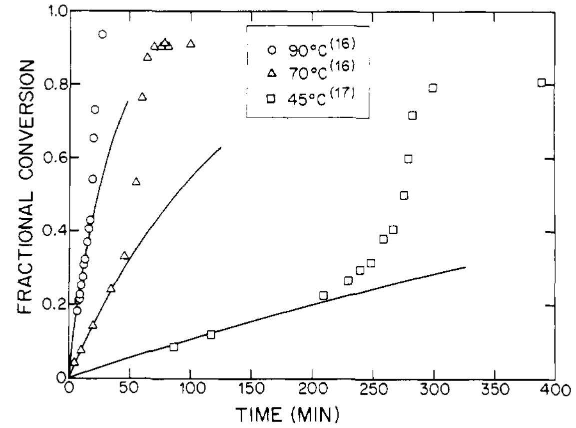

Figure 1. Fractional conversion vs. time data for bulk polymerization of MMA *initiated by AIBN on real time coordinates.*

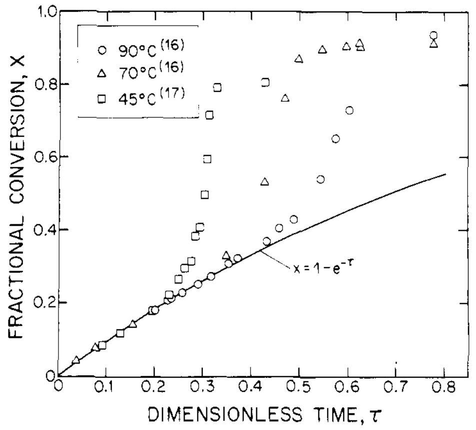

Figure 2. Fractional conversion vs. scaled time for bulk polymerization of MMA initiated by AIBN, illustrating data superposition at low conversion.

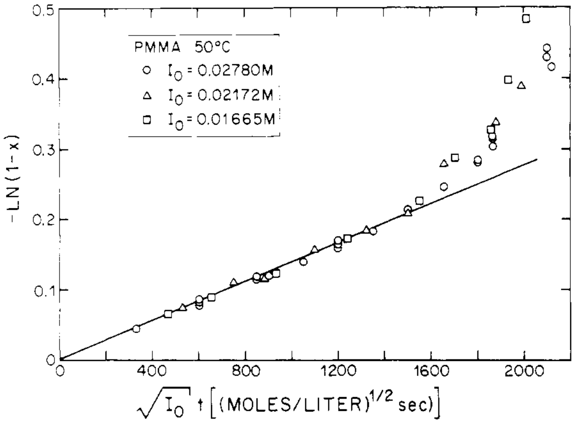

Figure 3. Constant-temperature data superposition used to extract the effective rate constant $(2fk_dk_p^2/k_{t0})^{1/2}$. Experimental data from Balke and Hamielec.[16]

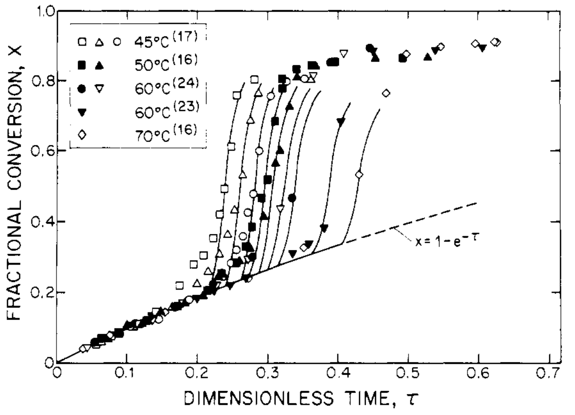

Figure 4. "Master curve" for the gel effect indicating low-conversion data superposition and systematic variation of onset of acceleration.

The utility of time scaling suggests a procedure both for empirical correlation of the gel effect data and for extracting information relevant to mechanistic understanding of the phenomenon. Integration of eq 13 yields

$$-\ln(1-x) = \left(\frac{2fk_dk_p^2}{k_{t0}}\right)^{1/2} I_0^{1/2}t \qquad (19)$$

By plotting $-\ln(1-x)$ vs. $I_0^{1/2}t$ for data at a single temperature, the slope of the line at low conversion yields the effective rate constant $(2fk_dk_p^2/k_{t0})^{1/2}$ involved in the time scaling. The use of such plots to superpose data at different initiator concentrations has been reported previously by Crosato-Arnaldi et al. for suspension polymerization of poly(vinyl chloride).[21] An illustration of the application of this procedure to the data of Balke and Hamielec[16] is seen in Figure 3. The ability of the time scaling procedure to superpose data from different laboratories under very different conditions is illustrated in Figure 4 for representative data. An Arrhenius plot for the effective rate constant is presented in Figure 5.

Quantification of Gel Effect Onset

In order to quantify the dependence of the gel effect onset on the molecular weight of the polymer produced, the kinetic model developed previously[14] was used. The primary aspect of this model is the concentration and chain length dependence of the termination rate constant

$$k_t \sim 1/\bar{N}'^2c^{1.75}$$

at polymer concentrations greater than a critical concentration, c^{**}, for the onset of reptative diffusion. In the present work, values of the critical concentration, c^{**}, were adjusted to allow fit of experimental conversion vs. τ data for each data set.

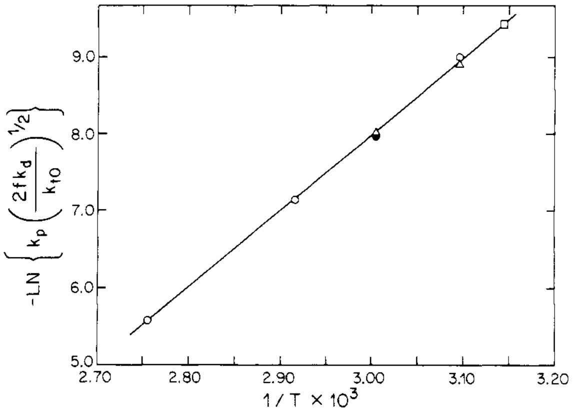

Figure 5. Arrhenius plot for polymerization of MMA initiated by AIBN.

In dimensionless form eq 3–10 become

$$\frac{dI^*}{d\tau} = -\frac{k_d}{k_p}\left(\frac{k_{t0}}{2fk_dI_0}\right)^{1/2} I^* + I^*\frac{\lambda_0^*}{1-\epsilon x}\epsilon(1-x) \qquad (20)$$

$$\frac{dx}{d\tau} = (1-x)\lambda_0^* \qquad (21)$$

$$\frac{d\lambda_0^*}{d\tau} = \frac{k_{t0}}{k_p}I^* - \frac{k_{t0}}{k_p}g(x,\bar{N},\bar{N}')\lambda_0^{*2} + \lambda_0^{*2}\frac{\epsilon(1-x)}{1-\epsilon x} \qquad (22)$$

$$\frac{d\lambda_1^*}{d\tau} = \frac{M_0(1-x)}{1-\epsilon x}\left(\frac{k_{t0}}{2fk_dI_0}\right)^{1/2}\lambda_0^* - \frac{k_{t0}}{k_p}g(x,\bar{N},\bar{N}')\lambda_1^*\lambda_0^* + \lambda_0^*\lambda_1^*\frac{\epsilon(1-x)}{1-\epsilon x} \qquad (23)$$

$$\frac{d\lambda_2^*}{d\tau} = M_0\left(\frac{k_{t0}}{2fk_dI_0}\right)^{1/2}\frac{1-x}{1-\epsilon x}(2\lambda_1^* + \lambda_0^*) - \frac{k_{t0}}{k_p}g(x,\bar{N},\bar{N}')\lambda_0^*\lambda_2^* + \lambda_2^*\lambda_0^*\frac{\epsilon(1-x)}{1-\epsilon x} \qquad (24)$$

$$\frac{d\mu_0^*}{d\tau} = \frac{k_{t0}}{k_p}\lambda_0^{*2}g(x,\bar{N},\bar{N}') + \mu_0^*\lambda_0^*\frac{\epsilon(1-x)}{1-\epsilon x} \qquad (25)$$

$$\frac{d\mu_1^*}{d\tau} = \frac{k_{t0}}{k_p}g(x,\bar{N},\bar{N}')\lambda_0^*\lambda_1^* + \mu_1^*\lambda_0^*\frac{\epsilon(1-x)}{1-\epsilon x} \qquad (26)$$

$$\frac{d\mu_2^*}{d\tau} = \frac{k_{t0}}{k_p}g(x,\bar{N},\bar{N}')\lambda_0^*\lambda_2^* + \mu_2^*\lambda_0^*\frac{\epsilon(1-x)}{1-\epsilon x} \qquad (27)$$

where $I^* = I/I_0$, $\lambda_k^* = \lambda_k(2fk_dI_0/k_{t0})^{-1/2}$, and $\mu_k^* = \mu_k(2fk_dI_0/k_{t0})^{-1/2}$ for $k = 0, 1, 2$. Here the termination rate constant has been factored in a form

$$k_t = k_{t0}g(x,\bar{N}',\bar{N}) \qquad (28)$$

where the dimensionless function g contains any dependence of the termination constant on fractional conversion and number-average degree of polymerization of the radicals, $\bar{N}'$, and dead polymer, $\bar{N}$, which results from the gel effect. Since it has been shown that the effect of diffusion-controlled termination on fitting conversion–time data at low conversion is quite small, the following form of the termination constant is used (see ref 14):

$$k_t = k_{t0}(1 + g_{\min}) \qquad c < c^{**} \qquad (29a)$$

$$k_t = k_{t0}\left\{\frac{\bar{N}^{**2}c^{**1.75}}{\bar{N}'^2c^{1.75}} + g_{\min}\right\} \qquad c > c^{**} \qquad (29b)$$

Table I
Kinetic Parameters for
Methyl Methacrylate Polymerization

T, °C	k_p, L/(mol s)	k_{t0}, L/(mol s)	k_d, s^{-1}	f	ref
50	558	3.50×10^7	2.14×10^{-6}	0.50	16
70	828	3.67×10^7	3.40×10^{-5}	0.49	16
90	1178	3.83×10^7	3.98×10^{-4}	0.50	16
50	558	3.50×10^7	2.14×10^{-6}	0.42	23
60	684	3.59×10^7	8.89×10^{-6}	0.49	23
60	684	3.59×10^7	8.89×10^{-6}	0.51	22
60	684	3.59×10^7	8.89×10^{-6}	0.51	24
45	501	3.45×10^7	1.02×10^{-6}	0.46	17

T, °C	V_M,[25] cm^3/g	V_P,[25] cm^3/g	M_0,[26] mol/L
45	1.096	0.8327	9.13
50	1.102	0.8350	9.07
60	1.115	0.8399	8.95
70	1.128	0.8448	8.83
90	1.154	0.8546	8.58

Here, prior to the onset of reptative diffusion control of termination at c^{**} a constant rate constant is used to describe termination. At polymer concentrations greater than c^{**} the control of termination by reptation results in the strong concentration and chain length dependence of the termination rate constant described in eq 29b. $k_{t0}g_{\min}$ is a minimum value of the termination constant introduced to account for termination by any small fraction of small, nonreptating radicals present in any chain length distribution.[14]

When a single critical concentration for the onset of reptative behavior is used, the model loses some ability to fit data precisely near the upswing in rate of polymerization. The overall fit during acceleration, however, is good. Values of rate constants used in eq 20–27 were extracted from various literature data.[16,17,22-24] The expressions used are

$$k_d = 8.46 \times 10^{14} \exp\{-30439/RT\} \quad (\mathrm{s}^{-1}) \qquad (30a)$$

$$k_p = 4.92 \times 10^5 \exp\{-4353/RT\} \quad (\mathrm{L/(mol\ s)}) \qquad (30b)$$

$$k_{t0} = 7.93 \times 10^7 \exp\{-525/RT\} \quad (\mathrm{L/(mol\ s)}) \qquad (30c)$$

Using these expressions, values of the initiator efficiency, f, were used to correct each data set to match the effective rate constants reported in Figure 5. The actual values used are found in Table I. The type of fit to data attained with the model is illustrated in Figure 4 for a part of the data studied. A complete list of the critical concentrations and degrees of polymerization for the data studied is presented in Table II and Figure 6.

Discussion

From the values in Table II several things are immediately evident. First, within data sets from a single laboratory there is a systematic variation of the critical concentration with average degree of polymerization. Comparison of data between laboratories shows that some minor discrepancies occur; however, the general trend of decreasing c^{**} with increasing $\bar{N}^{**}$ remains intact. Also, the data do not indicate any direct temperature effect on c^{**}. A least-squares fit of the data in Figure 6 to a power law

$$K = c^{**}\bar{N}^{**a} \qquad (31)$$

yields an exponent of $a = 0.24$ with a standard deviation of the exponent equal to 0.007.

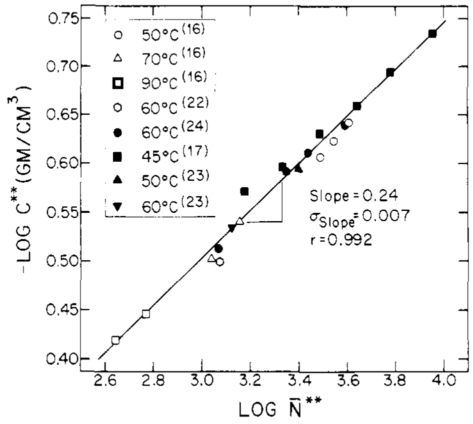

Figure 6. Plot of log c^{**} vs. log $\bar{N}^{**}$ according to eq 30.

Table II
Dependence of the Critical Conversion and Critical Polymer Concentration for Onset of Reptative Chain Termination on Number-Average Degree of Polymerization

T, °C	I_0, mol/L	x^{**}	c^{**}, g/cm^3	$\bar{N}^{**}$	ref
50	0.02780	0.256	0.2477	3093	16
50	0.02172	0.247	0.2384	3519	16
50	0.01665	0.237	0.2282	4044	16
70	0.02706	0.326	0.3148	1099	16
70	0.01620	0.301	0.2887	1448	16
90	0.02630	0.395	0.3814	441	16
90	0.01575	0.374	0.3589	588	16
50	0.05	0.263	0.2549	2513	23
60	0.05	0.302	0.2927	1347	23
60	0.06090	0.325	0.3169	1172	22
60	0.06090	0.316	0.3074	1178	24
60	0.01827	0.267	0.2564	2225	24
60	0.01218	0.256	0.2451	2750	24
60	0.00609	0.241	0.2298	3943	24
45	0.2	0.275	0.2688	1513	17
45	0.1	0.261	0.2542	2159	17
45	0.05	0.242	0.2345	3089	17
45	0.025	0.227	0.2192	4411	17
45	0.0125	0.211	0.2029	6303	17
45	0.00625	0.193	0.1847	9017	17

Rheological theories and experiments have established that the onset of "entangled" polymer dynamic behavior obeys a power law of the form of eq 31; however, in rheological measurements values of the exponent range from 0.5 to 1.0. The value obtained from the kinetic data, therefore, is significantly different. A plausible explanation for this difference may be developed by considering the diffusive processes which occur on a microscopic level in the different experiments, particularly when viewed within the framework of reptation theory. The basic premise underlying the idea of reptation is that the motion of a given macromolecule is confined within a virtual "tube" defined by the locus of its intersections with adjacent molecules. Under the assumption that the tube is essentially stationary on time scales over which diffusion within the tube occurs, the familiar results of reptation theory are derived. Klein[27] has tested the validity of the fixed-tube assumption by analyzing the interactions between a macromolecule and the "environment" chains surrounding it. By recognizing that the "environment" chains which form the tube around a given macromolecule are themselves reptating in similar tubes, Klein has applied a self-consistency relation to determine the dominant modes of motion in a multichain system. For a *monodisperse polymer system* this analysis predicts that a sharp, cooperative transition between a rapid Rouse-like[28] relaxation mode and a slower reptative mode will occur at a concentration which depends upon chain length in a simple power law form, with an exponent of 0.8 for very good solvents in the "semidilute" concentration regime.[27] For the general case of the onset of reptation in a polydisperse polymer system, Klein's approach does not lend itself to simple quantitative analysis. Qualitatively, however, the analysis points out an intrinsic difference between the observed variables in kinetic and rheological experiments.

In the kinetic context a very complex problem is presented: dual populations, radicals and dead polymer, each polydisperse but of different average sizes, are present. A relatively small number of radicals of average size $\bar{N}'$ are diffusing in tubes formed by the predominant environment (dead) chains of average size $\bar{N}$. In such a system the macroscopically observed variable k_t is dependent upon the diffusion behavior of the *radical species*. In general, the diffusion coefficient of a radical depends upon its own length, as well as the total concentration and size distribution of the dead polymer chains in whose environment it moves.[14] In the formulation of the present kinetic model the dependence of the diffusion coefficient of a particular radical on its own size has been decoupled from any dependence on the size distribution of the dead polymer chains surrounding it. It has been assumed that (1) the *mode of diffusion* (equivalently, the mode of radical termination) is determined primarily by the concentration and average size of the *dead* polymer, while (2) the average termination rate constant for the radicals in a reptating system depends upon some average *radical* size and is independent of the size distribution of the dead polymer. The success of the kinetic model in fitting experimental data during acceleration indicates that the second part of this assumption appears valid. Additionally, diffusion experiments on systems in which reptation is the dominant relaxation mechanism have also shown that the diffusion coefficient of a "tagged" macromolecule depends upon its own length and is virtually independent of the size distribution of the environment in which it moves.[29,30]

The first assumption above corresponds to a supposition that the transition to a fixed tube around the radicals occurs at a concentration c^{**} which depends upon the average size of the dead polymer chains only. As the environment chains undergo a transition from a Rouse-like to a reptative motion (as would be observed in a rheological measurement), the mode of motion of the radicals will most certainly be affected also. However, in the application of a self-consistency relation to the motion of a radical in a dual-population system, the transition to reptation for the radical should depend upon the sizes of both the radical and the dead polymer. Though the data examined in this report indicate that a good correlation of the kinetic manifestation of reptation to a power law form (eq 31) based on the dead polymer molecular weight can be made, the effective exponent of 0.24 obtained from this correlation reflects the complications involved in analyzing the onset of reptation for a "tagged" molecule as its environment is changed. This makes a simple, direct correspondence between rheological and kinetic results inconsistent in the sense that the sensitivities to the various chain lengths involved are fundamentally different in the two experiments. If the view we have presented here is correct, then we might expect to observe a consistent exponent if it was possible to perform both the kinetic and rheological experiments with strictly monodisperse polymers.

Conclusion

In this report we have presented a procedure by which the onset of the gel effect for a variety of experimental conditions may be studied in a systematic manner. By using a previously developed kinetic model, we have quantified the dependence of this onset on the average size of the polymer generated. Due to the complexity of the interactions present in the dual-population, polydisperse kinetic situation, a simple power law fit to experimental data yields an exponent which is inconsistent with rheological measurements and theoretical developments designed for monodisperse systems. Given the current level of theoretical understanding, a systematic experimental study of the relationship between kinetic and rheological manifestations of polymer entanglement under controlled conditions appears in order. In particular, for the present application it would be interesting to know how the self-diffusion coefficient of a "tagged" chain of length N' changes with increasing concentration of an "environment" chain of length N.

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References and Notes

(1) Turner, D. T. *Macromolecules* **1977**, *10*, 221.
(2) Lee, H. B.; Turner, D. T. *Macromolecules* **1977**, *10*, 226.
(3) Lee, H. B.; Turner, D. T. *Macromolecules* **1977**, *10*, 231.
(4) High, K. A.; Lee, H. B.; Turner, D. T. *Macromolecules* **1979**, *12*, 332.
(5) Lee, H. B.; Turner, D. T. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977**, *18*, 539.
(6) Lee, H. B.; Turner, D. T. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19*, 603.
(7) O'Driscoll, K. F.; Wertz, W.; Husar, A. *J. Polym. Sci., Part A-1* **1967**, *5*, 2159.
(8) Abuin, E.; Lissi, E. A. *J. Macromol. Sci., Chem.* **1977**, *A11*, 65.
(9) Lachinov, M. B.; Simonian, R. A.; Georgieva, T. G.; Zubov, V. P.; Kabanov, V. A. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 613.
(10) Dionisio, J. M.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3199.
(11) Trommsdorff, E.; Kohle, H.; Lagally, P. *Makromol. Chem.* **1948**, *1*, 169.
(12) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(13) Ferry, J. D. "Viscoelastic Properties of Polymers"; Wiley-Interscience: New York, 1970.
(14) Tulig, T. J.; Tirrell, M. *Macromolecules* **1981**, *14*, 1501.
(15) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(16) Balke, S. T.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1973**, *17*, 905.
(17) Ito, K. *J. Polym. Sci., Part A-1* **1975**, *13*, 401.
(18) Schurz, J.; Hochberger, H. *Makromol. Chem.* **1966**, *96*, 141.
(19) Yu, T. L.; Reihanian, H.; Jamieson, A. M. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 695.
(20) Yu, T. L.; Reihanian, H.; Jamieson, A. M. *Macromolecules* **1980**, *13*, 1590.
(21) Crosato-Arnaldi, A.; Gasparini, P.; Talamini, G. *Makromol. Chem.* **1968**, *117*, 140.
(22) Robertson, E. R. *Trans. Faraday Soc.* **1955**, *52*, 426.
(23) Nishimura, N. *J. Macromol. Chem.* **1966**, *1*, 257.
(24) Rokudai, M.; Toyooka, Y.; Saitou, Y.; Imoto, T. *Nippon Kagaku Kaishi* **1972**, *8*, 1768.
(25) Schulz, G. V.; Harborth, G. *Angew. Chem.* **1947**, *59*, 90. *Makromol. Chem.* **1947**, *1*, 106.
(26) Matheson, M. S.; Auer, E. E.; Bevilacqua, E. B.; Hart, E. J. *J. Am. Chem. Soc.* **1949**, *71*, 497.
(27) Klein, J. *Macromolecules* **1978**, *11*, 852.
(28) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(29) Klein, J. *Nature (London)* **1978**, *271*, 143.
(30) Klein, J. *Macromolecules* **1981**, *14*, 460.