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A Critical Experimental Examination of the Gel Effect in Free Radical Polymerization: Do Entanglements Cause Autoacceleration?

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ABSTRACT: Over the past two decades, a substantial case has been made associating and/or attributing the "gel" effect or autoacceleration in free radical polymerization and its onset to entanglement of polymerizing chain radicals, resulting in a marked reduction in the termination rate parameter, k_t. This case has often been made by modeling a limited range of free radical polymerization data using the assumption that in the neighborhood of the gel effect k_t is controlled by polymer self-diffusion which in turn exhibits entangled polymer dynamics. The present study provides critical experiments involving both bulk methyl methacrylate and styrene polymerizations which contradict the widely held belief that the gel effect onset is related to the formation of chain entanglements. By employing experimental conditions which tend to delay or eliminate the formation of chain entanglements, i.e., high initiator and/or chain transfer agent concentrations and addition of low molecular weight polymer prior to reaction, it is shown that the gel effect readily occurs in the absence of entanglements and that delaying the onset of entanglements does not necessarily delay the onset of the gel effect. Critical examination of the molecular weights produced in these and other experiments often indicates values too low for entanglement formation in solution (polymer plus monomer) and sometimes even in bulk polymer, not only at the onset but also throughout the gel effect. This fact illustrates the importance of understanding the relationship between molecular weight and entanglements in bulk polymer and solution in performing a critical examination of the relationship between the origin of the gel effect and entanglement formation. Furthermore, even under conditions where entanglements are likely to exist, the gel effect onset does not correlate with polymer molecular weight, either of the chains produced or the matrix, in a manner consistent with entanglement arguments. Although the present results indicate that the *onset* of the gel effect is unrelated to entanglement formation, whether the kinetics *during* the gel effect may be affected by entanglements if they do form remains an open question; experimental tests to investigate this issue are outlined. Other theories which purportedly explain the origin of the gel effect are also discussed in the context of data from this study and future experimental tests.

Introduction

A central problem encountered in free radical polymerization of such monomers as methyl methacrylate, styrene, vinyl acetate, methyl acrylate, and other acrylates and methacrylates is the autoacceleration in the polymerization rate at intermediate to high conversions called the "gel" effect. Also known as the "Norrish−Smith"[1] or "Trommsdorff"[2] effect, this phenomenon can lead to difficulties ranging from undesired final properties to reactor explosion, as the exothermic nature of the reaction can cause an uncontrolled temperature rise. Avoiding this effect through use of large quantities of chain transfer agent and/or solvent often proves costly or environmentally unsafe. In addition, as well-understood "classical" kinetics no longer apply during autoacceleration, efforts to model the polymerization may not be entirely predictive (in the sense that adjustable parameters are necessary to fit experimental data) due to what is an incomplete understanding of the physical origin of the gel effect.

Experimental evidence for the gel effect usually takes the form of a rise in the slope of a plot of monomer conversion versus time. At low conversion, where classical kinetics (including the quasi-steady state approximation) apply, the slope is nearly constant. At some conversion, the magnitude of which depends on the monomer and other factors, the polymerization rate begins to increase to a much higher level, resulting in a higher slope. The increased conversion rate usually leads to a temperature rise, which causes a yet higher conversion rate, which causes a higher temperature, etc. Thus, the magnitude of the conversion vs time slope during the gel effect depends on the effectiveness of heat transfer. Although this nonisothermal character causes some of the problems previously stated, it also provides a second means by which the time of the gel effect can be identified, as a plot of temperature versus time will generally exhibit a spike[3,4] during this period. (Since the gel effect can be observed under isothermal conditions,[5] the absence of a temperature rise does not necessarily imply the absence of the gel effect.)

The cause of the gel effect has been the subject of debate in the literature for over 50 years. Early work[1,2,6−9] established that the increase in rate of polymerization was related to a decrease in the rate of chain termination, which was immediately linked to diffusion-control issues. Qualitatively, it is well accepted that the termination reaction between two growing chains becomes more hindered as mobility in the system becomes restricted due to conversion of monomer to polymer. The debate lies in the details of exactly what type of mobility is important as well as how best to account quantitatively for the decrease in the termination rate. Here, we provide critical tests for one of the main pictures used to explain the origin of the gel effect, i.e., that formation of chain entanglements hinders diffusion of the center-of-mass of radical chains,

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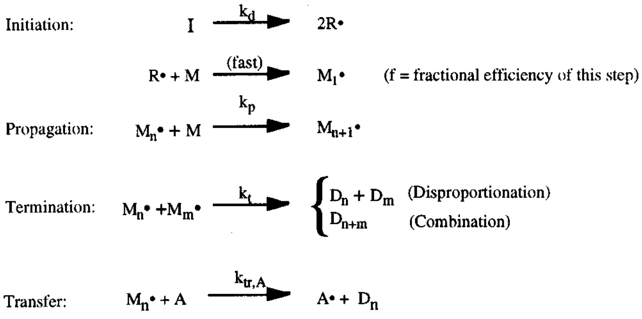
Scheme 1



where I = initiator; R• = initiated radical, M = monomer, M_n• = growing chain of length n, D_n = dead polymer chain of length n, A = chain transfer agent.

causing a decrease in the rate of termination. We also comment on other possible mechanisms for the gel effect and offer approaches for testing these pictures. First, a review of the history of this subject is in order.

Background

In classical free radical polymerization (Scheme 1), it is assumed that the rate of initiation balances the rate of termination. This "quasi-steady state assumption" is reasonable if the radical lifetimes are relatively short, since virtually all radicals formed are killed in a fraction of a second or seconds. The kinetic expression resulting from this assumption is the following:

$$R_p = k_p[\mathrm{M}](fk_d[\mathrm{I}]/k_t)^{1/2} \qquad (1)$$

where R_p is the rate of polymerization, [M] and [I] are the monomer and initiator concentrations, f is the initiator efficiency, and k_p, k_d, and k_t are the propagation, initiation, and termination rate constants, respectively. Equation 1 describes accurately the low conversion kinetics of a wide range of monomers.[10,11] In 1939 Norrish and Brookman[12] reported a deviation from this kinetic theory in the bulk polymerization of methyl methacrylate (MMA). At approximately 10−20% conversion, R_p was observed to undergo a sharp increase, with an accompanying rise in system temperature. It was later noted that the degree of polymerization of the formed polymer also underwent a sharp increase during this regime.[1] This observation led to the conclusion that this effect was associated with a decreased termination rate constant. This conclusion was subsequently confirmed by direct measurement of individual rate constants.[6−9]

Norrish and Smith[1] asserted that the cause was the increasing bulk viscosity, which apparently slowed the diffusion of propagating chains enough to restrict the termination reaction, leading to a higher radical population and, consequently, an increased R_p. They proposed this explanation based on the observation that MMA polymerizations carried out in poor solvents resulted in longer chain lengths (and higher solution viscosities) as well as earlier gel effect onset conversions as opposed to polymerizations carried out in good solvents. Trommsdorff et al.[2] studied MMA polymerization and found that the gel effect occurred earlier when preformed poly(methyl methacrylate) (PMMA) or cellulose tripropionate was predissolved in the reaction mixture. As addition of high molecular weight species markedly increases bulk viscosity, they concluded that higher viscosity causes an earlier gel effect. Studies showed a later gel effect with increasing amounts of solvent.[13] Chain transfer was shown to suppress or eliminate the gel effect, presumably because the lower molecular weights formed led to lower viscosities.[8] Theories were presented which predicted characteristic viscosities at which termination in a polymerizing solution may become diffusion controlled.[14,15] This and other evidence led to the prevailing theory of the time[10,11] that the gel effect onset corresponded to the onset of diffusion control of the termination reaction, caused by the increase in viscosity with increasing conversion.

The bulk viscosity picture presumes that termination is chemically-controlled at the beginning of polymerization. However, this was shown to be incorrect by Benson and North,[16] who found that k_t for MMA polymerization in dilute solution was inversely proportional to the viscosity over a range of 2 orders of magnitude in viscosity, which was varied by addition of a poly(ethylene oxide)−poly(propylene oxide) copolymer. Subsequently, it was realized that the friction a chain experiences in the polymerizing medium depends on microviscosity rather than bulk viscosity, the latter of which can be affected by polymer molecular weight and chain entanglements.[17,18] Thus, it was shown that the conclusions of these studies as well as those of Trommsdorff et al.[2] were potentially flawed, as factors other than bulk viscosity may have been altered by the addition of polymer to the reaction medium. (Despite this, further work attempted to correlate the termination reaction with bulk viscosity by use of predissolved polymer.[19−21]) These experiments were repeated using low molecular weight esters of similar solvent power but varying viscosity, and the same conclusion was reached, i.e., that k_t for MMA polymerization is inversely dependent on solvent viscosity in dilute solution.[22] Similar results were shown for other methacrylates, although a slightly less than inverse viscosity dependence was observed.[23]

A rather ambiguous notion of what was meant by "diffusion control" existed until North and co-workers[22,24] outlined a three-step process for termination. In this picture, two propagating chains first undergo translational diffusion until they are within proximity of one another. Next, the radicals themselves (attached to chain ends) come within a given reaction radius via chain-end motion, termed segmental diffusion. Third, the two radicals react. If one step were much slower than the others, this process would be said to be rate controlling.

North and Reed[22] showed that the concentration dependence of k_t for MMA in dilute solution follows that of the mutual diffusion coefficient for PMMA but not that of the self-diffusion coefficient; i.e., k_t rises with conversion. According to the Smoluchowski relation for diffusion-controlled interactions,[25] k_t should be proportional to the diffusion coefficient. (Although this is strictly derived for translational diffusion coefficients, it has been used in the context of segmental diffusion.[26]) From this evidence, North and Reed asserted that segmental diffusion and not translational diffusion is controlling at the early stages of polymerization. Inherent in this explanation is the presumed correspondence of "chain-end segmental diffusion" with mutual diffusion. The validity of this correspondence is not clear if one takes "segmental diffusion" to be equivalent to segmental mobility, which slows with polymer concentration.[27] Conversely, the mutual diffusion coefficient is expected to rise with conversion, at least until rather high concentrations (20–50%).[28–30] The connection between segmental diffusion, which is not precisely defined, and mutual diffusion, which is, comes from the notion that chain segments may experience some *local* concentration gradient across a polymer coil. However, since mutual diffusion occurs in the presence of a *macroscopic* concentration gradient (over distances much larger than the coil radius of gyration), this must be considered suspect; O'Shaughnessy[31] has shown that the rise in k_t at low conversion can be explained entirely by excluded volume.

With this evidence came a shift in the discussion of the cause of the gel effect. The debate that arose from the work of North et al.[16,17,22–24] was whether the gel effect is caused by a gradual slowing down of segmental mobility with conversion or whether some change in the mechanism of termination, such as the shift from segmental to translational control, is associated with the onset of autoacceleration. This debate has never been experimentally resolved, although most current work assumes that termination is translational diffusion-controlled at gel effect conversions.[32–41]

This view appears to originate with the classic result of Hayden and Melville[9] that k_t (above a critical conversion) depends on initiator concentration and thus molecular weight of the chain radicals. This molecular weight dependence of k_t is more consistent with translational control because the self-diffusion coefficient is expected to vary with chain length, while segmental motions should not, at least for long enough chains.[42] However, examination of this work reveals that the reported trend is very weak and, more importantly, that the conclusion is based on only two data points. Furthermore, their numerical analysis has been criticized by Ito[43,44] on the basis that they calculate k_t values using classical kinetics despite the fact that their R_p data do not exhibit the expected $[I]^{1/2}$ dependence. In contrast to this result, Fischer et al.[45] have reported that k_t for MMA polymerization is independent of polymer molecular weight in the dilute regime. This is consistent with segmental control, but no results were reported for higher concentrations.

More recent evidence has suggested a dependence of k_t on molecular weight, albeit not as strong as expected for translational diffusion control. O'Driscoll and Mahabadi[46] reported that in dilute solution k_t depends on the degree of polymerization for values less than about 1000. Results at higher concentration have been reported for ethylene,[47,48] styrene,[49] methyl methacrylate,[50] and butyl acrylate[51] polymerization. Of those studies testing chain length dependence, Buback and Schweer[47] have noted that k_t at 9.5% conversion in ethylene polymerization is approximately constant for chain lengths longer than about 400 and rather strongly dependent for shorter chains; Sack et al.[50] have claimed a chain length dependence for PMMA at intermediate conversions but not at high or low conversion. These results, though interesting, are not conclusive, given the known inconsistencies associated with rate parameters reported by different groups,[52,53] and the fact that experiments carried out through the gel effect regime are often nonisothermal.[5]

The fact that translational diffusion control has never been conclusively established has not deterred the notion that the gel effect onset is simply the concentration at which translational diffusion becomes the controlling step. This was popularized by O'Driscoll[54,55] who proposed that the onset be defined as the "conversion at which the rate of segmental diffusion of the polymeric radicals equals the rate of their translational diffusion."[54] This definition can be seen as a consequence of the misunderstanding of the concentration dependence of segmental dynamics, resulting from North and Reed's treatment[22] correlating segmental diffusion to mutual diffusion in dilute solution. If the rate of segmental diffusion always increases with concentration, as is often asserted, then some other effect must cause the decrease in k_t associated with the gel effect. However, there is no reason why chain-end diffusion rates should increase with concentration beyond the point at which chains begin to overlap, as no effective concentration gradient of chain segments should be present, i.e., excluded volume effects are screened out.

This desire to invoke some fundamental change in chain diffusion characteristics has led to the theory that the gel effect onset corresponds to the onset of entanglements in solution. Although entanglements have long been considered a potential contributing factor to diffusion-controlled termination,[9,56] the first work outlining a definitive relationship between the gel effect and entanglements was the model of Cardenas and O'Driscoll.[57] They explained that entanglements led to two populations of polymerizing radicals: those that are unentangled and thus free to diffuse and terminate, and those that are entangled and thus immobile. Despite the lack of any effect of concentration on termination other than through a varying entanglement density, this model was shown to fit MMA polymerization data. A second entanglement-based model by Tulig and Tirrell,[58] which related k_t to the self-diffusion coefficient of the propagating chains, D_{self}, and included molecular weight and concentration scaling for D_{self} based on a reptation model,[59] also fitted data up to relatively high conversion, beyond which the model failed.

These results would be encouraging for the entanglement picture were it not for the fact that most models presented to explain the gel effect[57,58,60–66] have proven adequate to fit experimental conversion–time data, despite entirely different physical assumptions. Several models which base the conversion dependence of rate parameters only on the change of free volume with conversion[60–66] have proven to fit experimental data adequately, in some cases better[64–66] than the entanglement models. The success of at least some of these models is no doubt related more to the presence of adjustable parameters or to critical conversions where the physical assumptions are changed than to the validity of these physical assumptions. Clearly, the ability of a model to fit experimental data does not prove the validity of its assumptions. Therefore, any effort to *prove* various physical pictures of the gel effect based on modeling has been frustrated by the fact that many different models have been found adequate to fit the limited range of experimental data tested. (A complicating factor has been that some of the gel effect data used for modeling purposes may have been taken under nonisothermal conditions,[5] a detail not accounted for by such models.)

Experimental evidence has also been offered in an attempt to link entanglements to the gel effect. Several authors[67–70] have noted that there appears to be a slight trend for a higher gel effect onset concentration when lower molecular weight polymer is formed. This is qualitatively consistent with the entanglement theory, as entanglements should form at higher conversions for lower molecular weights. Critical examination of the literature indicates that such a trend apparently exists in some results,[2,13,71] but not in others.[72−74] However, even for those data that follow this trend, it has been noted that there is a much weaker dependence of onset concentration on molecular weight than expected based on reptation arguments.[67,75] In addition, this evidence is suspect as there is no unambiguous method for determining the onset concentration. In fact, the notion that the gel effect is characterized by a sharp change in rate of polymerization and is characterized by an easily-identified onset concentration is incorrect. This is evident from the room temperature polymerization of styrene by Ito.[76] These polymerizations, which last as long as 252 days and therefore facilitate very accurate determination of conversion−time curves, clearly show the gel effect, but with a very gradual transition from low conversion to gel effect kinetics.

Further evidence has been offered in the form of critical conversions for the formation of entanglements in solution taken from "break" points in log−log plots of bulk viscosity as a function of conversion.[54,58,70] These onset concentrations are then shown to be similar to the gel effect onset conversion. However, this method is incorrect, as such plots do not show two distinct scaling regimes as is the case with viscosity−molecular weight plots for a given concentration.[77] Rather, since such plots simply show continuous curvature over the entire concentration range, the value of the "critical conversion" so defined depends on the range of viscosity data used. This practice has been strongly criticized[77] for this very reason.

It is interesting to note that at least two studies have reported that the gel effect can occur under conditions where the molecular weight of the polymer formed is too small to be considered entangled.[68,73] In both cases the authors concluded that the gel effect is still caused by entanglements, except when the polymer chains are too small, in which case the cause must be related to free volume. This explanation is unappealing if it is believed that the gel effect onset is caused by a single physical phenomenon.

A different picture to describe termination kinetics on the basis of "short−long" termination has emerged recently.[32−40] O'Shaughnessy[34] has advanced a theory to explain the kinetics during the gel effect on the basis of short−long termination. "Long" chains are those for which k_t decays with chain length N more strongly than N^{-1}; "short" chains are those for which k_t decays less strongly. Since the only reasonable physical picture for which k_t may show this strong a dependence on N is for translational diffusion control of entangled chains, the difference between "short" and "long" is said to be "entangled" or "unentangled". This picture postulates that during the gel effect the termination of a long chain becomes so hindered due to diffusional limitations that it can only terminate when a short chain diffuses into its vicinity. As the population of short chains is presumably small at this point, the overall rate of termination decreases strongly.[78] This theory deviates from classical kinetics with two major results: R_p in the gel effect regime is independent of initiation rate, and the mean living chain length is inversely proportional to the initiation rate. Experimental tests of this model have not yet appeared. A second model related to "short−long" termination[79] comes from the work of Gilbert and co-workers[36−38] and Russell,[39] who have also provided limited experimental evidence[38,80] which seems to correlate well with their model but does not constitute convincing proof of the short−long hypothesis. (The success of a model in fitting data does not constitute strong evidence for the validity of the model, as discussed previously.) Faldi et al.[41] have also suggested short−long termination as a means of describing their data, which shows that the concentration dependence of k_t for MMA polymerization more closely resembles that of the self-diffusion of short PMMA chains than that of the self-diffusion of longer chains.

It is clear that experimental tests are needed to distinguish critically among the theoretical pictures claiming to explain the origin of the gel effect. Given the more than 50-year history of this area, surprisingly few studies report even conversion as a function of time over a range of experimental conditions. (An outstanding review of such work has recently appeared.[81]) Of the available studies, most have not used conditions conducive to discerning between models or theories. If the gel effect is said to be linked to a specific physical phenomenon, it is only logical to work under experimental circumstances where this phenomenon is reduced or eliminated and to investigate whether the gel effect disappears or remains present. The purpose of the present work is to perform such critical tests, in particular with regard to the concept of entanglements forming the physical basis for the origin of the gel effect.

Experimental Section

Styrene and methyl methacrylate (Aldrich) were purified and dried by mixing with commercial inhibitor remover replacement packing and calcium hydride for several hours, and then filtering. 2,2-Azobis(isobutyronitrile) (AIBN) (Pfaltz and Bauer) and benzoyl peroxide (Aldrich) were used as received. Monodisperse polymer was purchased from Pressure Chemical or synthesized anionically.

Free radical polymerization was performed by combining monomer, initiator, and (if applicable) predissolved polymer, and placing a known amount of this solution (typically ~5 mL) into several test tubes (typically ~15 mL tubes). The tubes were sealed with rubber stoppers, purged of oxygen by a nitrogen stream, and placed in a constant temperature water bath, with one of the tubes containing a wire thermocouple. The tubes were then removed from the bath at different times and frozen with liquid nitrogen to stop the reaction. The contents were dissolved in methylene chloride, precipitated in methanol or hexane, dried in a vacuum oven at 110 °C, and weighed for conversion. The tube containing the thermocouple provided a temperature profile throughout the polymerization. (The presence of the thermocouple had no observable effect on the reaction, in contrast to previous reports using a different experimental setup.[60]) Molecular weight characterization was performed by gel permeation chromatography (GPC) using tetrahydrofuran as solvent and monodisperse polystyrene and PMMA standards for calibration.

Results and Discussion

It is well accepted that formation of entanglements is intimately related to polymer molecular weight, M. Therefore, if formation of entanglements is at the heart of the gel effect, certain relationships are expected to exist between M and the conversion level at which the gel effect onset occurs. Specifically, in bulk polymer, it is believed that entanglement phenomena are present only if M is above some critical value, defined as $M_{c,bulk}$. Thus, at a minimum, free radical polymerization systems with $M < M_{c,bulk}$ cannot be entangled and would not be expected to undergo the gel effect if the entanglement explanation is valid. In addition, even chains of high molecular weight ($M > M_{c,bulk}$) cannot be entangled at low polymer concentrations, as solvent dilutes out entanglement contacts. A simple estimate of the critical molecular weight for entanglement formation in solution, $M_{\mathrm{c,soln}}$, is given by the following:[82,83]

$$CM_{\mathrm{c,soln}} \approx (\rho M_{\mathrm{c,bulk}})^{a} \qquad (2)$$

where C is the polymer concentration, ρ is the bulk polymer density, and a is in the range 1.0−1.2. Equation 2 illustrates that $M_{\mathrm{c,soln}}$ is considerably higher than $M_{\mathrm{c,bulk}}$ for low polymer concentrations, which is important as bulk free radical polymerization occurs in solution with monomer as solvent. Thus, for the gel effect to be related to entanglements, M must not only exceed $M_{\mathrm{c,bulk}}$ but should be higher than $M_{\mathrm{c,soln}}$.[84] In addition, it is clear from eq 2 that the entanglement explanation predicts that the gel effect should occur at lower conversions when higher molecular weight polymer is formed, as entanglements form at lower polymer concentrations for higher M. Since M is easily accessible experimentally, these principles offer the opportunity to define experiments which critically examine the relationship between the gel effect and M, thus testing the relationship between the gel effect and entanglements.

Figure 1A illustrates such a test. Conversion−time results are presented for bulk MMA polymerizations at 50 °C with five initiator (AIBN) concentrations. The polymerizations at the two lowest initiator concentrations are from the classic data of Balke and Hamielec,[60] while the three at higher initiator concentrations are from the present work. This type of plot, using data taken at a common polymerization temperature with a varying initiator concentration, is fairly common in the gel effect literature and offers a first test of the relationship between the gel effect and entanglements. In particular, since higher initiator concentrations result in lower M, as is the case here (Table 1), one would expect on the basis of entanglement arguments to observe the gel effect occurring at lower conversions when lower initiator concentrations are used. It has been argued[58] that the critical polymer concentration for the gel effect onset, C_{crit}, should scale as $M_{\mathrm{n}}^{-0.5}$, where M_{n} is the number-average molecular weight, if entanglements control the onset. (This is a conservative estimate of the molecular weight dependence as eq 2 would suggest $C_{\mathrm{crit}} \sim M_{\mathrm{n}}^{-1}$.) Whether or not this trend exists can thus serve as a potential test of the entanglement theory.

This leaves us with the problem of how exactly to define C_{crit} experimentally. This is troublesome given that the gel effect onset is actually a gradual phenomenon which cannot be characterized by an easily determined onset conversion, despite various attempts to do so.[67,75] One possibility is to use the fact that these polymerizations are typically nonisothermal during the gel effect, as seen in the temperature−time data presented in Figure 1B. Since a temperature spike is usually a characteristic of the gel effect, it may seem possible to define the onset time based on the time at which this spike commences. However, like the conversion data, the temperature data reveal a gradual transition to gel effect kinetics, making it difficult to define a specific time for the onset. In addition, the temperature data are affected by heat transfer, and thus are influenced by the position of the thermocouple in the tube and the experimental time scale.

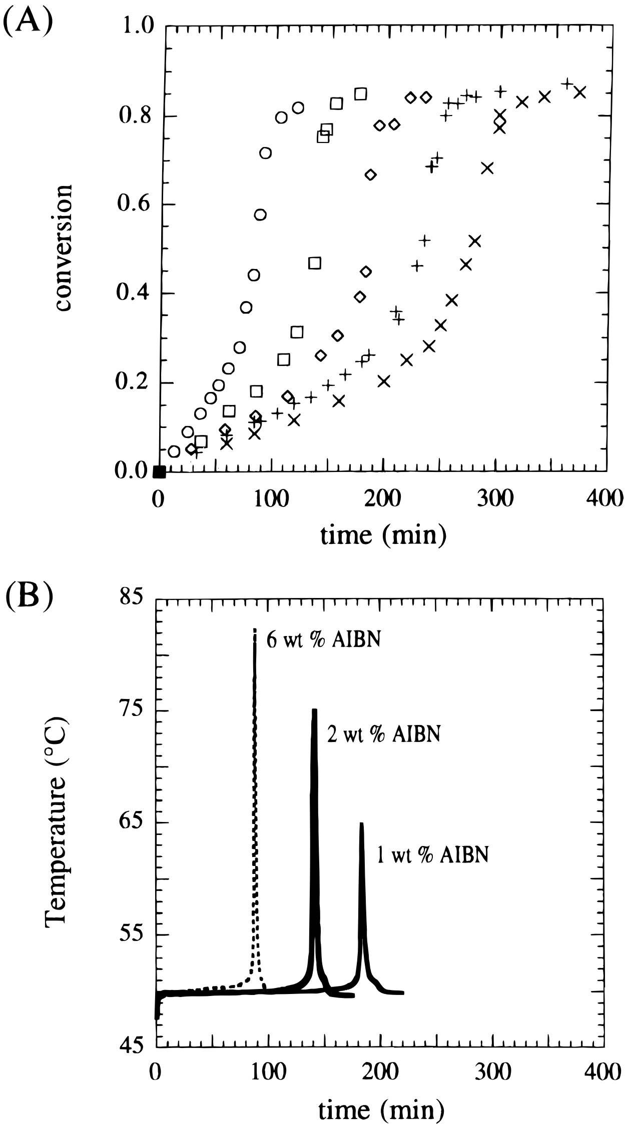


Figure 1. (A) Conversion and (B) temperature as a function of time for MMA polymerizations at 70 °C and five different initiator (AIBN) concentrations: (○) 6 wt %; (□) 2 wt %; (◇) 1 wt %; (+) 0.5 wt %; (×) 0.3 wt %. Data at the two lowest initiator concentrations are taken from Balke and Hamielec.[60] Temperature data in (B) are not reported for these conditions. Note that the height of the temperature peak in this and all subsequent figures is not necessarily a reliable measure of the severity of the gel effect, as it depends on such factors as placement of the thermocouple in the test tube.

Another possibility is to define an onset concentration as the intersection of two straight lines, one drawn through the low conversion data on a conversion−time plot, the other drawn through the data during the gel effect regime. This method is flawed because it depends on the slope of conversion−time data taken during the gel effect, which may be unreliable because of the short time scales involved and the nonisothermal nature of the system, which can cause a higher slope than if the system were perfectly isothermal.[5] This can lead to a high estimate for C_{crit}.

A third potential method has been outlined by Lee and Turner,[75] who defined the gel effect onset as the conversion at which the conversion−time data first deviate from the classical kinetics defined in eq 1. This method takes advantage of the fact that eq 1 can be solved in terms of fractional monomer conversion, x, to the following form:

$$-\ln(1 - x) = (fk_{\mathrm{d}}[\mathrm{I}]/k_{\mathrm{t}})^{1/2}k_{\mathrm{p}}t \qquad (3)$$

Table 1. Molecular Weight and Conversion Data for MMA Polymerizations at 50 °C[a] and Varying AIBN Concentrations (from Figure 1)

conditions	time (min)	fractional conversion	M_n	M_w
1 wt % AIBN	58.5	0.094	160 700	387 100
	114	0.168	151 100	393 300
	143	0.260	164 800	407 300
	158	0.304	177 200	769 500
	182.5	0.447	186 400	1 150 000
	193	0.777	234 900	1 309 000
	220	0.839	250 100	1 445 000
2 wt % AIBN	62	0.136	121 200	258 100
	86	0.180	115 700	250 600
	110	0.251	119 400	283 400
	137	0.466	143 400	726 400
	146	0.769	145 000	789 200
	175	0.849	168 900	973 000
6 wt % AIBN	25	0.090	71 100	147 400
	45	0.165	68 000	138 000
	52.5	0.194	70 800	140 000
	61	0.232	73 800	149 000
	76	0.367	76 600	156 700
	88	0.576	93 100	404 000
	105	0.796	89 200	374 700

[a] Note that during the gel effect the polymerizations do not remain isothermal (see Figure 1).

where *t* is time. From eq 3, a plot of $-\ln(1 - x)$ versus time should be linear as long as classical kinetics apply and initiator concentration is nearly constant. Although this method is systematic and independent of mechanistic descriptions of the gel effect, it assumes a constant k_t, ignoring the effects of increasing polymer concentration in reducing k_t due to increasing resistance to diffusion. As a result, this method probably gives a somewhat low estimate for the onset concentration.[85]

Tulig and Tirrell[58,67] approached this problem in the context of their computational model, which has as one of its adjustable parameters a critical concentration at which the kinetics are switched to a reptation-based description. Since this "switch" in the physical basis of the model at an adjustable conversion level invariably results in a sharp increase in the predicted R_p, the model is able to exhibit the characteristic change in slope of a conversion−time curve, with the conversion level at which this switch is executed offering an obvious estimate of the onset conversion. However, this method of estimation is dependent on the validity of the model's architecture, which is unclear at this time. In fact, since this method of estimating C_{crit} is based on a description derived from reptation, the resulting numbers may be biased toward an entanglement picture and therefore may not be suitable for testing the validity of this picture.

Given the options available, we have chosen simply to estimate both a high and low value for C_{crit} in order to define an effective range of values over which the gel effect onset occurs. To this end, we have analyzed the data using the second and third methods outlined above. The results appear in Figure 2 as a function of number-average molecular weight, M_n. In the form given, a negative slope would indicate the expected (based on entanglement arguments) trend of a lower C_{crit} for higher M_n. In our opinion, the data as illustrated in Figure 2 exhibit no clear trend, i.e., *C_{crit} is not a significant function of M_n*. In any event, the most that could be said is that if such a trend exists, then it is very weak. Tulig and Tirrell,[58,67] who analyzed data by other researchers, determined a much weaker dependence than predicted by reptation scaling. Although their results have been used to justify the entanglement picture, such data clearly do not support the idea that the gel effect is caused by a slowing of the translational diffusion of entangled chains.[86] In fact, even for systems which are clearly entangled, such as the room temperature styrene polymerizations of Ito[76] in which the *M* values are in the millions, there is no strong trend for C_{crit} as a function of *M*.

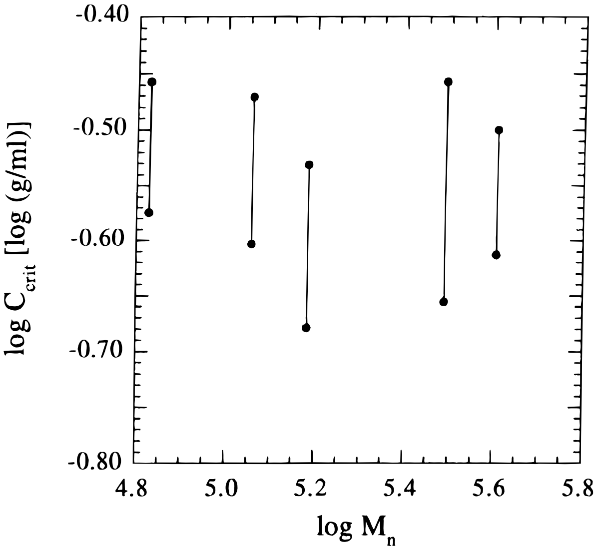


Figure 2. High and low estimates for the critical concentration at the onset of the gel effect for the data in Figure 1 as a function of number-average molecular weight of the polymer in the system prior to the gel effect onset.

In addition to these issues, the *M* values in Table 1 are not necessarily high enough to support the claim of entanglement effects. In particular, the data for 6 wt % AIBN ($M_n \sim 70\,000$; $M_w \sim 140\,000$) are probably too low for entanglement formation for PMMA in a 25 wt % solution, roughly the conversion level for the gel effect onset in this case. Given eq 2 and a value of $M_{c,bulk} \approx 31\,000$[87] for PMMA, one would expect $M_{c,soln}$ to be at least 150 000 for this case. Thus, the *M* values for these experiments must be considered borderline at best in relation to entanglement formation. Furthermore, critical examination of the work of Balke and Hamielec[60] indicates that some of their *M* values are not high enough to strongly support entanglement arguments, particularly those taken at 90 °C, where M_n values as low as 40 000−50 000 and M_w values as low as 90 000 are reported prior to the gel effect. As has been pointed out[88] in the context of viscoelasticity experiments, caution should be exercised in attributing effects to entanglements when the systems cannot possibly be entangled. Although the cases outlined above do not necessarily support such a strong statement, it is clear that the *M* values in gel effect systems should be examined carefully before assumptions are made about entanglements.

Chain transfer is cited as a means by which to delay or eliminate the gel effect.[10,89] The explanations given for this usually relate to the shorter chain lengths present in such systems, in accordance with the view that higher *M* values result in lower values of C_{crit}. Those wishing to explain the gel effect in terms of entanglements can point to chain transfer as a means of eliminating or delaying entanglement formation. However, chain transfer can also be used to test whether the gel effect occurs in the absence of entanglements. Figure 3 shows conversion and temperature as a func-

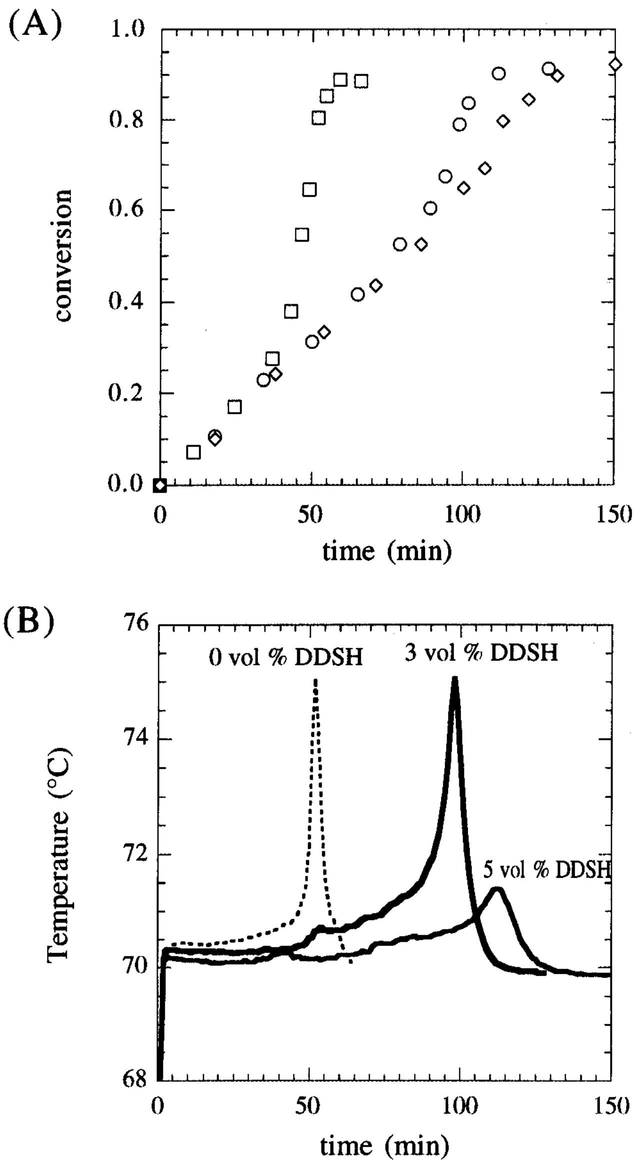


Figure 3. (A) Conversion and (B) temperature as a function of time for MMA polymerization at 70 °C, 0.5 wt % AIBN initiator, and three different concentrations of dodecanethiol (chain transfer agent): (□) 0 vol %; (○) 3 vol %; (◇) 5 vol %.

Table 2. Molecular Weight and Conversion Data for MMA Polymerizations at 70 °C[a] with 0.5 wt % AIBN and Varying Chain Transfer Agent (DDSH) Concentrations (from Figure 3)

conditions	time (min)	fractional conversion	M_n	M_w
no DDSH 0.5 wt % AIBN	11	0.072	73 500	138 500
	24.5	0.169	81 100	139 500
	37	0.276	73 000	153 300
	43	0.379	78 100	159 400
	46.5	0.546	74 800	293 200
	49	0.644	76 400	350 200
	52	0.804	67 600	315 000
	54.5	0.853	69 100	335 500
	59	0.885	74 200	330 600
3 vol % DDSH 0.5 wt % AIBN	18	0.105	5400	14 800
	34	0.229	5200	15 800
	50	0.312	4900	14 900
	65	0.416	4500	14 500
	79	0.524	5200	15 000
	89	0.603	4900	15 400
	98.5	0.789	4600	15 100
	101.5	0.836	4700	14 700
	128	0.913	4400	15 100
5 vol % DDSH 0.5 wt % AIBN	18	0.100	4000	9 100
	38	0.242	3800	9 200
	54	0.333	3900	8 900
	71	0.435	4000	9 600
	86	0.524	3800	9 200
	100	0.648	3600	8 900
	107	0.692	3300	8 700
	113	0.797	3400	9 100
	121.5	0.845	3600	8 900
	131	0.913	3400	9 000

[a] Note that during the gel effect the polymerizations do not remain isothermal (see Figure 3).

tion of time for MMA polymerizations at 70 °C with 0.5 wt % AIBN and three different chain transfer agent (*n*-dodecanethiol) concentrations: 0, 3, and 5 vol %. The gel effect clearly occurs at higher conversions when more chain transfer agent is present, as expected. More importantly, although the "severity" of the gel effect is mitigated by chain transfer in the latter two systems, the conversion and temperature data clearly indicate that autoacceleration was present in both systems containing chain transfer agent. These systems, particularly the 5 vol % run, are interesting because they represent the extreme case where the gel effect is significantly delayed but not eliminated. If one is interested in the origin of the gel effect, it is perhaps more instructive to investigate such cases rather than the typical experiments where the gel effect is more prevalent. If the gel effect is related to entanglements, one would expect M in these two experiments to correspond roughly to the value necessary to begin to observe entanglement effects. Thus, M data for these studies, shown in Table 2, are particularly useful. As $M_{c,\mathrm{bulk}} \approx 31\,000$[87] for PMMA, at the gel effect onset M must be considerably higher than 31 000 for entanglements to affect these systems. Using eq 2[90] with $a = 1.0$, $M_{c,\mathrm{soln}}$ for 60% PMMA in MMA (roughly the onset conversion for the 3 vol % case) is estimated to be about 48 000, and that for a 70% solution (roughly the onset conversion for the 5 vol % case) to be about 42 000. However, Table 2 reveals that the molecular weights formed in these polymerizations were far below these levels, with M_w about 15 000 and 9000, respectively. In fact, these values are far below even $M_{c,\mathrm{bulk}}$. These systems could not have been entangled either at the onset of or during the gel effect.[84] Thus, the absence of entanglements does not eliminate the gel effect.

A *classic* signature of the gel effect, the pronounced increase in M_w and polydispersity at high conversion, is not present in the data in Table 2 with excessive chain transfer agent. However, this should not be taken to indicate the absence of the gel effect. Rather, this is exactly what would be expected on the basis of simple kinetic arguments. In particular, chain lengths are related to the ratio $R_p/(R_t + R_{tr})$ where R_t is the rate of termination and R_{tr} is the rate of chain transfer. If R_{tr} is much greater than R_t, i.e., chain transfer is the dominant mechanism for dead chain formation, then a decrease in R_t associated with the gel effect would be expected to have little effect on chain lengths. Since these systems have extremely high chain transfer agent concentrations, the observed results are as expected. This fact illustrates a flaw in recent attempts[91] to characterize the gel effect on the basis of changing molecular weight distributions. Clearly, this method cannot be generally used, as an increased polydispersity is not a *universal* signature of the gel effect.

Figure 4 illustrates further MMA chain transfer experiments in which the chain transfer agent concentration is maintained at a constant level (3 vol % dodecanethiol) while the initiator concentration is var-

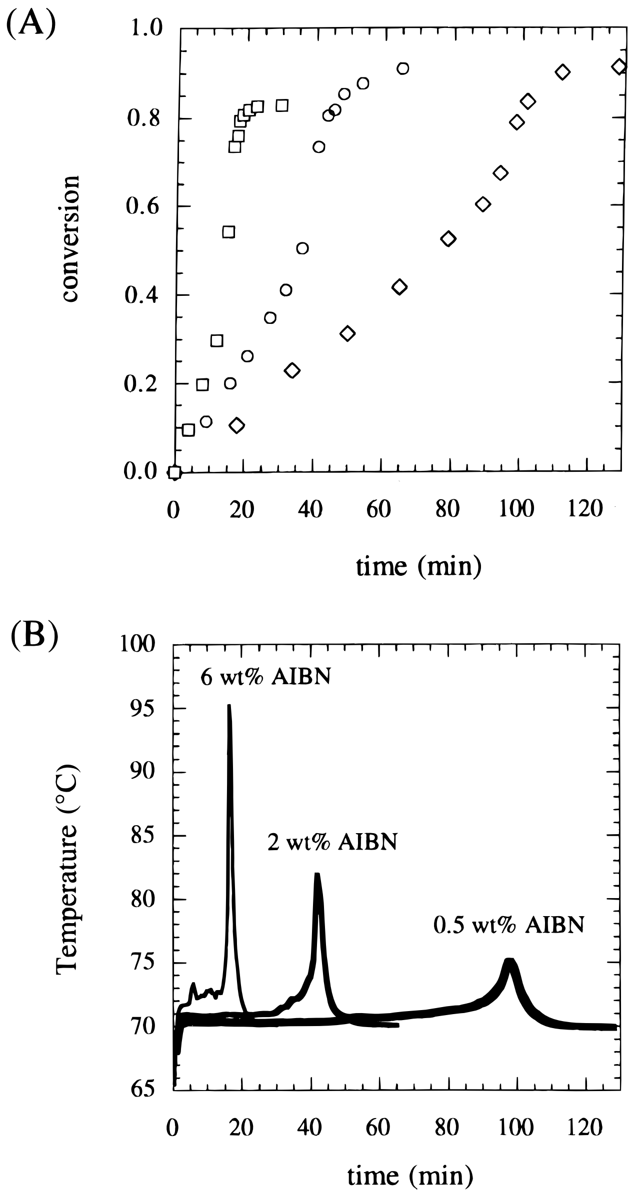


Figure 4. (A) Conversion and (B) temperature as a function of time for MMA polymerization at 70 °C, 3 vol % dodecanethiol, and three different AIBN concentrations: (◇) 0.5 wt %; (○) 2 wt %; (□) 6 wt %.

ied. All data were taken at 70 °C, and three initiator (AIBN) concentrations were employed: 0.5, 2, and 6 wt %. M data are presented in Table 3. As before, both the conversion and temperature data irrefutably indicate the presence of the gel effect in all three cases. Two important points arise. First, the M data for these systems are far below the levels necessary to begin to consider entanglement phenomena. In fact, these data indicate the absence of entanglements even more strongly than those in Figure 3, with M_n and M_w as low as 3000 and 8000, respectively. (Polydispersities do not change appreciably during the gel effect due to excessive chain transfer, as described above.) Second, analysis of the three conversion−time curves reveals that the trend for C_{crit} as a function of initiator concentration (and thus M) is actually reversed from that expected from the entanglement theory, with the 6 wt % AIBN case (lowest M) undergoing the gel effect onset at roughly 35−40% conversion, the 2 wt % AIBN case at roughly 50−55% conversion, and the 0.5 wt % AIBN case (highest M) at roughly 60−65% conversion. This also refutes the notion that the gel effect onset is related to entanglements.

Table 3. Molecular Weight and Conversion Data for MMA Polymerizations at 70 °C[a] with 3 vol % Chain Transfer Agent (DDSH) and Varying AIBN Concentrations (from Figure 4)

conditions	time (min)	fractional conversion	M_n	M_w
3 vol % DDSH 2 wt % AIBN	9	0.114	4600	11 400
	16	0.200	4400	11 600
	21	0.261	4700	11 900
	27.5	0.347	4200	10 900
	32	0.410	4300	10 800
	36.5	0.504	4200	11 300
	41	0.734	3800	11 100
	45.5	0.818	3900	10 800
	48	0.854	3800	10 700
	65	0.909	3700	10 900
3 vol % DDSH 6 wt % AIBN	4	0.095	3500	9 100
	8	0.197	3600	9 300
	12	0.298	3200	8 100
	15	0.542	3400	7 900
	16.5	0.736	3000	7 600
	19	0.807	2900	7 400
	23	0.827	3000	7 500
	30	0.829	3100	8 200

[a] Note that during the gel effect the polymerizations do not remain isothermal (see Figure 4).

It may be possible to explain these data on the basis of short−long termination, in accordance with other recent work,[38,41] in the following manner. If termination is dominated by short−long events, then the "short" radicals in these systems are only a few monomer units long. Since addition of one monomer unit onto a very short chain will affect its diffusion more so than an equivalent addition onto a somewhat larger chain, the diffusion of "short" chains may be slowed significantly at an earlier conversion for the systems with higher initiator concentrations. Thus the gel effect occurs earlier. However, such an explanation for these results requires that "short" and "long" not be related to entanglement phenomena. Since these polymerizations, particularly the 6 wt % AIBN case, occurred over rather short time scales compared to typical systems, this series of experiments was repeated at 50 °C. These data appear in Figure 5 and Table 4. In all three cases, the gel effect occurs despite low M values. At 50 °C, it appears that the onset conversion is approximately independent of initiator concentration, with a C_{crit} of 45−50% monomer conversion. The fact that the trend at 70 °C apparently is absent at 50 °C indicates that the onset of the gel effect is influenced by factors more complicated than just the molecular weight produced.

These results conclusively show that the gel effect can occur in a variety of conditions in the absence of entanglements. Still unclear is whether the molecular weight of the "dead" polymer in the system has any effect on the gel effect onset. To test this, the effect of predissolved polystyrene (PS) on styrene polymerization was studied. Such experiments have a long history in the gel effect literature,[2,19−21,75] as many have sought to investigate the effect of addition of high molecular weight polymer prior to polymerization. However, our focus is on the addition of low molecular weight polymer. Addition of unentangled polymer has two effects: it decreases the free volume (increases the microviscosity) relative to pure styrene while delaying the onset of entanglements to a higher overall polymer concentration. Thus, if addition of low molecular weight, unentangled PS prior to styrene polymerization delays the

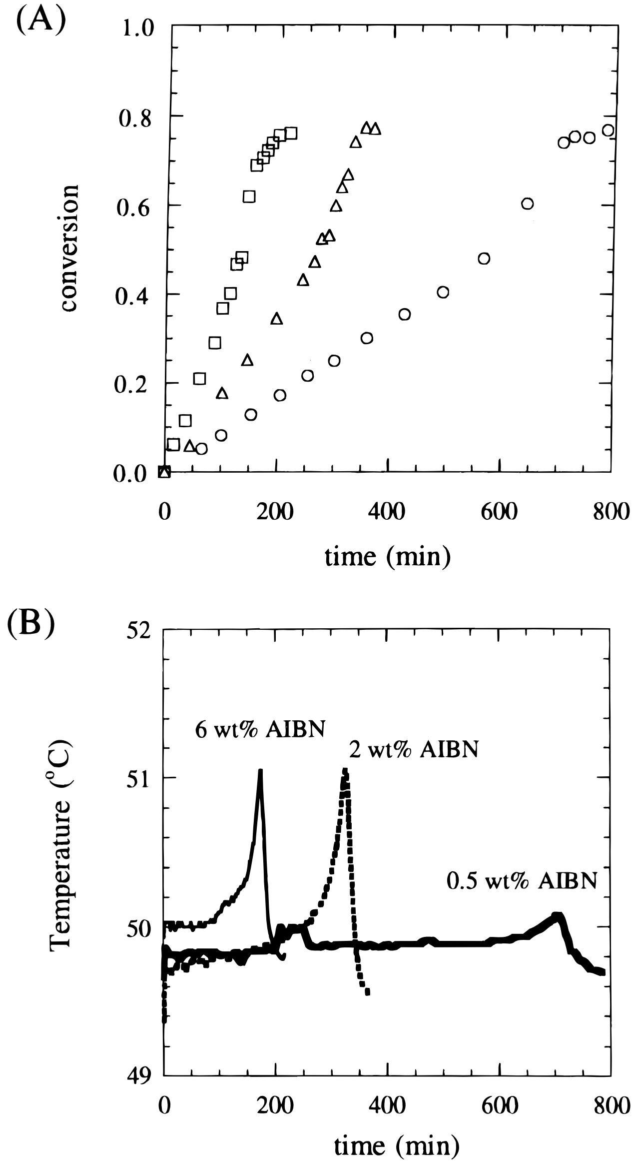


Figure 5. (A) Conversion and (B) temperature as a function of time for MMA polymerization at 50 °C, 3 vol % dodecanethiol, and three different AIBN concentrations: (○) 0.5 wt %; (△) 2 wt %; (□) 6 wt %.

gel effect, this would be consistent with entanglement theories; in contrast, an earlier gel effect would be consistent with free volume, as free volume should be relatively unaffected by M.

Figure 6 shows the effect of addition of 20 wt % monodisperse 4k PS ($M_n = 3600$; $M_w = 3800$) on styrene polymerization at 60 °C with 0.1 M (1.8 wt %) AIBN. Data with and without predissolved polymer are shown, and the data for the system with predissolved PS are plotted in two ways: total polymer concentration versus time and percent conversion of monomer versus time. The molecular weights produced are not reported in detail because the predissolved PS contributes to the overall distribution, making it difficult to discern the exact molecular weight of only the polymer formed during the polymerization. However, since the 4k PS is represented by a large peak on one end of a GPC chromatogram of these samples, it was possible to subtract out much of this contribution to the overall distribution. Estimates of the molecular weights of the formed PS using this technique indicate that predissolved PS has no significant effect, with both systems producing molecular weights on the order of M_n = 80 000 and M_w = 150 000 prior to the gel effect. Several points arise from these data. First, the presence of the predissolved PS had relatively little effect on the initial R_p. Second, the gel effect onset for the system with predissolved PS occurred at an earlier conversion level, and at approximately the same overall polymer concentration, as the system with no predissolved PS. Since the overall molecular weights in the first system were lower due to the presence of the 4k PS, entanglements would have formed later for this system. The fact that the gel effect occurs earlier contradicts the notion that entanglements are a major factor in determining C_{crit}. Furthermore, the fact that the overall polymer concentrations at the time of onset were roughly equal is consistent with free volume pictures.

Table 4. Molecular Weight and Conversion Data for MMA Polymerizations at 50 °C[a] with 3 vol % Chain Transfer Agent (DDSH) and Varying AIBN Concentrations (from Figure 5)

conditions	time (min)	fractional conversion	M_n	M_w
3 vol % DDSH 0.5 wt % AIBN	101	0.081	6900	14 200
	154.5	0.128	6800	14 400
	205	0.172	6600	15 600
	302	0.250	6400	14 800
	360	0.301	5500	12 500
	495.5	0.403	4700	11 700
	568	0.481	5500	11 900
	644	0.604	4900	11 600
	708	0.741	4800	11 400
	786	0.768	4600	11 200
3 vol % DDSH 2 wt % AIBN	45	0.058	6300	14 600
	102	0.178	6300	14 800
	147	0.251	5800	14 100
	198	0.346	6100	14 300
	265	0.473	5300	13 900
	290	0.532	6000	13 800
	311	0.640	5000	12 400
	334	0.742	4500	12 200
	368	0.772	4600	12 000
3 vol % DDSH 6 wt % AIBN	36	0.114	6900	14 100
	61	0.209	6600	13 800
	88	0.290	6200	14 300
	115	0.402	5900	13 600
	135	0.483	6100	13 900
	145	0.620	5700	12 900
	169	0.706	5400	12 300
	198	0.757	4900	11 700
	217	0.761	5500	12 500

[a] Note that during the gel effect the polymerizations do not remain isothermal (see Figure 5).

The same experimental circumstances were used to study the effects of molecular weight and concentration of predissolved polymer. In one series of experiments, three different predissolved, monodisperse PS molecular weights were used: 4k, 76k (M_n = 69 800; M_w = 76 000), and 314k (M_n = 276 300; M_w = 314 000). These results, presented in Figure 7, indicate that the molecular weight of the background polymer has essentially no effect for this system, with the gel effect onset occurring at roughly the same time and onset conversion, within experimental error. The effect of predissolved PS concentration was studied by repeating the conditions in Figure 6 with 50 wt % 4k PS. These results, shown in Figure 8, also indicate that the gel effect is related more closely to the overall polymer concentration, as the onset was at roughly 70 wt % polymer, only slightly higher than the level observed when 20 wt % 4k PS was added. Also, since so much 4k PS was predissolved, most of the polymer in the system at the time of the gel

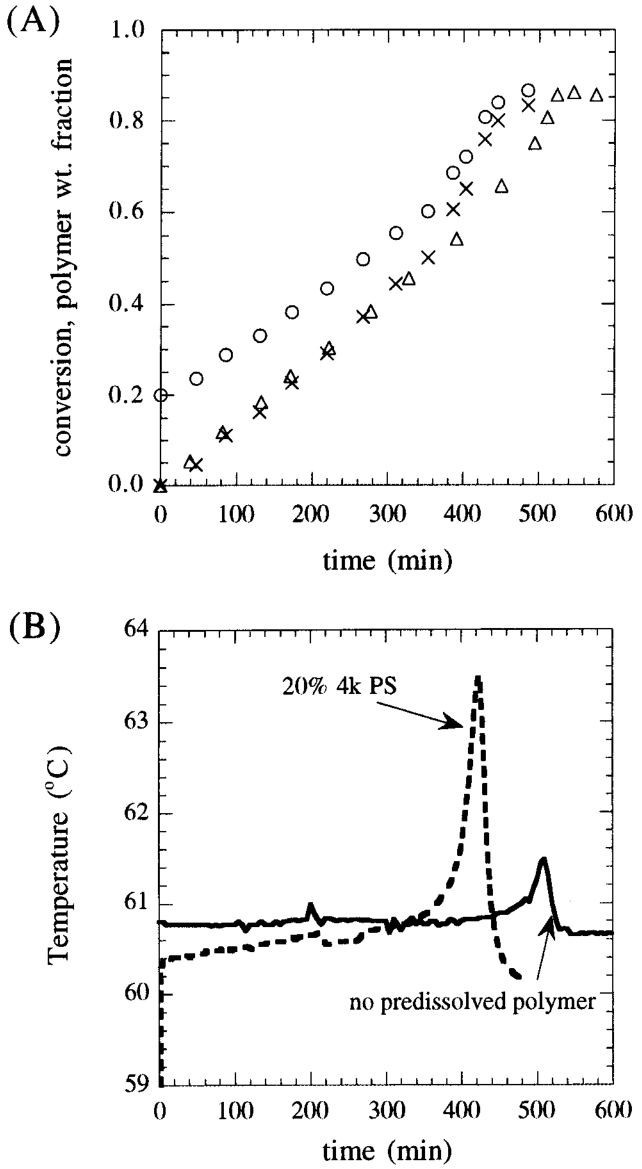


Figure 6. Comparison of styrene polymerization at 60 °C with 0.1 M AIBN with a polymerization run under the same conditions with 20% 4k PS predissolved in the reaction mixture. (A) shows (△) fractional conversion of monomer when no polymer is predissolved, (×) fractional conversion of monomer when 20% 4k PS is predissolved, and (○) total polymer weight fraction when 20% 4k PS is predissolved as a function of time. (B) reports temperature data for these two polymerizations.

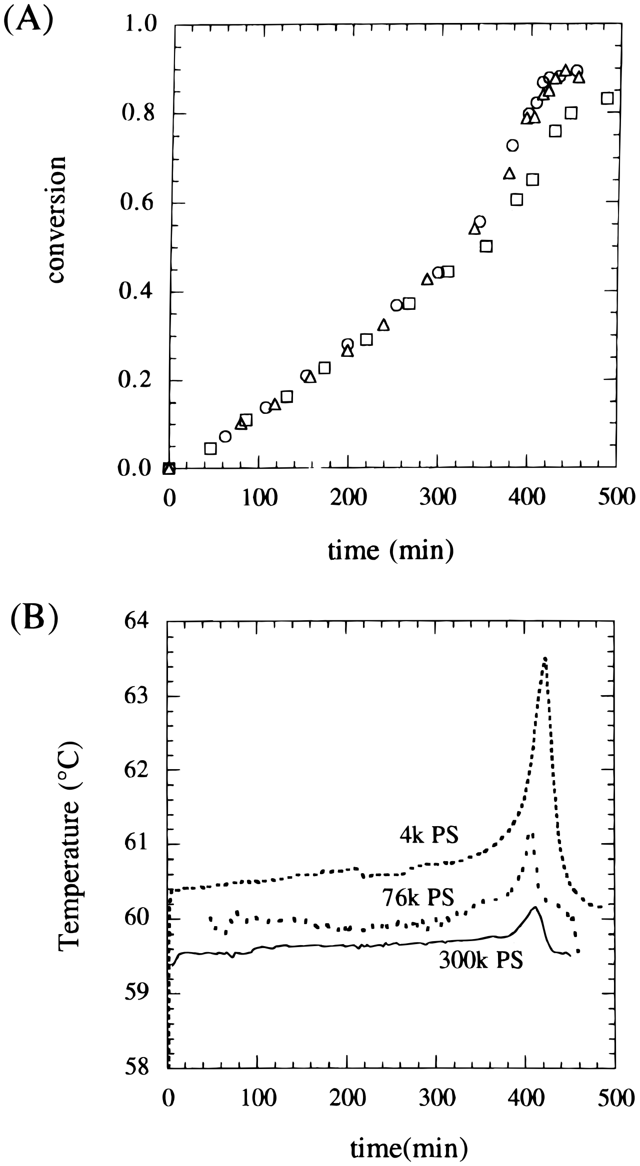


Figure 7. Styrene polymerization at 60 °C with 0.1 M AIBN with 20% PS of three different monodisperse molecular weights predissolved in the reaction mixture. (A) shows fractional conversion of monomer for (□) 4k PS, (○) 76k PS, and (△) 300k PS. (B) reports temperature data for all three polymerizations.

effect onset was far too low in molecular weight to contribute to entanglement formation.

These results conflict with the common idea that the molecular weight of the polymer in the system plays a significant role in determining the gel effect onset conversion. In retrospect, most of the experimental evidence used to support this belief has been taken by varying either the initiator concentration or the temperature in the system, both of which affect *M*. However, these types of experiments also affect other parameters which may play some role in causing the gel effect, such as microviscosity or free volume (when temperature is varied) or the distribution of "short" and "long" growing chains in the system (when initiator concentration is varied). Therefore, interpretation of such results may be misleading. One interesting result that may indicate some dependence of the gel effect onset concentration on *M* has been reported that avoids these specific uncertainties. Abuin et al.[92] have claimed that, when the rate of initiation is switched via photoinitiation effects from high to low during an MMA polymerization, the gel effect occurs at a higher conversion than when the initiation rate is maintained low throughout. Comparison of these two polymerizations suggests that the chain lengths of the propagating radicals are the same at their respective onset conversions but that the molecular weight of the dead polymer is lower for the first system. However, since the onset conversion identified by their technique for the lower initiation rate is anomalously low (~12 wt % conversion for polymerization at 77 °C), the meaning of these results is in question. While it is clear that the data reported in the present work do not constitute conclusive proof that *M* has absolutely no effect on the gel effect onset, it is equally clear that no strong evidence has been reported that establishes this link either. This is central to understanding the origin of the gel effect, especially given that a strong *M* dependence would support the idea of translational diffusion control of k_t while a lack of *M* dependence would support the idea of

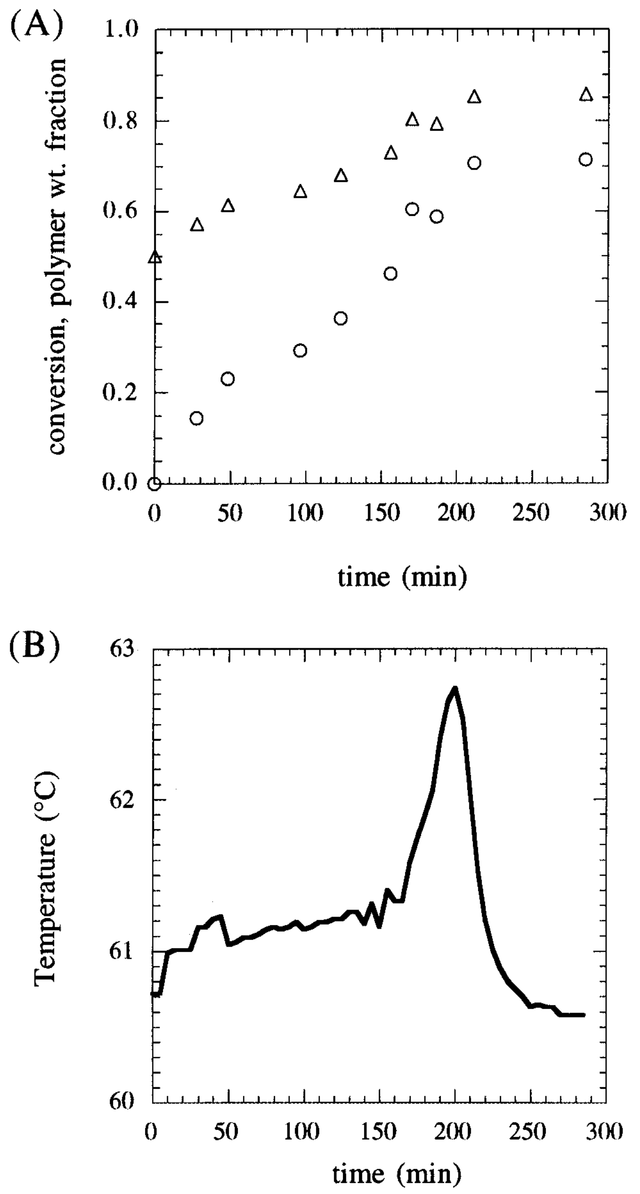


Figure 8. Styrene polymerization at 60 °C and 0.1 M AIBN in which 50 wt % monodisperse 3k PS is predissolved into the reaction mixture. (A) shows both (○) fractional conversion of monomer and (△) total polymer weight fraction as a function of time. (B) shows temperature as a function of time.

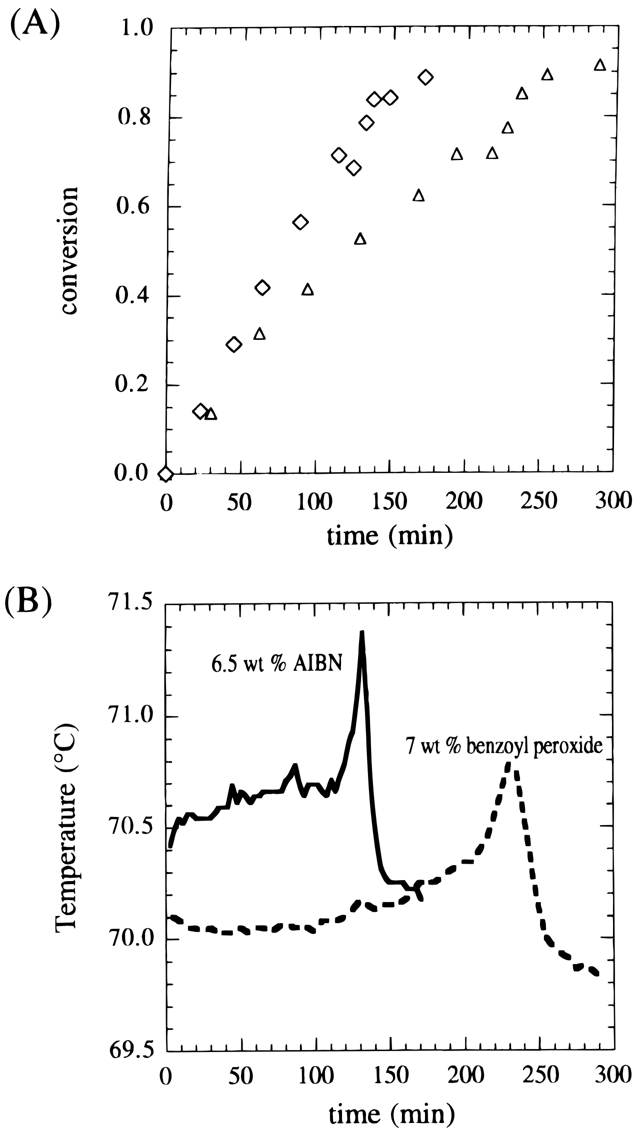


Figure 9. (A) Conversion and (B) temperature as a function of time for styrene polymerizations at 70 °C using two different initiator conditions: (◇) 6.5 wt % AIBN; (△) 7 wt % benzoyl peroxide.

segmental diffusion control of k_t at conversions typical of the gel effect onset.

The gel effect can be observed in the absence of entanglements for styrene polymerizations just as in MMA polymerizations. However, since styrene exhibits a much less dramatic gel effect than MMA under normal circumstances, and since running under extreme conditions where very low molecular weights are formed (high temperature and/or initiator concentration) tends to suppress the gel effect somewhat for styrene, the conversion−time data do not always provide compelling evidence of autoacceleration. Under these circumstances, monitoring the temperature as well as conversion can provide the necessary evidence for the gel effect, as the presence of a temperature peak is another indicator of this phenomenon. Such cases are shown in Figure 9 for styrene polymerizations at 70 °C with 6.5 wt % AIBN and 7 wt % benzoyl peroxide. Molecular weight data appear in Table 5. The temperature peak in each case indicates the presence of the gel effect, albeit at high conversion. As $M_{c,\mathrm{bulk}}$ for PS is approximately the same as for PMMA (31 000),[87] the molecular weight data in Table 5 are too low to consider the system entangled, either before or during the gel effect. These results are interesting in that addition of chain transfer agent was not necessary to achieve low *M* values (styrene polymerizations generally produce smaller chains than many other monomers under identical conditions).

Thus, the results presented here for MMA and styrene strongly indicate that the gel effect onset is not related to entanglements and that the gel effect is not caused by entanglement formation. The most compelling evidence for this is that many conditions involving high initiator concentration or the presence of chain transfer agent result in polymerizations where the gel effect is obviously present but where the molecular weight of the polymer produced is too low for entanglement formation not only in solution, i.e., polymer in monomer, but even in bulk polymer. (The neglect of the molecular weight requirement for entanglement may be the reason for the general misunderstanding of the lack of connection between the gel effect and entanglements. For example, some have asserted in explaining the gel effect that “as w_p (weight fraction polymer) increases,

Table 5. Molecular Weight and Conversion Data for Styrene Polymerizations at 70 °C[a] with Different Initiator Conditions (from Figure 9)

conditions	time (min)	fractional conversion	M_n	M_w
6.5 wt % AIBN	23	0.140	10 400	21 200
	45	0.289	10 500	20 200
	64	0.418	10 700	21 500
	89	0.564	10 100	22 700
	114	0.713	10 900	27 000
	124	0.684	10 200	27 000
	132	0.786	14 100	43 700
	137	0.837	15 800	55 000
	171	0.887	19 500	76 600
7 wt % BPO	30	0.135	9 200	23 900
	62	0.315	10 700	24 300
	94	0.414	10 900	25 700
	129	0.527	7 800	24 000
	168	0.623	8 500	23 800
	193	0.715	8 800	24 100
	217	0.717	10 200	24 900
	227	0.774	8 900	23 900
	236	0.851	8 600	22 900
	288	0.914	7 600	23 800

[a] Note that during the gel effect the polymerizations do not remain isothermal (see Figure 9).

short chains become entangled at lower and lower degrees of polymerization"[37] resulting in a lower average k_t, giving rise to autoacceleration. However, at typical gel effect onset conversions in MMA, only polymerizing chains with molecular weights of order 100 000 or greater could be entangled; few would claim such chain lengths to be short.[84])

Furthermore, even if it is asserted[68,73] that the gel effect is caused by entanglements for higher M systems and by free volume effects for lower M systems, the data presented here and in other studies do not support this claim. The "signatures" associated with the entanglement explanation are not present experimentally. For example, the expected significant M dependence of C_{crit} is not observed in polymerizations without chain transfer in this or other studies.[58,67] Where chain transfer is present, it is even possible to observe an M dependence of C_{crit} qualitatively opposite of that expected from entanglement arguments. In addition, no significant differences are observed in C_{crit} in studies employing different chain lengths and concentrations of matrix background polymer, some allowing for and others precluding entanglement of the polymerizing chains. Hence, the presence of autoacceleration over a broad range of polymerization conditions where entanglements cannot be present and, for conditions where entanglements may be present, an absence of the expected signatures of entanglement effects associated with the autoacceleration onset lead us to conclude that the gel effect is not caused by entanglements.

We note that this conclusion does not preclude the possibility that *during* the gel effect in some polymerizing systems entanglement effects may be able to play a role in determining the kinetics. This remains an open question, one that is invariably linked to the debate over whether the termination reaction is controlled by translational or segmental diffusion at various conversion levels. (While it has often been assumed that translational diffusion controls k_t at the onset conversion, there is little compelling evidence for or against this notion.) A molecular level theory by O'Shaughnessy[34] predicts that *during* the gel effect R_p for an entangled system (with entanglements controlling k_t) should be independent of initiator concentration, [I], if the gel effect occurs isothermally; this contrasts with the $[I]^{1/2}$ dependence given by eq 1. This prediction is difficult to test because of the nonisothermal nature of most gel effect systems as well as the uncertainties with taking conversion–time data during the fast kinetics associated with the gel effect. However, these problems can be avoided by performing slow polymerizations, over days or weeks. Such slow polymerizations result in very high molecular weights, virtually ensuring entanglements, a necessary condition of O'Shaughnessy's model. Although Ito[76] has performed such experiments for styrene, MMA is a better system to study, since the gel effect in MMA occurs over a much wider range of conversion. Tests of this type are underway in our laboratory.

Finally, many results of this study are seemingly consistent with explanations based on free volume. However, it is not our intention to leave the impression that such a simple picture can alone account for the whole range of gel effect phenomena. On the contrary, the results observed for MMA polymerizations with significant chain transfer (Figure 4) cannot be reduced to simple free volume explanations. In addition, a set of experiments reported in the classic paper by Norrish and Smith[1] also may indicate an inadequacy associated with simple free volume models. These authors studied MMA solution polymerizations with solvents of different thermodynamic quality. They observed a trend for a lower gel effect onset concentration with poorer solvent. Their explanation was that poorer solvents result in higher molecular weight polymer, increasing the bulk viscosity of the system, leading to an earlier gel effect. However, it has since been established that bulk viscosity is not an indicator of the gel effect, as previously explained. Furthermore, the results of the current work cast doubt on the validity of the belief that polymer molecular weight and gel effect onset concentration are related in a simple fashion. An alternative explanation of their results is that the solvent quality itself plays some nontrivial role in determining termination kinetics, a factor not considered by free volume models. (It has been shown that k_t in poor solvents is diminished compared with that in bulk monomer;[93] effects of solvent on free radical polymerization have been reviewed by Kamachi.[94] It has also been reported that solvent influences k_t significantly but in an unclear manner.[95]) A complicating factor is that closer examination of these data indicate that the solvents used by Norrish and Smith[1] line up in the same order whether they are arranged in terms of increasing solvent quality or increasing free volume in solution, as determined by parameters from the Vrentas–Duda free volume theory.[96] Preliminary results in our lab[97] indicate that even for solvents with similar free volume parameters, such as toluene and hexane, the thermodynamic quality has the same qualitative effect on the gel effect onset concentration as that reported by Norrish and Smith. More critical studies of the gel effect as a function of solvent thermodynamic quality/free volume and monomer species, as well as model experimental studies of chain-end reactions in polymer solutions, are ongoing[98–100] in order to establish a clearer understanding of the physical basis of the gel effect.

Summary

Perhaps the most commonly held view about the onset of the gel effect is that it is related to entanglements. This notion, popularized over the last 20 years, based on modeling of a limited range of experimental data, has not been adequately tested from an experimental standpoint. In the present work we have critically tested this theory and found it lacking. Simply put, eliminating or delaying the formation of chain entanglements does not result in a corresponding elimination or delay of the gel effect onset. The gel effect can and does occur in the absence of entanglements. Furthermore, even for systems which are most likely entangled, the onset of the gel effect does not correlate with molecular weight in a manner consistent with entanglement arguments. (Note that our scope in the present work is limited to the gel effect *onset*; entanglements, if present, may play a role in the kinetics of *some* systems *during* the gel effect.)

Previous work has sometimes suffered from misconceptions which have hindered progress in understanding the origin of the gel effect. One such mistaken notion is that polymer segmental diffusion is equivalent to mutual diffusion and thus increases in rate with polymer concentration. This idea leads inevitably to the belief that translational diffusion must control k_t at conversions typical of the gel effect,[54] as k_t is known to be decreasing at these conversions. However, since segmental diffusion rates decrease with conversion,[27] albeit not as rapidly as translational diffusion rates, the debate over which of these processes controls k_t remains unresolved. A second misconception has been the idea that the gel effect is characterized by a sudden and catastrophic drop in the termination rate at a specific conversion. If one believes this picture, then the entanglement explanation *sounds* right, as the onset of entanglements is a phenomenologically identifiable physical transition which can justify a sharp change in polymer diffusion rates. However, the reality is that there is a smooth rather than sudden transition involved in the gel effect. The rate of termination only needs to slow down enough with increasing polymer concentration that it falls out of balance with the rate of initiation. Once this happens, the situation becomes progressively worse: R_p rises due to the increased number of growing chains, causing the polymer concentration to rise at a higher rate, in turn causing termination to slow down yet further. With this explanation, any approach which provides for a significant enough dependence of k_t on concentration could potentially account for the gel effect without invoking some sudden change in the physics of the system. Further critical experiments examining free radical polymerization in the region of the gel effect[100] and the dependence of model chain-end interactions[98,99] on polymerization parameters are needed to determine the physical basis of this phenomenon.

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(78) In O'Shaughnessy's[34] original work, the gel effect onset was said to be caused by the depletion of short chains in the system, with the implication that entanglements are necessary for this to occur. However, the purpose of this theory is to predict kinetics during the gel effect; the onset could be related to some other factor such as the increasing microviscosity in the system rather than the formation of entanglements (O'Shaughnessy, personal communication, 1995) without changing the predictions of the model, as long as it is understood that short−long termination as described by the model would then dominate the kinetics only if the system became entangled during the gel effect.

(79) A troubling aspect of this model is the fact that k_t is said to be proportional to the *mutual* diffusion coefficient of the growing polymer chain ends, which, as explained in the Background, should have nothing to do with termination kinetics, at least beyond the dilute regime. This problem also arises elsewhere (Strukelj, M; Martinho, J. M. G.; Winnik, M. A.; Quirk, R. P. *Macromolecules* **1991**, *24*, 2488). However, we believe this to be largely a problem with terminology; it is apparent from refs 36−39 that the authors do not have in mind the classical definition of mutual diffusion, i.e., diffusion in the presence of a macroscopic concentration gradient, but instead calculate the mutual diffusion coefficient as the sum of the translational diffusion coefficients of two growing polymer chains. Since k_t should in fact be proportional to this sum if translational diffusion controls the termination rate, it appears that their model is not invalidated by this methodology. However, given the misunderstanding of mutual diffusion that has existed in this area since the groundbreaking work of North and Reed,[22] we point out what may be a minor point in order to promote the rigorous use of correct terminology.

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(84) For polydisperse samples, some of the chains may have $M > M_{c,soln}$ even if the overall molecular weight is too low for entanglements. However, these chains will *not* exhibit reptation scaling behavior or any other signature of entanglement if the *matrix* is not entangled.

(85) Equation 3 also assumes a constant k_p. Data supporting this assumption up to conversions of 0.6 or higher for MMA polymerization are available in the literature (see for example: Parker, H.-Y.; Westmoreland, D. G.; Chang, H.-R. *Macromolecules* **1996**, *29*, 5119).

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(90) The bulk and solution values for M_c have been determined for PMMA by measuring zero-shear rate viscosity as a function of molecular weight (see ref 77). As PMMA has been observed to exhibit different solution behavior depending on how the samples have been synthesized (Balloge, S.; Tirrell, M. *Macromolecules* **1985**, *18*, 817), it is important that some of these measurements have in fact been done using free radically produced samples (Bueche, F.; Coven, C. J.; Kinzig, B. J. *J. Chem. Phys.* **1963**, *39*, 128. Graessley, W. W.; Pennline, H. W. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2347.) Dependencies slightly different from eq 2 have been observed, but it is well established that $M_{c,soln}$ is clearly higher than $M_{c,bulk}$. Results in our lab indicate a critical M_w of approximately 150 000 for free radically produced PMMA in MMA at 35 wt % polymer concentration.

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