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An Evaluation of Free Volume Approaches to Describe the Gel Effect in Free Radical Polymerization

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ABSTRACT: This paper examines the use of free volume approaches to describe the gel effect in free radical polymerization, specifically testing the consistency of free volume in describing the effect of temperature on the critical onset conversion for the gel effect, X_{crit}. Experimental polymerization results for both methyl methacrylate (MMA) and styrene in which the temperature, T, is varied while the molecular weight, M, is held nearly constant show that the critical onset conversion for the gel effect, X_{crit}, is affected by T; i.e., a higher T leads to a higher X_{crit}, consistent with free volume. Other studies purported to show a link between X_{crit} and M did not account for variations in T in the data analyzed, and it is highly likely that part of the X_{crit} trend reported to be caused by M was in fact related to T variations. Further examination of this issue via modeling indicates that the experimental results are consistent with the quantitative trend predicted by free volume for X_{crit} as a function of T as well, indicating that free volume is an appropriate basis for modeling the gel effect as it adequately handles effects of temperature on termination. However, as it does not describe the concentration or potential molecular weight dependence of termination, free volume is not a complete theory for the gel effect. For this task, additional molecular-level insight is needed, a fact underscored by certain experimental trends not predicted by free volume, such as the effects of chain transfer and solvent quality on termination.

Introduction

Investigation into the details of chain termination in free radical polymerization that lead to the phenomenon known as the "gel" or "Trommsdorff" effect continues to be the subject of active research[1−30] despite decades of effort. The history of this effort has been recently reviewed.[1,30] While it is well understood that the characteristic autoacceleration in polymerization rate associated with the gel effect is due to a decrease in the termination rate parameter, k_t, which in turn is related to a restriction of chain mobility as monomer is converted to polymer, a quantitative understanding of this autoacceleration remains elusive for a variety of reasons. Chief among these is the fact that the cause of the onset of the gel effect has never been conclusively isolated.

Several theories have been presented that could potentially explain this phenomenon, but experimental tests to discern among these theories have been lacking. In recent years, three pictures have emerged that may offer a good chance of quantitatively explaining the gel effect onset, either singly or in combination with one another. The first is that the formation of chain entanglements plays a pivotal role in restricted chain mobility, leading to the decrease in k_t. While this explanation has received considerable attention,[2−9] recent work[1] has indicated clearly that the gel effect occurs readily in the absence of chain entanglements and that quantitative trends that would be expected if entanglements were the main cause of the gel effect are not observed experimentally. A second theory is that termination at intermediate conversion levels is dominated by short active chains (unentangled) reacting with long active chains (entangled), a process governed by the diffusion of the shorter, more mobile chains. The gel effect then can potentially be related to a depletion of short chains in the system.[10−13] While an interesting idea, this does not explain the presence of the gel effect in the absence of entanglements and has not been significantly tested experimentally. A third theory is related to free volume. Although several versions of gel effect free volume models exist with minor and sometimes major variations,[14−20] the essential idea is that the restricted mobility associated with decreasing the free volume as monomer is converted to polymer is adequate to account quantitatively for the observed decrease in k_t. The purpose of this paper is to explore the consistency of this assertion with experimental results.

Background

Relating the gel effect onset to decreasing free volume has its roots in early work[21−23] correlating this phenomenon with increasing bulk viscosity as monomer is converted to polymer. While it was realized that bulk viscosity can be affected by factors not necessarily affecting k_t (e.g. molecular weight, M, of dead polymer), the potential relationship between the diffusion-controlled k_t and *microviscosity* remained promising, and it was shown that k_t at low conversion decreases when low molecular weight species are added to increase the solution viscosity.[24] This provided evidence that k_t is diffusion-controlled. The accepted picture of the termination process was first presented by North and coworkers.[24,25] In this explanation, two propagating chains undergo translational diffusion until they are in close proximity. Next, the radicals (attached to chain ends) come within a reaction radius via chain-end motion, termed segmental diffusion. Third, the radicals react. If one step were much slower than the others,

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this step would be said to be rate controlling. As diffusion is related to microviscosity, which seems to correlate with system free volume, a logical progression was to discuss the gel effect in terms of free volume.

Since this link was established, there has followed a series of models seeking to predict quantitatively the entire course of polymerization for given conditions by relating k_t and often other kinetic parameters to the level of free volume in the system as a function of conversion.[14-20] Most notable has been work by Hamielec and co-workers,[14,16] Arai and Saito,[15] Soh and Sundberg,[17] Chiu, Carratt, and Soong,[18] Achilias and Kiparissides,[19] and Panke,[20] all of whom have included some type of free volume formulation in their models, often in conjunction with other factors also claimed to affect the relevant kinetics. (Recently, other groups[31,32] have published extensive modeling efforts that can be said to combine what appear to be the best aspects of previous models. References 31 and 32 constitute significant reviews of the general topic of modeling of free radical polymerization and provide insight into the current state of this area; they are recommended to those interested in a detailed modeling overview.) The bulk of the evidence for relating the gel effect to free volume comes from the success of these models in fitting experimental data.

While these models have achieved an impressive record in matching experimental results for several monomers, they have not been without criticism. To fit experimental data accurately, most models have introduced one or more adjustable parameters that are often tenuously linked to recognized physical quantities and, thus, may be seen to serve as curve-fitting parameters. Given the complex array of factors potentially affecting free radical polymerization, a process in which many of the kinetic parameters are thought to vary nontrivially with conversion and are notoriously difficult to measure reliably,[33-35] it is perhaps inevitable that a certain amount of curve fitting is necessary to match experimental data, particularly at high conversion where the underlying chemical physics is least well understood. However, this reliance on adjustable parameters comes with the penalty that the success of these models in fitting polymerization data does not in itself constitute proof that the gel effect onset is related to free volume, either by itself or in conjunction with other effects. Key experimental tests are needed to aid in this issue.

The main difficulty with testing the free volume concept as it relates to the gel effect is in determining exactly what free volume predicts in terms of conversion−time results. Free volume does not *predict* how k_t will change with conversion unless additional physics is imposed on the system, such as an assumption about the molecular process controlling k_t. Therefore, free volume alone cannot predict how conversion varies with time. However, as a first approximation, what can be stated is that free volume would predict that temperature plays a significant role in determining the gel effect onset conversion, X_{crit}. In particular, the gel effect should occur earlier at lower temperatures because there is less free volume under these circumstances. Thus, a minimal test of the validity of the free volume picture is to test for consistency with this prediction.

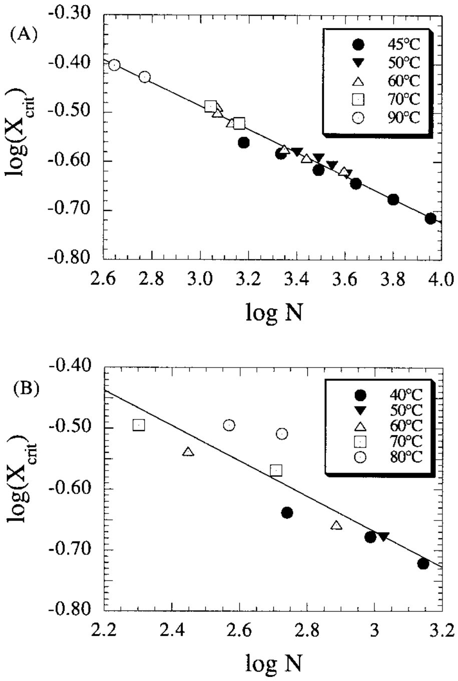

Figure 1. Critical fractional conversion for the gel effect onset, X_{crit}, as a function of chain length, N, as determined by (A) Tulig and Tirrell[7] for MMA and (B) Lee and Turner[26] for styrene. Note that in general the higher X_{crit} values occur for systems at higher temperatures. Note also that the X_{crit} values in Figure 1B are anomalously low for styrene, owing to the identification of the gel effect onset in ref 26 at conversions with very small deviations from classical kinetics.

This issue has been approached indirectly in the context of testing for the *molecular weight* dependence of X_{crit}. Theories for the gel effect onset relating it to the onset of entanglements predict that the gel effect occurs at much lower conversion when higher M polymer is formed. (From entanglement theory one may expect[36] $X_{\mathrm{crit}} \sim M^{-1}$.) In support of these theories, X_{crit} (or a related parameter such as polymer concentration), has been linked to M (or chain length, N) of the polymer formed prior to the gel effect for several systems, notably methyl methacrylate[7] (MMA) and styrene.[26] Figure 1 illustrates the cases made in refs 7 and 26 for the chain length dependence of X_{crit} in MMA and styrene polymerizations. X_{crit} reportedly varied as $M^{-0.24}$ for MMA[7] (Figure 1a) and as $M^{-0.35}$ for styrene[26] (Figure 1b). (Our best fit of the data from ref 26 yields $M^{-0.29}$.) While these scaling relationships are far less strong than expected on the basis of the theories they are sometimes used to support, they seemingly point to some effect of M on the gel effect onset. However, what is generally not recognized is that the data used in these studies were not all acquired at the same temperature. Other factors being equal, a higher free radical polymerization temperature results in lower M polymer; this is how much of the variation in M was realized in these studies, with MMA polymerized over the range 45−90 °C and styrene over the range 40−80 °C. By ignoring these variations, these studies have implicitly assumed that temperature does not affect X_{crit}. Thus, it is possible that effects attributed to M could be due, in part or entirely, to temperature, consistent with the free volume concept. This idea forms much of the basis of the present study, in which we decouple experimentally the effects of molecular weight and temperature on X_{crit} and compare the results to free volume predictions, offering a test of the general concept of free volume in describing the gel effect onset.

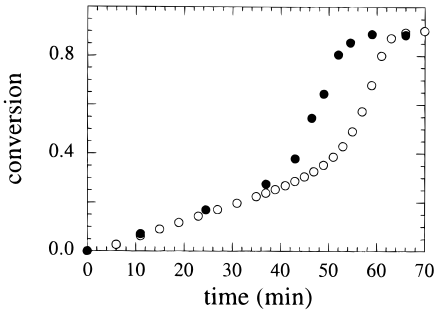

Figure 2. Experimental fractional conversion−time curves for the same MMA polymerization (70 °C, 0.5 wt % AIBN) carried out with two different methods having different heat transfer characteristics: (●) polymerization done via the "ampule" method, which results in a temperature rise during the gel effect, and (○) polymerization done via DSC, which results in an isothermal experiment.

Experimental Section

Styrene and MMA (99% purity, Aldrich) were purified and dried by mixing with commercial inhibitor remover replacement packing and calcium hydride for several hours, and then filtering. The initiators benzoyl peroxide (97% purity, Aldrich) and 2,2-azobis(isobutyronitrile) (AIBN) (Pfaltz and Bauer) were used as received. Free radical polymerization was performed by either differential scanning calorimetry (DSC)[28,37] or the "ampule"[1] method. In the ampule polymerizations, 15 mL test tubes were used, with approximately 5 mL of monomer in each. Molecular weight characterization was done by gel permeation chromatography (GPC) using tetrahydrofuran as solvent and monodisperse polystyrene (PS) and poly(methyl methacrylate) (PMMA) standards for calibration.

Results and Discussion

A. Bulk Polymerization. The goal of the first part of this study is to test the effect of temperature on X_{crit}. However, this presents a potential problem related to heat transfer effects on polymerization. Almost all past gel effect studies[1,8,14,21−23,38−40] have reported data gathered using "test-tube" or ampule polymerizations, which are not typically isothermal throughout the gel effect regime (possible exceptions include ref 28 done with DSC where reactions are believed to be isothermal and refs 41 and 42 where selected polymerizations were done in annular tubes in order to improve heat transfer as compared to polymerization in ampules). The reason that ampule polymerizations are typically nonisothermal is related to inadequate heat transfer, which can cause problems with interpretation of a series of experiments. An example of the effect of nonideal heat transfer on the course of polymerization is shown in Figure 2. This figure reports conversion−time data for the same system (MMA at 70 °C with 0.5 wt % AIBN) polymerized via two different methods, DSC and the ampule method. (A greater than 10 °C temperature rise was observed during the gel effect for the ampule polymerization.) At low conversion, the data overlap, but the gel effect apparently occurs earlier for the ampule experiment. This shows the importance of maintaining isothermal (or nearly isothermal) conditions in comparing X_{crit} values among a series of experiments; if some experiments have different heat transfer characteristics than others, the results could be of limited value. As faster kinetics allow less time for sufficient heat transfer, this problem is worse for faster polymerizing systems (MMA as opposed to styrene) or for any system at higher temperature.

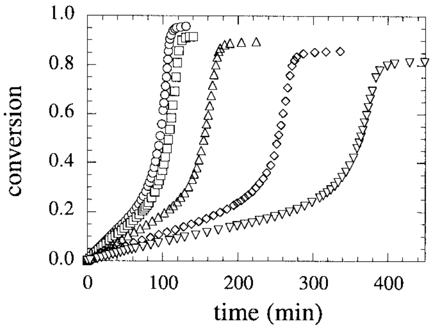

Figure 3. Experimental fractional conversion−time curves for MMA polymerizations at different temperatures but roughly constant molecular weight. Five conditions are shown: (▽) 40 °C with 0.1113 M benzoyl peroxide (BPO); (◇) 50 °C with 0.0430 M BPO; (△) 60 °C with 0.0214 M BPO; (□) 75 °C with 0.0039 M BPO; (○) 85 °C with 0.0012 M BPO.

Table 1. Molecular Weight Averages Prior to the Gel Effect for the Experiments in Figures 3 and 5

T(°C)	[I] (mol/L)	M_n	M_w
	MMA (Figure 3)		
40	0.111_3	321 000	640 000
50	0.043_0	316 000	644 000
60	0.021_4	346 000	614 000
75	0.003_9	345 000	608 000
85	0.001_2	413 000	676 000
	Styrene (Figure 5)		
45	0.197_5	42 400	75 000
60	0.124_1	48 000	81 400
70	0.076_6	32 500	58 300
80	0.041_7	34 000	60 600
90	0.011_3	40 500	70 200

With this issue in mind, the free volume concept is tested by investigating whether temperature alone affects X_{crit}. Since changing the temperature changes M, it can be difficult to decouple the effects of temperature and M on X_{crit}. To accomplish this, experiments must be done at different temperatures but at *constant polymer molecular weight*. Of course, this is more difficult than maintaining a constant temperature and varying M; nonetheless, it is possible to achieve this by varying initiator concentration so as to counteract the effect of temperature on M. This study reports such data for both MMA and styrene, with all reactions carried out isothermally (or very nearly isothermally). For MMA, conversion−time results at temperatures ranging from 40 to 85 °C (but approximately constant M) are shown in Figure 3. Because of the fast MMA kinetics, these reactions were done via DSC in order to maintain isothermality. Initiator concentrations needed to achieve a nearly constant M (at conversions below the gel effect) as well as the M values appear in Table 1. Note that the slight variations in M are far too small to cause a noticeable variation in X_{crit}, even if the variations in X_{crit} reported previously[7,26] were entirely the result of M and not affected by temperature.

To determine whether these experimental data exhibit the X_{crit}/temperature trend expected from free volume, X_{crit} must be calculated systematically. To accomplish this, one must calculate the conversion−time data as they would have occurred had k_t remained constant from the beginning of the reaction (the classical kinetics prediction) and compare this result to the actual data. The conversion at which the experimental data deviate from the classical kinetics prediction by a certain percent can then be defined as X_{crit}. One approach is to use the initial k_t as a fitting parameter to fit the low-

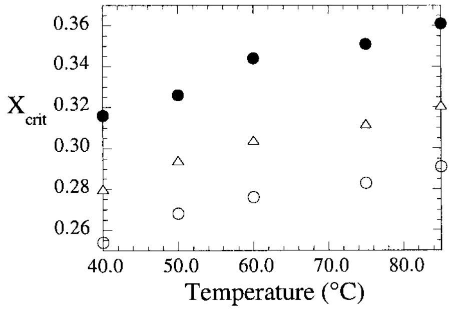

Figure 4. Experimental X_{crit} values as a function of temperature for the MMA systems in Figure 3, determined as the percent deviation from classical kinetics, using three different deviation levels[44] to define the gel effect onset: (○) 5% deviation from classical kinetics; (△) 7% deviation; (●) 10% deviation.

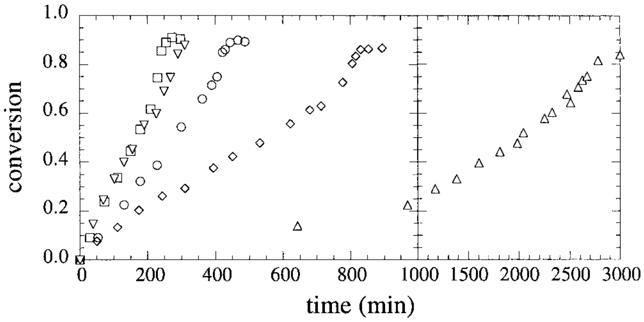

Figure 5. Experimental fractional conversion−time curves for styrene polymerizations at different temperatures but roughly constant molecular weight. Five conditions are shown: (△) 45 °C with 0.1975 M benzoyl peroxide (BPO); (◇) 60 °C with 0.1241 M BPO; (▽) 70 °C with 0.0766 M BPO; (□) 80 °C with 0.0417 M BPO; (○) 90 °C with 0.0113 M BPO. Note the collapsed time scale for the last two-thirds of the 45 °C case, necessary to represent meaningfully all of the data on one plot.

conversion data to the standard kinetic equations[18,43] (including volume contraction effects). Once the appropriate initial k_t has been thus determined, the entire predicted conversion−time curve may be calculated and used to determine X_{crit} as outlined above. Following this approach, Figure 4 presents results for MMA using 5%, 7%, and 10% deviations from classical kinetics.[44] Clearly there is an experimental trend for a higher X_{crit} at higher temperature. Therefore, independent of M, temperature affects the gel effect onset conversion, an observation supporting free-volume-based pictures. Furthermore, the observed experimental variation in X_{crit} is comparable to the magnitude of the reported[7,26] effect of M on X_{crit}. Thus, the trend previously attributed to molecular weight was at least partially due to temperature variations.

To confirm this result for another system, Figure 5 illustrates conversion−time data for styrene polymerizations performed under similar circumstances. These data were taken via the ampule method (styrene polymerizations are far slower than MMA polymerizations and, when run sufficiently slowly, can be approximately isothermal). These data, taken over a range in temperature from 45 to 90 °C, represent systems polymerized at different temperatures but at approximately constant M, owing to the variation in initiator concentration. Initiator concentrations needed to achieve an approximately constant M (at conversions below the gel effect) as well as the M values themselves are shown in Table 1. As with MMA, these data were analyzed to obtain X_{crit} values as a function of temperature, and these data appear in Figure 6, showing a clear trend for a higher X_{crit} at higher temperatures, consistent with expectations based on free volume.

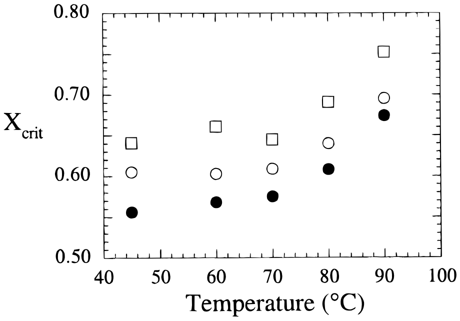

Figure 6. Experimental X_{crit} values as a function of temperature for the styrene systems in Figure 5, determined as the percent deviation from classical kinetics, using three different deviation levels to define the gel effect onset: (●) 5% deviation from classical kinetics; (○) 7% deviation; (□) 10% deviation.

These results serve as an initial test of the consistency of free volume pictures with experiment. As such, it can be stated that the experimentally observed effect of temperature on X_{crit} is qualitatively consistent with free volume, and therefore that free volume appears to be an appropriate framework with which to begin to describe the gel effect. However, two key issues still remain which must be examined more closely. The first has to do with the question of *quantitative* consistency: does the magnitude of the trend in X_{crit} as a function of temperature observed experimentally correspond to that expected on the basis of free volume? The second issue involves explaining the differences between the two systems examined in this manuscript, MMA and styrene. Any complete theory for the gel effect must account for the unmistakable fact that the gel effect occurs at much higher conversions in styrene polymerization as compared to MMA polymerization. These two issues are discussed in more detail in the next section.

B. Predicting X_{crit} Trends with Free Volume. To test for quantitative consistency with free volume, it is necessary to know what trend is predicted for X_{crit} as a function of temperature based on free volume. In other words, it is clear that the gel effect should occur at lower conversion with lower temperature based on free volume arguments, but how much lower? This requires the ability to model the course of polymerization (up to and slightly beyond the gel effect onset) via free volume, which is more ambiguous than modeling based on, for example, an entanglement picture, because free volume is not a molecular-level description of chain diffusion in the same sense as the entanglement theory. Although it is possible to use the existing gel effect free volume models to predict X_{crit} for a given set of conditions, this requires knowledge of the appropriate adjustable parameters for the model, which in turn come from fitting existing polymerization data, leading in some sense to a circular argument. Because such models are therefore not predictive, it is necessary to formulate a new modeling approach aimed specifically at predicting the temperature dependence of X_{crit}.

Although the requirement that the model must be predictive makes the task more difficult than other modeling efforts, the fact that we are interested only in predicting X_{crit}−temperature trends makes the task much simpler. For example, since the model need only work up to conversions slightly beyond X_{crit}, it can ignore such high-conversion complexities as the glass effect,[45] termination by reaction−diffusion,[17,46] and conversion-dependent propagation rate parameters,[47] and fractional initiator efficiencies,[48] as well as potential system heterogeneity,[49] observed to be important at fractional conversions of roughly 0.7 and higher. This means that k_t is the only system parameter that changes significantly with conversion over the range of interest, and the only one that need be accounted for. In addition, since determination of X_{crit} requires knowledge only of how the rate parameters change with conversion, reproducing the time scale of polymerization is not important. More explicitly, for a given temperature, the initial values of the rate parameters are irrelevant; only their relative change with conversion must be considered.[50] Finally, since we have eliminated M variations in the experimental cases illustrated in the previous section, and since M does not change significantly with conversion prior to the gel effect, the potential dependence of k_t on molecular weight (which is poorly understood, at best) can be ignored by modeling the same experimental circumstances outlined previously.

Thus, for the systems explored experimentally in the previous section, the only factors potentially having a serious effect on X_{crit} are the temperature and concentration dependencies of k_t. To predict X_{crit}, these are the factors that must be examined in our modeling. Both can be handled within the context of free volume. The temperature variation can be handled by assuming the temperature dependence of monomer diffusion, readily predicted from the Vrentas−Duda[51,52] free volume theory. This is tantamount to saying that k_t is diffusion-controlled, as free volume theory merely provides a means of describing the temperature dependence of monomeric friction, which should apply to a variety of types of diffusion.

The concentration dependence of k_t is a more difficult problem. It is not enough to say that k_t changes with concentration according to free volume; additional physics must be imposed on the system to achieve any modeling results. In particular, one must decide which molecular diffusive process should control termination or, at a minimum, what the concentration dependence of that process is. It is true that data on the concentration dependence of small molecule diffusion, segmental diffusion, and translational diffusion of chains of a variety of different lengths can all be fit with a free volume framework.[53] However, each of these processes has a different concentration dependence, and it is not clear which of them controls termination.

What can be done is to consider a variety of different concentration dependencies for k_t and predict via a free volume model X_{crit} vs temperature trends for each. To accomplish this, it is necessary to represent the differences in concentration dependence within a free volume framework. This type of variation has been handled before, in the context of the Vrentas−Duda free volume theory, for small-molecule diffusion in polymer solutions. Experimental results[54] and analysis[55] of the effect of small-molecule probe or solvent size on diffusion in polymer solutions indicate that larger molecules have a stronger concentration dependence. In terms of Vrentas−Duda free volume theory, this relationship may be expressed by

$$\frac{D_1(c)}{D_1(0)} = \left(\frac{D_2(c)}{D_2(0)}\right)^{\xi_{1,2}} \tag{1}$$

where c is the polymer concentration and $\xi_{1,2}$ accounts for the difference in concentration dependence of two given species, the species of interest ("1"), and the reference species ("2"). (In the context of Vrentas−Duda theory, $\xi_{1,2}$ may be interpreted as the ratio of the "jumping-unit size" of species 1 to that of species 2.) With this formulation, it is clear that larger $\xi_{1,2}$ values are associated with molecules with stronger concentration dependences (larger molecules); experimental results[54] indicate that for a situation where molecule 1 is of the order of 3−6 times larger than molecule 2 (in terms of molar volume), $\xi_{1,2}$ is typically in the range 1.2−1.7.

From the above discussion, it seems that the "ξ" parameter is a convenient way of expressing the differences in concentration dependences of various species, relative to some reference species. Therefore, this formulation appears promising to express the relative differences in concentration of the various types of diffusion that could control k_t. Extending this approach to these other types of diffusion, one may attempt to fit the concentration dependence of such processes as segmental diffusion or polymer translational diffusion with a similar equation, using monomer diffusion as the reference species:

$$\frac{D_x(c)}{D_x(0)} = \left(\frac{D_m(c)}{D_m(0)}\right)^{\xi_{x,m}} \tag{2}$$

where the subscripts "x" and "m" refer to the species and process of interest and monomer, respectively. In our experience,[27,53,56] eq 2 can be used to effectively fit data on the concentration dependence of segmental diffusion with an $\xi_{x,m}$ value in the range 1.0−1.2, data on translational diffusion of unentangled polymer chains with an $\xi_{x,m}$ of 3.0−3.5, and data on translational diffusion of entangled polymer chains with an $\xi_{x,m}$ of 9.5−10.0.

We do not wish to overemphasize the physical meaning of such curve fits; it may well be fortuitous that such an equation can fit such a wide range of data. However, it is clear that the $\xi_{x,m}$ parameter is an effective means of portraying the concentration dependence differences observed for the various molecular processes that may control termination, all within the general framework of the free volume picture. As such, this formulation can be used to model k_t:

$$\frac{k_t(c)}{k_t(0)} = \frac{D_x(c)}{D_x(0)} = \left(\frac{D_m(c)}{D_m(0)}\right)^{\xi_{x,m}} \tag{3}$$

where "x" now refers specifically to whatever species and process controls the termination reaction. D_m can be predicted[52] from the Vrentas−Duda model with existing or readily calculable parameters.[27,52] With eq 3, one can now predict X_{crit} as a function of temperature for a given system, using nothing more than the classic kinetic equations[18,43] for free radical polymerization. Details on the parameters used for modeling are given elsewhere.[27]

Using this approach, the predicted X_{crit}−temperature trends have been calculated for both MMA (Figure 7) and styrene (Figure 8) for four values of $\xi_{x,m}$: 1, 2, 3, and 5. (This range of $\xi_{x,m}$ values encompasses the range of realistic values for actual k_t data.[27,53]) All calculations assume a gel effect onset occurring when the conversion deviates from classical kinetics (k_t constant) by 5%. The

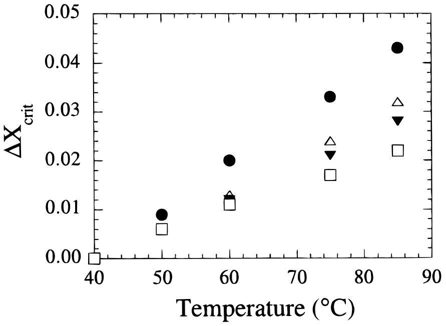

Figure 7. Simulated values of the change in X_{crit} (relative to data at the lowest temperature reported, 40 °C), ΔX_{crit}, as a function of temperature for the MMA experimental systems illustrated in Figures 3 and 4. Four values are used in the simulations for $\xi_{x,m}$: 1.0 (□), 2.0 (▼), 3.0 (△), and 5.0 (●).

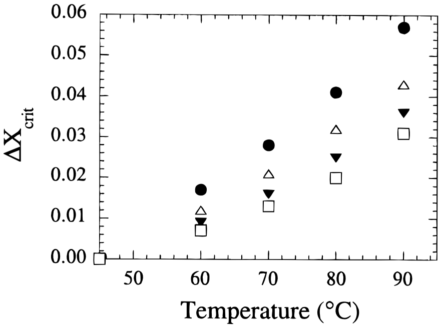

Figure 8. Simulated values of the change in X_{crit} (relative to data at the lowest temperature reported, 45 °C), $\triangle X_{\text{crit}}$, as a function of temperature for the styrene experimental systems illustrated in Figures 5 and 6. Four values are used in the simulations for $\xi_{x,m}$: 1.0 (□), 2.0 (▼), 3.0 (△), and 5.0 (●).

data are presented in the form of *change* in X_{crit} (relative to the lowest temperature considered), ΔX_{crit}, vs temperature.[57] Comparing these data to the experimental data in Figures 4 and 6, it is clear that free volume does a reasonably good job of predicting quantitatively the magnitude of the trend in X_{crit} as a function of temperature. For MMA, although the concentration dependence of k_t (as expressed by the parameter $\xi_{x,m}$) affects the results to some degree, the simulations effectively reproduce the ~4% range (for example, from $X_{\text{crit}} \approx 0.25$ to $X_{\text{crit}} \approx 0.29$ for the 5% deviation case in Figure 4) in X_{crit} as the temperature changes from 40 to 85 °C. For styrene, the experimental range may appear somewhat larger (roughly a 10% range in X_{crit} from 45 to 90 °C) than the simulation results. However, with the exception of the 90 °C data, the simulations approximately reproduce the experimental range.

From this evidence it can be convincingly argued that free volume is an appropriate framework with which to handle temperature effects on X_{crit}. This information, as well as previous work,[1] indicates that free volume, as far as it goes, is a better means of explaining the gel effect than competing theories related to entanglements, which have been significantly discredited. However, one must remember that free volume alone is not enough to predict the course of polymerization and thus is less ambitious than molecular-level theories. Much more information is needed to achieve this level of predictive capability, and there are many questions that cannot be readily handled with only the notion that k_t depends on free volume.

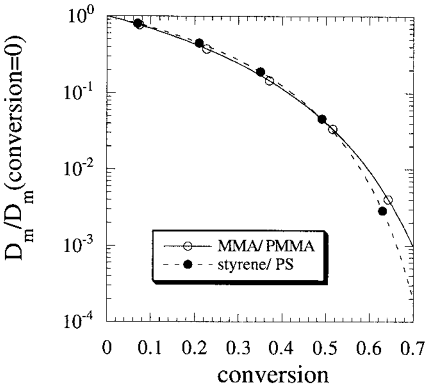

Figure 9. Vrentas–Duda free volume theory calculations for the monomer diffusion coefficient, D_m, normalized to the value at zero conversion, as a function of conversion for (○) the MMA–PMMA system, and (●) the styrene–PS system.

One such issue is the fact that styrene undergoes the gel effect onset at much higher conversion than MMA under similar conditions.[1,17,19,31,41,42] (This is confirmed by inspection of experimental data presented earlier.) While similar trends for the temperature dependence of X_{crit} are observed for the two monomers, the values of X_{crit} for styrene are roughly double those for MMA. If free volume effects are to account for the gel effect onset, these significant differences in X_{crit} between monomers must make sense within a free volume framework.

The simplest explanation for this difference in X_{crit} would require that k_t be much less concentration dependent for styrene than for MMA. In terms of our model, this means that the concentration dependence of PS diffusive motion (which should be related to that of styrene diffusion) must be much weaker than the concentration dependence of PMMA diffusive motion (which should be related to the concentration dependence of MMA diffusion) or that different processes control termination for the two different monomers. To test this, appropriate Vrentas–Duda free volume parameters were obtained (see ref 27 for parameters) and used to determine the free volume prediction for the polymer concentration dependence of styrene diffusion in styrene–PS solutions; this was compared with the polymer concentration dependence of MMA diffusion in MMA–PMMA solution at 25 °C. The results, presented in Figure 9, indicate only a very slight difference between MMA and styrene for the conversion dependence of monomer diffusion. This means that for a given value of $\xi_{x,m}$, the difference in the predicted values of X_{crit} for the two monomers at similar temperatures would be negligible. Therefore, it appears that the difference in concentration dependences for k_t between the two monomers is related somehow to differences in the fundamental process controlling k_t.

Does this imply that one set of physical assumptions could be applicable with one monomer type but inapplicable with a second? While not impossible, this is not likely the case. However, it does imply that circumstances that result in slowing down or suppressing the gel effect phenomenon in styrene, beyond the onset conversion expected from a simple free volume picture alone, must be of much less importance in MMA polymerization. A significant possibility has to do with chain transfer and its effect on "short-long" termination processes[10−13] hypothesized to be of importance in the gel effect regime. It is well-known that in free radical polymerization styrene exhibits much higher chain transfer effects than does MMA.[58,59]

This significantly higher level of chain transfer in styrene may result in effects leading to suppression of the gel effect relative to MMA. At equivalent chain lengths, the relative amount of production of "dead" polymer via chain transfer effects as compared to termination involving combination or disproportionation of two polymer radicals is greater in styrene than MMA. This means that under conditions where disproportionation/combination reactions are impeded, as at intermediate conversions associated with the gel effect onset in MMA, a much higher concentration of very "short" (including monomeric) radicals, resulting from chain transfer to monomer and initiator, will be present in styrene polymerizations than in MMA polymerizations. It has been shown via experimental photophysical simulations[60] of the diffusion-limited termination reaction for polystyrene that, when one of the terminating chains is ~10 repeat units long or shorter, there is a very significant increase in simulated k_t with decreasing chain length. In particular, these photophysical studies indicate that at a concentration of 300 g/L polystyrene k_t is 1 order of magnitude higher for a termination process involving a high molecular weight polymer radical and a monomer radical than for a high molecular weight polymer radical and a radical with 10 repeat units. Thus, a significantly increasing level of very short radicals with conversion in styrene polymerizations will result in an apparently higher k_t value at intermediate conversion than would be expected in the absence of significant chain transfer, suppressing the gel effect. (Examples of suppression of the gel effect via chain transfer agent addition, consistent with the arguments above, are given in Figure 3 of ref 1 and in ref 61.)

Also contributing somewhat to a suppression of the gel effect in styrene relative to MMA is the fact that the termination rate involving a monomeric radical with a polymer radical should be less conversion or polymer concentration dependent than the termination rate involving two polymeric radicals. This is due to the fact that monomeric radical, which dominates its diffusion-controlled reaction with polymeric radical, would be expected to have an $\xi_{x,m}$ value of 1.0 while a polymeric radical may be expected to have a significantly higher value. Other arguments associated with recent short−long termination pictures[10−13] also indicate that the gel effect could be suppressed if the relative population of short radicals increased.

C. Solution Polymerization Data. It is clear that free volume is effective in predicting the effects of temperature on termination (and thus on X_{crit}). However, it is equally clear that free volume alone is not adequate to predict conversion−time curves; a more molecular-level picture is required for this task. Details on the effects of molecular weight and chain transfer on the mechanisms and species involved in the termination reaction must be imposed onto the general framework of free volume in order to capture effectively the range of observable polymerization behavior. In addition, there may be a further complexity in solution polymerization unaccounted for by typical free volume models. In the classic work of Norrish and Smith[21] a trend was noted for an earlier gel effect when poorer solvents were used in MMA solution polymerizations at 40 °C with 60% MMA and 40% 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. An alternative explanation is that solvent quality itself plays a nontrivial role in determining termination kinetics, a factor of potential importance in diffusion but not described by free volume models. However, the effect is not clear, as examination of the Norrish and Smith data indicates that the solvents used line up in the same order whether arranged in terms of increasing solvent quality or increasing free volume in solution, as determined from Vrentas−Duda free volume parameters.[52]

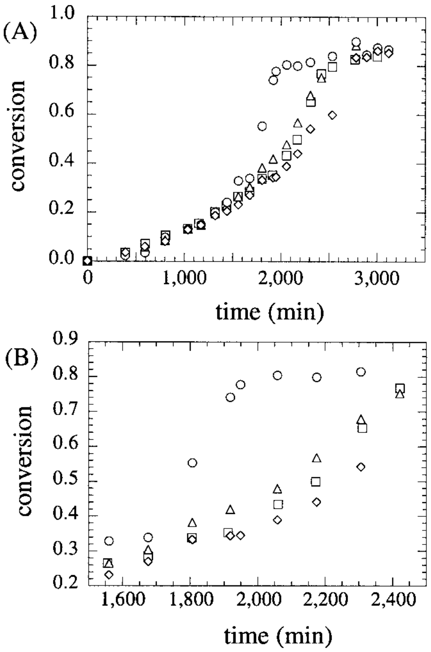

Figure 10. Experimental fractional conversion−time results for MMA solution (60 vol % MMA, 40 vol % solvent) polymerizations at 40 °C with 0.0094 M BPO as initiator. The solvents used, toluene and hexane, were chosen because they are very similar in terms of free volume parameters but very different in terms of thermodynamic quality in dissolving PMMA. Four different cases are shown, with the following mixed solvents employed: (○) 50% toluene/50% hexane, (△) 75% toluene/25% hexane, (□) 87.5% toluene/12.5% hexane, and (◇) 100% toluene. Figure 10A shows the entire results, while Figure 10B shows an expanded view of the gel effect region.

To investigate whether solvent quality affects the gel effect onset independent of free volume considerations, solvents must be identified that are similar in terms of free volume but vary considerably in terms of solvent quality. Toluene, a good thermodynamic solvent for PMMA, and hexane, a very poor thermodynamic solvent for PMMA, are similar in terms of their free volume parameters.[52] Therefore, if experiments show a measurable difference in the conversion−time behavior (and specifically, the gel effect onset) when different mixtures of these solvents are used, this would indicate that a factor of importance in chain diffusion but not described by any free volume theory may need to be considered in describing phenomena near the gel effect onset in some solution polymerizations.

Parts A and B of Figure 10 test for this potential trend. MMA solution polymerizations using the same conditions as Norrish and Smith (60% MMA and 40% solvent at 40 °C) have been run with four different mixed solvents: 50% (vol) toluene/50% hexane, 75% toluene/25% hexane, 87.5% toluene/12.5% hexane, and

100% toluene. It should be noted that phase separation occurred prior to the gel effect for the 50% toluene/50% hexane case, which obviously caused the sharp autoacceleration at anomalously short polymerization time; no phase separation was observed at any conversion for the other three cases. Considering only those polymerizations done in the absence of phase separation, there is a measurable, although slight, trend for an earlier gel effect when more hexane is used, seen more clearly in Figure 10B. Therefore, at approximately identical free volume conditions, solvent quality can apparently have a measurable effect on the termination reaction, leading to an earlier gel effect for poorer solvents.

Solvent quality effects on termination were also discussed by Cameron and Cameron[62] over two decades ago. While their study did not approximately equalize the effects of free volume, as done here, their conclusion that termination is hindered in poor solvents due to formation of more tightly coiled polymer radicals is consistent with the results of the work described here. Such effects are consistent with diffusion arguments as long as it is realized that a more compact coil will result in a slightly higher local polymer segment density in the neighborhood of a polymer radical chain end, reducing the chain-end local free volume and mobility and thereby the free radical termination rate. (Related effects have also been discussed by Tsutsumi et al.[63] for free radical polymerization of polystyrene macromonomer.) Thus, although it can be said that typical free volume models do not account for this solvent quality issue, even this effect can be understood in terms of a free volume picture, provided it accounts for such local effects.

Summary

The purpose of this study was to test the validity of the free volume picture for describing the gel effect in free radical polymerization, taking a similar approach to previous work[1] testing (and disproving) the entanglement theory. To test critically the applicability of free volume theory, it is necessary to attempt to disprove it by searching for discrepancies between experiment and fundamental predictions of the theory. This requires identifying specific predicted outcomes or trends, which in the case of free volume can be difficult.

The main area in which we have chosen to focus is that of the predicted effect of temperature on X_{crit}. The reason for this choice is that past work[7,26] has suggested that the effect of temperature on X_{crit} can be ignored, which is certainly inconsistent with free volume pictures for the gel effect. Thus, this is an opportunity to identify a discrepancy between experiment and theory. The problem with this past work (which sought to link X_{crit} to M) is that both M and temperature were varied, leaving uncertain which was responsible for the observed changes in X_{crit}. To alleviate this difficulty, we have designed experimental systems for both MMA and styrene for which temperature is varied while M is held approximately constant. Analysis of these systems confirms that temperature alone has a significant effect on X_{crit}, with higher X_{crit} values associated with higher temperatures, qualitatively consistent with free volume. To delve further into the issue, we have performed simulations on free volume predictions of the effect of temperature on X_{crit} and found that, although assumptions about the process controlling termination affect the results to a certain degree, the predicted trends are quantitatively consistent with experiment. Thus, free volume has passed the test designed for it; it appears in this sense to be an appropriate framework with which to describe the gel effect.

Despite this success, it is clear that free volume is an effective but incomplete theory for the gel effect, as evidenced by two issues which are not describable by standard free volume theories but are not necessarily inconsistent with them either. The first is the observed trend for a lower X_{crit} in MMA than in styrene polymerization. Since monomeric diffusive properties depend similarly on concentration in these two systems, free volume alone does not predict such a discrepancy. However, the differences can be explained, at least qualitatively, by increased chain transfer in styrene polymerization and its effect on the chains involved in termination. Although this issue deserves more attention, it seems reasonable to postulate that chain transfer may delay the gel effect until higher conversion through production of very short radicals with enhanced mobility, increasing k_{t} beyond that expected without chain transfer and reducing its concentration dependence. The second issue is that solvent quality appears to have a measurable effect on X_{crit}, another trend unaccounted for by standard free volume theories. This observed trend of an earlier gel effect when poorer solvents are used is an example of another area that deserves attention, but is understandable in a qualitative sense, in this case, if one considers the effect a poor solvent can have in contracting a polymer coil and the impact that this could have on chain mobility.

This relative success of free volume as a theory for describing the gel effect should not be overinterpreted. The present work is clearly significant in that it shows that temperature affects X_{crit} (not accounted for in previous studies), in a manner qualitatively and quantitatively consistent with free volume. However, the specifics of the effects of molecular weight and concentration on termination (and on X_{crit}) must still be dealt with using additional molecular-level insight.[27,53] In addition, it should be explicitly noted that the fact that free volume handles temperature effects does not necessarily imply that it is fundamentally correct on a mechanistic level. Free volume is designed to provide a means of describing frictional properties in polymer systems but is not the only option in that regard. It could be argued that any theory that can account for such frictional properties could be effective as a framework for describing the gel effect and that the use of free volume is more an issue of convenience than of scientific significance. While this may be the case, the results we have shown indicate that free volume may be justifiably used as a modeling basis and that this practice should help, rather than hinder, the effort to offer a complete description of the gel effect on a molecular level.

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