Nonidealities Exhibited by Cross-Linking Copolymerization of Methyl Methacrylate and Ethylene Glycol Dimethacrylate[†]

Neil A. Dotson, Tim Diekmann,[‡] Christopher W. Macosko,* and Matthew Tirrell

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

Received October 15, 1991; Revised Manuscript Received April 30, 1992

ABSTRACT: The predictions of classical theory for the establishment of a network by free-radical polymerization have been tested under conditions for which those predictions should be simple, i.e., short pregel regimes in which the composition and chain length distribution of the primary chains should be nearly invariant and for a nearly equally reactive system (methyl methacrylate/ethylene glycol dimethacrylate). At the moderate to high concentrations of cross-linker used, the classical theory is inapplicable, each of its predictions being disobeyed. Gelation occurs 1-2 orders of magnitude later than predicted, the gel point is relatively insensitive to the amount of cross-linker, the dependence on the primary chain length is weaker than the predicted inverse dependence, and the divergence of the weight-average molecular weight is more consistent with the percolation picture. All of these point to a violation of the mean-field picture, probably through cyclization and (size-dependent) reduction in the reactivity of the pendants.

Introduction

The theory of ideal network formation[1] formulated by Flory and Stockmayer is based upon random reaction of functional groups, an assumption often divided into three facets: equal reactivity, independent reactivity, and the prohibition against cyclization in finite species. An equivalent restatement of these is that the nonlinearity of the reaction introduces no new reactions or reaction kinetics beyond those which would characterize a corresponding linear polymerization (not denying, of course, that the resulting *structure* is quite different). This broader definition permits nonidealities, such as unequal reactivity, not tied to the branching nature of the polymerization (as both substitution effect and cyclization would be). It also allows intrinsically nonrandom chemistries, such as free-radical polymerization, in which polymerization is contingent upon initiation. In this particular case, ideality requires that the pendant unsaturations behave in all ways like their monomeric counterparts, differing neither in reactivity nor in available reactions. The former would constitute a substitution effect; an example of the latter would be cyclization, which, although chemically identical to cross-linking, is topologically distinct and obeys a different rate law (based on intramolecular static or dynamic properties of the polymer).

The actual behavior of cross-linking free-radical copolymerizations, however, diverges seriously from that predicted by these ideal models, a fact known since the work of Walling in 1945.[2] This study exposed the discrepancy between the predicted and actual gel points for the systems methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA) and vinyl acetate/divinyl adipate. The years since have witnessed numerous studies addressing this and other differences between the actual and predicted behaviors, and thus the distance between the ideal theory and the realities of nonlinear free-radical polymerization is well appreciated.[3]

What has not been consistently appreciated is that the ideal classical theory, as it is usually formulated, is far too idealized for the realities of even the corresponding *linear* free-radical copolymerization. These models, either intrinsically or in implementation, assume that the composition and chain length distribution of the primary chains produced are not functions of conversion. The first will obviously be wrong for an unequally reactive system for which the composition drifts. The drift in primary chain length, on the other hand, can result from changes in the relative rates of any of the numerous reactions occurring during a free-radical polymerization (conversion-dependent kinetics[4]). This may result from depletion of monomer, initiator, or transfer agent, the decrease in termination rate constant (Trommsdorff effect), propagation rate constant, or initiator efficiency, temperature changes, and so forth. A framework broad enough to account for the latter has been presented by Dotson et al.,[4] and the straightforward extensions for unequal reactivity have been recently made.[5]

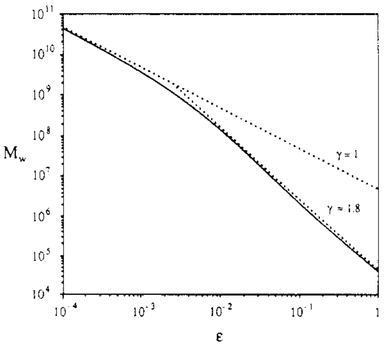

Figure 1. Theoretical prediction for the behavior of a late-gelling system (p_c = 1).[3,4] Monomer depletion is the sole source of conversion-dependent kinetics. Reaction involves a monounsaturated monomer of molecular weight 100 and a diunsaturated monomer of molecular weight 200, the latter contributing 0.5% of the double bonds in the mixture. Initial degree of polymerization of the primary chains is $DP_w^0(0)$ = 401; chains are ended by disproportionation only.

Because of these complications, if one wishes to compare experimental results with theory, either all of the conversion-dependent kinetics mentioned above must be thoroughly characterized or the aggregated effects on chain length and composition known. Failing this, the data may be misinterpreted. An example of this is given in Figure 1, where we see the evolution of the weight-average molecular weight M_w predicted for an equally reactive system

---

[†] Presented in part at the Spring 1992 ACS Meeting, San Francisco, CA, April 6-10, 1992.

[‡] Present address: 3M, St. Paul, MN 55144.

0024-9297/92/2225-4490$03.00/0

which gels at complete conversion, $p = 1$. Here, monomer depletion, the sole source of conversion-dependent kinetics, causes a linear decrease in the primary chain length with conversion; composition drift does not occur. Because of the decreasing primary chain length, when making a critical plot of M_w versus ϵ (a dimensionless distance to the gel point), an apparent critical exponent γ of $\sim$1.8 is seen in the first two decades of ϵ, before the true mean-field value of 1 is manifested. If this system could be realized experimentally, then, the results over the first two decades (and it is only here that experimental data could be obtained) would be attributed to non-mean-field behavior (specifically, percolation behavior[6]) when in fact something as mundane as monomer depletion was the cause.

This should not be interpreted as a suggestion that observed non-mean-field exponents spring from such prosaic roots. What is being insisted upon, rather, is that in order to compare properly with theory, one needs either to characterize rigorously the effects of conversion-dependent kinetics or to work in regimes for which those effects are absent. Else, one runs the risk of attributing to the cross-linking aspect of the polymerization deviations from theory which in fact are common to the corresponding linear polymerization. Because of the difficulties in doing the former (even for linear polymerizations), in this paper we do the latter. The effects of drifts will vanish if the conversion interval is sufficiently short,[7] so that essentially both average primary chain length and composition do not change. This necessarily excludes the study of the entirety of the postgel regime; in this paper only the pregel regime is examined.

For polymerization of equally reactive monomers forming long primary chains, the general equations[4,5] for the weight-average molecular weight of the polymer simplify to give several key predictions, *if the pregel regime is short*. First, M_w diverges from its initial value $M_w(0)$ as follows:

$$M_w = M_w(0)\epsilon^{-1} \tag{1}$$

where the dimensionless distance to the gel point, ϵ, is given from the conversion, p, as

$$\epsilon = (p_c - p)/p_c \tag{2}$$

and the critical double-bond conversion is

$$p_c = 1/a_4\,\mathrm{DP_w}^0 \tag{3}$$

where a_4 is the fraction of double bonds in the comonomer mixture contributed by the cross-linker and $\mathrm{DP_w}^0$ is the weight-average degree of polymerization of the primary chains. From eq 3 we note that the gel point should exhibit the following scalings:

$$p_c \propto a_4^{-1} \tag{4}$$

$$p_c \propto (\mathrm{DP_w}^0)^{-1} \tag{5}$$

if $\mathrm{DP_w}^0$ is not itself a function of a_4. As is clear from eq 1, the molecular weight itself diverges as follows:

$$M_w \propto \epsilon^{-1} \tag{6}$$

which is expected to hold over the *entire pregel regime* ($0 \le \epsilon \le 1$) for short pregel regimes (contrary to Figure 1). This is a result of the high functionality of the primary chains; the same is seen for A_f step homopolymerization as $f \rightarrow \infty$. Finally, the pendant double-bond conversion (at low conversions) is half the overall conversion of double bonds:

$$p_p = p/2 \tag{7}$$

These simple predictions can be tested provided we have a chemical system which conforms to the restrictions mentioned. Fulfilling the requirement of equal reactivity is the most difficult since the reactive characteristics of monomer pairs are not easily varied. In this work, a system often considered equally reactive, but which is probably only nearly so, is used: MMA/EGDMA. Establishing conditions under which the primary chains are long and the pregel regime short is relatively straightforward, because long chains and moderate amounts of cross-linker should necessarily give early gelation, as eq 3 shows. The production of long primary chains is favored by small amounts of initiator and low temperatures. In this study the common thermal initiator 2,2′-azobis(isobutyronitrile) (AIBN) was used for bulk polymerization at the relatively low temperature of 40 °C. The somewhat extreme polymerization conditions—low temperatures and small amounts of initiator—were required to ensure that the pregel regime was short with respect to conversion but long with respect to time, so that the evolution of M_w could be easily resolved. These conditions required that a transfer agent, 1-dodecanethiol (lauryl mercaptan, LM), be used to control the length of the primary polymer chains. Moderate to high cross-linker content was ensured by working at volume fractions EGDMA, $\upsilon_{\mathrm{EGDMA}}$, between 0.10 and 0.80, corresponding to $0.111 \le a_4 \le 0.819$.

Under these conditions, then, the predictions expressed in eqs 3–6 should apply to the system MMA/EGDMA. How well the experiments conform to these predictions is the subject of this paper.

Experimental Section

Preparation of Reagents. MMA and EGDMA (Aldrich) were nominally 99% and 98% pure and were inhibited with 4-methoxyphenol (methyl ether of hydroquinone, MEHQ) at 10 and 100 ppm, respectively. Some EGDMA (Monomer–Polymer and Dajac Laboratories) was nominally 99% pure (dental grade) and inhibited with hydroquinone. Inhibitor was removed from these by extraction with a 10 wt % KOH solution (twice for MMA and thrice for EGDMA), followed by a rinsing with distilled water three times. Both monomers were then put over molecular sieve and stored in a refrigerator ($\sim$5 °C) to remove remaining water. Monomer, when dried, was taken off sieve, filtered through a 0.02-μm filter to remove dust from the sieve, and then stored in a freezer ($\sim$−12 °C) until use. One small batch of EGDMA was further purified by vacuum distillation, performed between 70 and 80 °C, in the presence of CuCl to prevent polymerization.

The initiator, AIBN (Kodak), was purified by twice crystallizing from methanol and then stored in the freezer ($\sim$−12 °C) until use. The chain-transfer agent, LM (Aldrich), was nominally 98% pure and was used as supplied. The inhibitor, MEHQ (Aldrich), was 98–99% pure and likewise was used as supplied.

Polymerization. Polymerizations were performed according to two different formulations: (a) 0.0188% by weight AIBN, 0.1% by weight LM, 40 °C; and (b) 0.3% by weight AIBN, 0.5% by weight LM, 40 °C. PMMA made by recipe a was found to have an M_w of 528K ± 12K, whereas that made by recipe b has an M_w of 122K ± 3K. (Error bars here, as elsewhere, indicate 95% confidence intervals.) Chain transfer largely determines the resulting molecular weights in these polymerizations; PMMA made under these two formulations but without the transfer agent are more than an order of magnitude longer (7380K and 1980K, respectively). This is to be expected from such a strong transfer agent; we estimate that C_s for the system MMA/LM is between 0.6 and 0.7,[5] somewhat higher than suggested by the Russian literature[8,9] and data obtained from polymerizations in the presence of a solvent.[10] Previous studies indicate that this transfer agent is ideal.[11,12]

In preparation for polymerization, monomers and transfer agent were pipetted into a round-bottom flask, either in a 100-mL batch into a 250-mL flask for recipe a or in a 40-mL batch into a 100-mL flask for recipe b. The amounts of the two monomers added were then more precisely determined by weighting the flasks. The appropriate amount of AIBN was then added. To eliminate oxygen from the system consistently, five freeze–pump–thaw cycles were used (bubbling nitrogen through the monomers to displace oxygen was found to be insufficient). A cycle comprised the reaction mixture being frozen in liquid nitrogen, removed and evacuated with a vacuum pump for approximately 4 min, and then warmed mildly. After the last thaw, reaction flasks were allowed to equilibrate in the freezer (~-12 °C) for at least 45 min before reaction. For most polymerizations, no gas was added to the flasks after the final thaw, so that the polymerizations were done under the vapor pressure of the monomer.

The reactions were carried out in a water bath at 40 °C. Because of the jump of over 50 °C there was a thermal lag of approximately 5 min (while swirling), during which negligible reaction should occur because of the large activation energy of the initiation step. Reactions were quenched by removal from the water bath, releasing the vacuum, adding MEHQ, and then cooling rapidly in liquid nitrogen (again while swirling). The solution was then precipitated dropwise into an agitated solution of cold (~-12 °C) methanol: ~850 mL containing ~0.7 g of MEHQ for the 100-mL batches and ~450 mL containing ~1 g of MEHQ for the 40-mL batches. The precipitated solution was then stored at -12 °C.

The gel point was always determined experimentally as the midpoint between the last time at which a soluble polymer was obtained and that at which the mixture was not soluble in toluene. Before doing such experiments with toluene, however, an upper bound on the gel time was found by the bubble rise method. For these polymerizations, reaction was done under argon at approximately 1 atm. Since activation volumes for the relevant reactions are on the order of 10 mL/mol,[13,14] changes in pressure in the range of 1 atm should thus have little effect on polymerization (note that this also implies that the change of pressure with a_4 should have negligible effect as well).

It should be noted that these polymerization conditions are not particularly robust, but are sensitive to small amounts of impurities not removed in the caustic wash (nor by vacuum distillation). This is especially true for recipe a, for which use of certain batches of monomer (generally EGDMA) caused reduced yield, the kinetics generally exhibiting an inhibition time beyond the 5-min thermal lag. That impurity, rather than poor technique, was the source of the problem was indicated by the correlation with certain batches of monomer. These problems are not of concern in this paper, as no data from polymerizations exhibiting an inhibition time are used.

Purification of Polymer. Polymer precipitated from the original reaction mixture was redissolved in a small amount of toluene, precipitated into cold methanol, again dissolved into toluene, and precipitated once more. Separation of the precipitated polymer from the liquid was usually done through a coarse sintered-glass filter. The polymer was finally put into benzene to form a 2–5% solution and then freeze-dried for 1–2 days. The mass yield of polymer was then determined by weight (with corrections for losses during filtering). That the purification resulted in neither a loss of the low molecular weight tail by inadequate precipitation nor an increase in the high molecular weight tail by cross-linking was shown by comparison of size exclusion chromatographs before and after purification. If these foams were merely stored as was, eventually the polymer would become insoluble, presumably due to oxidation. It was thus decided to store the polymers in inhibited MEK solution at a polymer concentration between 0.01 and 0.05 g/mL. Even then, a polymer stored for a sufficiently long time (months) would show a noticeable increase in molecular weight. Thus it was desirable to characterize the polymer as described below as soon as possible.

Static Light Scattering. Static light scattering was performed on a commercial multiangle light scattering photometer from Wyatt Technologies. The instrument had been modified by Kent to allow for temperature control and injection from a loop rather than directly.[15] Angles between 25.41 and 154.59° were used in data analysis. The source was a He–Ne laser from Melles Griot (λ_0 = 632.8 nm). Dark currents were measured from the detectors with the laser source off; solvent offsets were measured on solvent alone. Normalization was done by measuring the excess scattering from a solution containing an isotropic scatterer, a 17 500 polystyrene standard (Pressure Chemical). Absolute calibration of the instrument was done with pairs of solvents of known Rayleigh ratio; solvents used were toluene, methyl ethyl ketone (MEK), tetrahydrofuran (THF), acetone, and methanol.[16]

Light scattering was done from five solutions in MEK of nearly equally spaced concentrations, prepared by successive dilution. The concentration of the mother solution was chosen according to the anticipated molecular weight, but such that the lowest concentration sample would scatter sufficiently and the mother solution would be as far from the overlap concentration c^* as possible. The solvent had been thrice filtered through a 0.02-μm filter to remove dust. Solutions were stored at -12 °C until ready for scattering. Solutions were filtered through two filters (either 0.2 or 0.45 μm, again depending upon the anticipated molecular weight) upon entering the loop and once more through a filter of the same pore size on-line before the cell. All scattering was done at 25 °C.

Data were analyzed by the standard Zimm plots, the concentration dependence always being fit linearly and the angular dependence quadratically, the curvature arising from polydispersity.[17] Consistency of results was checked with PMMA samples, for which molecular weights by light scattering in both MEK and THF agreed well with those from size exclusion chromatography (calibrated with PMMA standards).

Differential Refractometry. A Brice-Phoenix type differential refractometer with a He–Ne laser source (λ_0 = 632.8 nm) was used to measure the refractive index increments of the polymers. Calibration of the instrument was regularly performed with two KCl/H_2O solutions of concentrations of approximately 0.04 and 0.1 g of KCl/g of H_2O, the refractive index differences ($\Delta n = n - n_{H_2O}$) of which were known from extrapolation from data at lower wavelengths[17] by the Cauchy dispersion relation. Determination of polymer dn/dc values was made with five solutions of concentrations between 0.002 and 0.01 g/mL. Because of the drift in zero values, the slope of the plot of Δn versus c was used as dn/dc, rather than the intercept of a plot of $\Delta n/c$ versus c. The data gathered, while suffering from scatter, do suggest that the polymer dn/dc is related to the initial comonomer volume fraction v_{EGDMA} by the following:[5]

$$\mathrm{d}n/\mathrm{d}c\ [\mathrm{mL/g}] = 0.113 + 0.006 v_{\mathrm{EGDMA}} \qquad (8)$$

This relation, used in interpreting all light scattering results, is in rough agreement with past results from PMMA[18] and poly(EGDMA).[19]

Experimental Tests of Equations 3–6

Gel Points. From eq 3, we may predict the gel points for the systems studied. We assume that the system is equally reactive, so that the copolymer composition F_B is given by the comonomer composition a_4. We do not, however, assume that the primary chain length $\mathrm{DP_w}^0$ is independent of a_4 but instead calculate this from the initial molecular weight found by extrapolation of the molecular weight data to $\epsilon = 1$. The predicted gel points, in terms of both the conversion of double bonds p and the mass yield x, are listed in Table I. Also listed are the measured gel points in terms of mass yield, calculated from the kinetics and from gel time measurements (or in the cases a_4 = 0.629 and 0.819, estimations from molecular weight data[20]). As expected,[2] the actual gel points exceed those predicted by 1–2 orders of magnitude.

Scaling with a_4. From eq 4, we would expect an inverse dependence of the gel point on a_4. This will not hold here, however, since $\mathrm{DP_w}^0$ has been seen to be a function of a_4 as well (see Table I). However, a plot of the theoretical and experimental values of x_c versus a_4 will address whether the dependence is as expected. From Figure 2, we note

Table I
Predicted and Experimental Gel Points for Conditions Studied

$M_w(0) \times 10^{-3}$	v_{EGDMA}	a_4	pred p_c (%)	pred x_c (%)	actual x_c (%)
			Recipe a		
796 ± 90	0.10	0.111	0.126 ± 0.014	0.140 ± 0.016	2.27 ± 0.08
964 ± 151	0.20	0.218	0.0580 ± 0.0091	0.0706 ± 0.0111	2.05 ± 0.13
1370 ± 110	0.40	0.427	0.0244 ± 0.0020	0.0348 ± 0.0028	2.17 ± 0.23
1600 ± 90	0.60	0.629	0.0162 ± 0.0009	0.0264 ± 0.0015	2.03 ± 0.22
1750 ± 190	0.80	0.819	0.0127 ± 0.0014	0.0231 ± 0.0025	1.93 ± 0.34
			Recipe b		
152 ± 32	0.10	0.111	0.66 ± 0.14	0.73 ± 0.15	6.58 ± 0.20

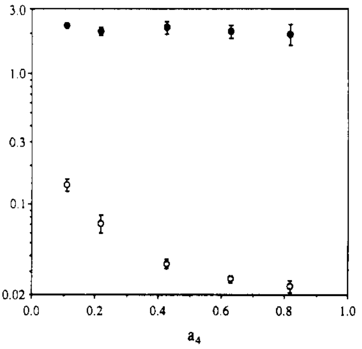

Figure 2. Critical yield, x_c, versus a_4 for recipe a: (●) experimental; (○) predicted. Error bars indicate 95% confidence interval (as in all other figures).

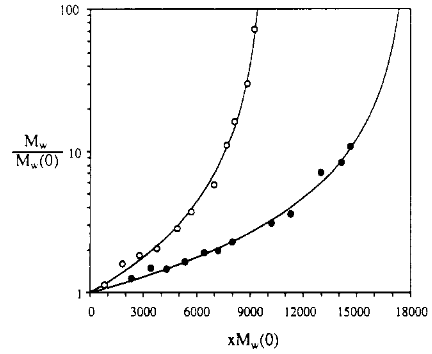

Figure 3. Reduced molecular weight versus reduced conversion for a_4 = 0.111: (●) recipe a; (○) recipe b.

that gelation is *largely insensitive* to the amount of cross-linker in the comonomer mixture over the range studied, rather than exhibiting the slightly greater than inverse dependence expected. Thus, the distance between theory and experiment increases with increasing amounts of cross-linker.

This widening gap was first noted by Walling[2] for both the system studied here and for the system vinyl acetate/divinyl adipate. The remarkable feature of a gel point invariant with the amount of cross-linker has been noted before and seems to be a feature manifested only at sufficiently high amounts of cross-linker. For example, in the work of Landin[12] on the same system as here (though under different reaction conditions), between v_{EGDMA} = 0.01 and 0.05, the gel point is seen to be a strong function of a_4. This distinction in behavior at low and high amounts of cross-linker is also seen by comparing the works of Storey,[21] Malinský et al.,[22] and Okasha et al.[23] for the system styrene/divinylbenzene. It is seen as well for styrene/dimethacrylate systems, as seen by comparing the work of Shah et al.,[24] for which invariance is seen as low as 2 mol % cross-linker in these solution polymerizations in toluene, and that of Vijayakumar and Fink[25] in which the expected dependence was found up to 3.5 mol % EGDMA. Perhaps even more dramatic is the data for the aqueous system acrylamide/methylenebisacrylamide,[26] where a minimum in the gel point at ~7 wt % bisacrylamide and a plateau past ~18% are seen. This stands in contrast to the data at lower concentrations of cross-linker for this system[26] or for the related acrylamide systems studied by Ulbrich et al.[27,28] A strong dependence at low cross-linker (up to 7.5 mol % cross-linker) was also seen by Wesslau[29] for styrene cross-linked by bis[4-(methacryloxy)benzylidene]-1,2-diaminoethane. The rule of a vanishing dependence at higher amounts of cross-linker is not without exceptions; e.g., Ito et al.[30] observed a strong dependence for the system styrene/poly(diallyl phthalate) up to a_4 = 0.5.

Scaling with $\mathrm{DP}_w{}^0$. From eq 5, we expect an inverse dependence of the gel point on the primary chain length. Because polymerizations at a_4 = 0.111 have been performed according to the two different recipes and have very different primary chain lengths as seen in Table I, we should be able to begin to answer the question of how the gel point changes with the primary chain length. The easiest way to visualize the answer is to prepare a plot of $M_w/M_w(0)$ (a reduced molecular weight) versus $xM_w(0)$, which should be universal at a given a_4. Figure 3 clearly shows that this universality is not the case and that the polymerization with the shorter primary chain length (recipe b) gels at an earlier *reduced* conversion than that with the longer chain length. Put another way, the dependence of the gel point on the primary chain length is much weaker than the inverse dependence predicted; a difference of primary chain length of a factor of 5.2 yields a difference in the gel point of 2.9. The polymerization with the shorter chain length thus exhibits less of a deviation from the ideal predictions.

This dependence of the gel point on primary chain length, weaker than expected, is in agreement with the recent results of Matsumoto et al.[31] on the same system, where a factor of 76 in primary chain length led to only a factor of 4 with respect to the gel point (here, though, the conversion range is much broader, and thus conversion-dependent kinetics confuse the interpretation). The only other investigations of the effect of primary chain length are at lower concentrations of cross-linker, and the results stand in contrast to these results. Vijayakumar and Fink[25] found the expected dependence on primary chain length for the system sytrene/EGDMA up to 3.5 mol % EGDMA, except at high dilution. Landin,[12] using the same system studied here, found that a fourfold decrease in primary chain length led to approximately a fourfold increase in gel point for v_{EGDMA} = 0.01 and 0.02. We may suppose that the weak dependence exhibited by our data is a characteristic of moderate to high concentrations of cross-linker, as was the weak dependence on a_4.

Divergence of M_w. From eq 6, we see that M_w should diverge as ϵ^{-1} (i.e., exhibit a critical exponent γ = 1) over the entire pregel regime. Because we know the gel points for a number of systems, we can easily determine the apparent exponents by which M_w diverges. The critical parameter, ϵ, was calculated on the basis of yield, x.

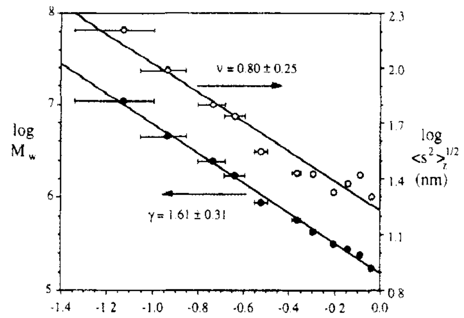

Figure 4. M_w (●) and $\langle s^2\rangle_z^{1/2}$ (○) versus ϵ for recipe b, $a_4 = 0.111$. In MEK at 25 °C.

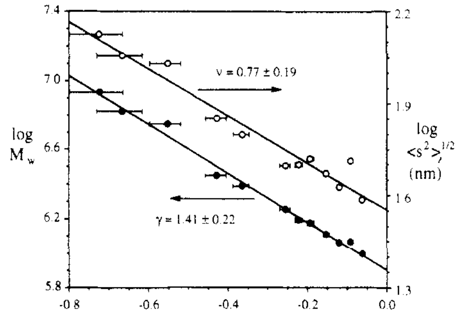

Figure 5. M_w (●) and $\langle s^2\rangle_z^{1/2}$ (○) versus ϵ for recipe a, $a_4 = 0.111$. In MEK at 25 °C.

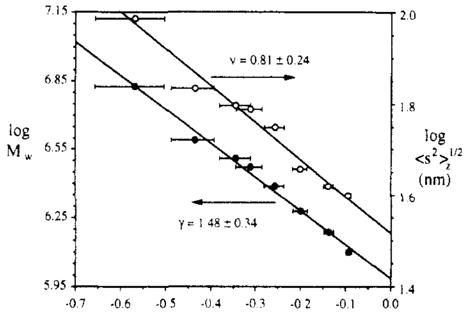

Figure 6. M_w (●) and $\langle s^2\rangle_z^{1/2}$ (○) versus ϵ for recipe a, $a_4 = 0.218$. In MEK at 25 °C.

The best set of data is that made under recipe b at $a_4 = 0.111$, for which the molecular weights measured span approximately 2 orders of magnitude. From Figure 4 we find that we do see an apparent power law divergence, but with an exponent γ much closer to the percolation[6,32,33] (or kinetic gelation[34,35]) value of 1.74 than to the classical value of 1. Moreover, as also shown in the figure, the radius of gyration $\langle s^2\rangle_z^{1/2}$ (in MEK at 25 °C) also diverges in a power law fashion and again with an exponent ν closer to the percolation value of 0.88 than to the classical value of $^1/_2$. Figures 5–7 show that the same behavior is seen for polymerizations performed under recipe a, $a_4 = 0.111$, 0.218, and 0.427. In all of these, the classical exponents are well outside the error bars, and values closer to percolation are seen. The rather large errors of these exponents are primarily a result of uncertainty in the gel point, which results in an uncertainty in ϵ as noted by the error bars; there is some contribution from the scatter of the data as well. Because both M_w and $\langle s^2\rangle_z^{1/2}$ diverge according to a power law, the latter is related to the former by a power law as well; Figure 8 illustrates this for recipe b, $a_4 = 0.111$. Similar plots for recipe a polymerizations yield similar exponents.

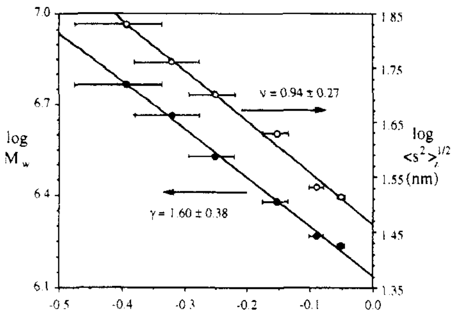

Figure 7. M_w (●) and $\langle s^2\rangle_z^{1/2}$ (○) versus ϵ for recipe a, $a_4 = 0.427$. In MEK at 25 °C.

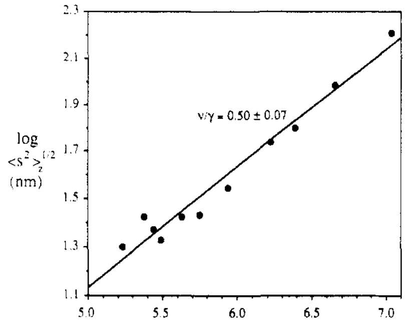

Figure 8. $\langle s^2\rangle_z^{1/2}$ versus M_w for recipe (b), $a_4 = 0.111$. In MEK at 25 °C.

It may be argued that studies in such small ranges of ϵ (a decade at most) provide no measure of critical exponents, because the critical regime has not yet been approached. Indeed, other cases are known where higher apparent exponents yield to mean-field values as $\epsilon \rightarrow 0$, both experimental[36] and theoretical (see Figure 1). Even so, such observations are still in quantitative disagreement with the theory since a value $\gamma = 1$ should be realized over the entire pregel regime. The nearness of the observed exponents with percolation values instead suggests non-mean-field behavior. The fact that the apparent exponents are somewhat lower than percolation values further suggests that we may be in a crossover regime to percolation behavior. That the critical regime may be quite broad is in agreement with recent results on an epoxy system[37] and by analogy with the cross-linking of long linear performed chains, for which the critical regime is expected to be quite small (and scale as $N^{-1/3}$) in the melt but depend strongly on concentration in the semidilute regime and be quite broad near c^* (very nearly our case near the gel point).[38]

For free-radical systems, the literature is not unanimous in supporting either classical or percolation behavior but is more heavily weighed toward the latter. For the same system as studied here, Whitney and Burchard[39] found fairly classical values for both γ and ν, although some doubts were raised about the determination of the gel point, so that a maximum value of γ of 1.5 was stated. On the other hand, the Strasbourg group, studying the system styrene/divinylbenzene, found exponents of $\gamma = 1.8$ and $\nu = 0.91$.[40] The only remaining relevant literature on free-radical systems concerns other critical exponents, and these as well support the percolation view. For example, for a polyacrylamide system, the gel fraction has been shown to grow with an exponent β of 0.5;[41] the expected percolation value is 0.4, while the classical value is 1.[6,32,33]

Values for γ and ν for other gelling systems are also split between percolation and classical values. Supporting the percolation viewpoint, Adam et al.[42] found $\gamma = 1.71$ and

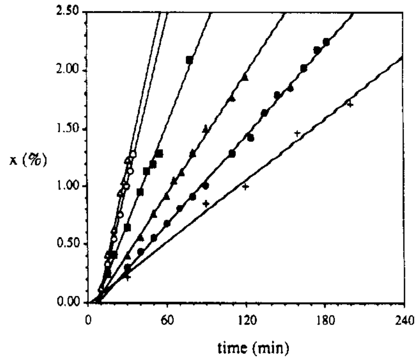

Figure 9. Kinetics of polymerization for recipe a: (+) $a_4 = 0$; (●) $a_4 = 0.111$; (▲) $a_4 = 0.218$; (■) $a_4 = 0.427$; (○) $a_4 = 0.629$; (△) $a_4 = 0.819$.

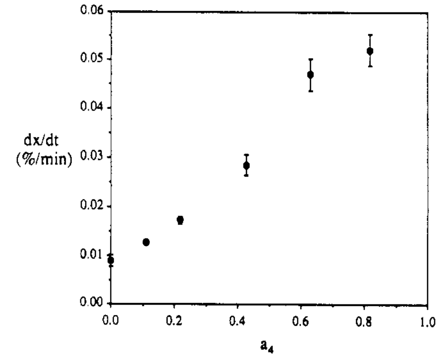

Figure 10. Rate of polymerization versus a_4 for recipe a.

$\nu = 0.86$ for a polyurethane system; Patton et al.[43] found $\gamma = 1.8$ and $\nu = 1.19$ for a polyester system, and Adolf et al.[44] found $\gamma = 1.7$ and $\nu = 1.4$ for an epoxy system (ν is a function of swelling both in the reaction bath and in subsequent dilution). On the other hand, for an epoxy system, Koňák et al.[45] found $\gamma = 0.97$ and $\nu = 0.50$. Kajiwara et al.[46] found for a polyurethane system classical exponents in bulk (over a small range of ϵ, though) but percolation exponents in dilution. Exponents much higher than those expected from percolation have been measured for sol–gel systems, for which $\gamma = 2.7$ and $\nu = 1.53$.[47] On the balance, then, nonclassical behavior seems to be the dominant result.

Other Features of MMA/EGDMA Polymerizations

We have found in the discussion above that all the theoretical predictions have been consistently frustrated. Before attempting an explanation of this, we first point out some other unusual features manifested by this chemical system.

Increase in Rate of Polymerization with a_4. Figure 9 shows a plot of the mass yield, x, versus time for recipe a polymerizations. We see an increase in the rate of polymerization with increasing amount of cross-linker; this is made even clearer in Figure 10, in which dx/dt is plotted versus a_4. Here, a factor of almost 6 separates the rate for $a_4 = 0$ and that for $a_4 = 0.819$. The same trend is noted as well for recipe b, where for $a_4 = 0$, $dx/dt = 0.0387 \pm 0.0026\%/\text{min}$, while for $a_4 = 0.111$, $dx/dt = 0.0440 \pm 0.0017\%/\text{min}$. This further points to the curious feature that the enhancement in rate appears to be dependent on the recipe or, we would suppose, chain length. This is seen by comparing the ratio of the rate dx/dt for $a_4 = 0.111$ to that for $a_4 = 0$ for recipes a and b. For recipe a, this ratio is 1.44 ± 0.20, while that for recipe b is 1.14 ± 0.08.

Enhancement of the rate of polymerization is a common observation in cross-linking free-radical systems. It is seen in the earlier results of Hayden and Melville[48] and of Horie et al.[49] and also in the more recent results of Li et al.[50] (although the effect is not as large here). Such enhancement in rate can even be observed even in the rather moderate range of 0–10% cross-linker. This occurs for styrene cross-linked by dimethacrylates,[24,51,52] for example, as well as in the system acrylamide/methylenebisacrylamide.[53] It should first be noted that this enhancement in rate occurs from the beginning of the polymerization and so is qualitatively different from the increase in rate with cross-linker at higher conversions due to shifting of the Trommsdorff effect to lower conversions because of gelation (an effect which can be seen in the range 0–1% cross-linker[27,28]).

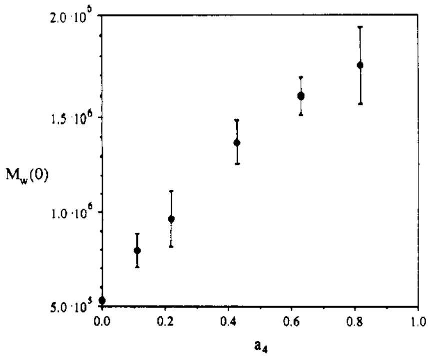

Figure 11. $M_w(0)$ versus a_4 for recipe a.

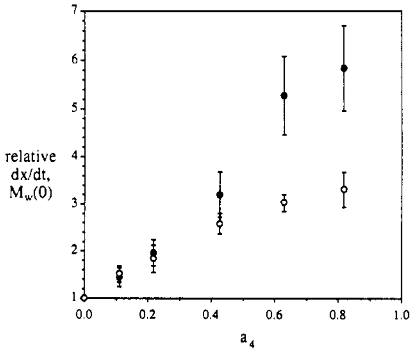

Figure 12. Relative rate and initial molecular weight versus a_4 for recipe a: (●) $(dx/dt)|_{v_{EGDMA}}/(dx/dt)|_0$; (○) $M_w(0)|_{v_{EGDMA}}/M_w(0)|_0$.

Increase in Primary Chain Length with a_4. The second unusual feature is that, like the rate of polymerization, the primary chain length, as obtained from the $\epsilon = 1$ intercept in the critical plots, also increases with a_4. This we have already noted in Table I, but in Figure 11 this is shown more clearly. The effect is sufficiently large that the increase cannot be attributed merely to the increase in average monomer mass (which is also true of the increase in the rate). The rate and primary chain length do not, however, increase proportionally, as seen in Figure 12. The increase in $M_w(0)$ is more modest.

Recently, there have been a number of works from the Osaka group supporting an increase of primary chain length with cross-linker for a number of reasons. For both MMA and styrene, cross-linking with oligo(ethylene glycol) dimethacrylates of successively longer oligo(ethylene glycol) bridges leads to progressively longer primary chain lengths.[54,55] Similarly, for MMA cross-linked by trimethylolpropane trimethacrylate, an increase is seen in primary chain length as well.[56] The explanation in these cases is that the cross-linker allows cycles to form which sterically suppress termination. Steric hindrance for the transfer to monomer reaction was suggested as the reason for longer primary chains in the polymerization of triallyl isocy-

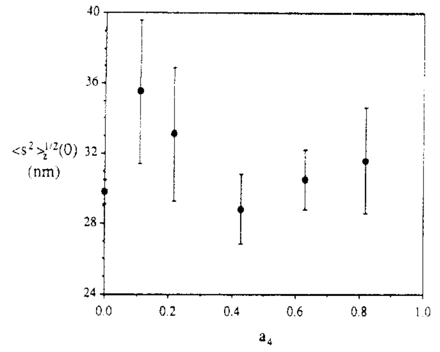

Figure 13. $\langle s^2\rangle_z^{1/2}(0)$ versus a_4 for recipe a. In MEK at 25 °C.

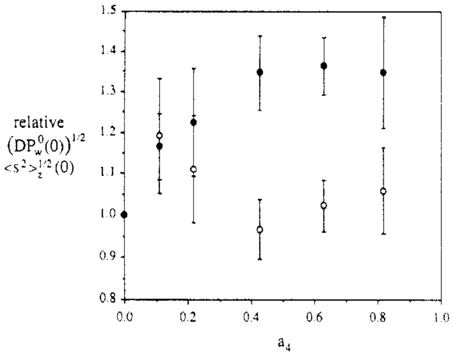

Figure 14. Reduced $(\mathrm{DP_w}^0(0))^{1/2}$ and $\langle s^2\rangle_z^{1/2}(0)$ for recipe a: (●) $(\mathrm{DP_w}^0(0))^{1/2}|_{\upsilon_\mathrm{EGDMA}}/(\mathrm{DP_w}^0(0))^{1/2}|_0$; (○) $\langle s^2\rangle_z^{1/2}(0)|_{\upsilon_\mathrm{EGDMA}}/\langle s^2\rangle_z^{1/2}(0)|_0$. In MEK at 25 °C.

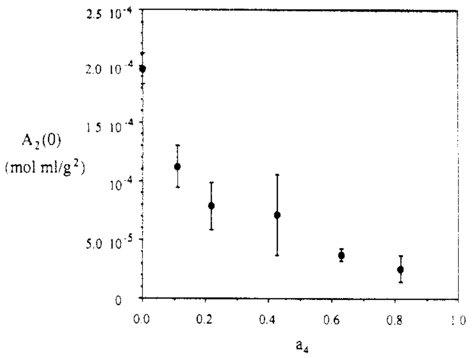

Figure 15. $A_2(0)$ versus a_4 for recipe a. In MEK at 25 °C.

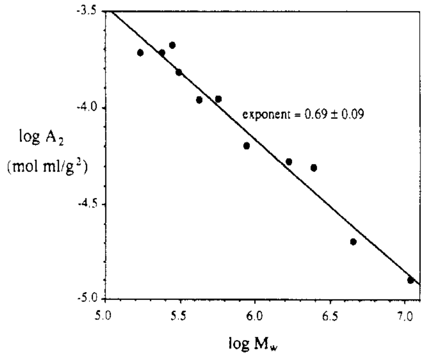

Figure 16. A_2 versus M_w for recipe b, $a_4 = 0.111$. In MEK at 25 °C.

anurate as compared to those of triallyl cyanurate.[57,58] In the copolymerization of tetraallylammonium chloride with diallylammonium chloride, increasing the amount of the latter (a monomer of lower functionality) increases the primary chain length, the cause simply being a higher k_p.[59]

Lack of Concomitant Increase of Primary Radius of Gyration with Primary Chain Length. Despite the strong increase in primary chain length with a_4, we find that the radius of gyration of the primary chains does not exhibit an accompanying increase. In Figure 13 the radius of gyration of the primary chains, found, like $M_\mathrm{w}(0)$, by extrapolation to $\epsilon = 1$, is plotted versus a_4. The radius of gyration is almost constant despite a fourfold increase in $M_\mathrm{w}(0)$, which implies at least a factor of 2 in $\mathrm{DP_w}^0$. This observation is substantiated by noting that the location of the peak in size exclusion chromatography (SEC) traces corresponding to the primary chains is invariant with a_4, within experimental error. These data indicate that the primary chains become denser with increasing a_4. This is made even clearer by comparing the radius of gyration with $(\mathrm{DP_w}^0(0))^{1/2}$, where the latter is calculated from $M_\mathrm{w}(0)$ assuming equal reactivity (as was done for the theoretical predictions in Table I). The results are shown in Figure 14 for recipe a. Although for $a_4 = 0.111$ the increase in size and mass correspond, this is not the case at the higher concentrations of cross-linker; there the chains show a noticeable, although not extreme, densification.

Such densification with cross-linker is also a common observation from intrinsic viscosity measurements. Probably the earliest indication of such behavior is found in the work of Zimm et al.,[60] in which the molecular weight dependence of the intrinsic viscosity was found to be quite weak. Perhaps more conclusive are data indicating that the intrinsic viscosity of the branched copolymer at low conversions far from the gel point is less than that of the corresponding linear polymer. The largest body of data of this type is from the Manchester group; such behavior was noted for styrene/p-divinylbenzene,[61] styrene/4,4′-divinylbiphenyl,[62] styrene/4,4′-diisopropenylbiphenyl,[62] and styrene/dimethacrylate systems.[51] It has been noted in the polymerization of commercial divinylbenzene mixtures[63] and in the reaction of linear poly(4-vinylstyrene).[64] In most of these cases, reaction was performed in solution so as strongly to encourage cyclization, but this behavior is not limited to solution polymerizations. It has also been noted in the bulk polymerization of EGDMA[19] and in the bulk polymerization of MMA/EGDMA.[12] Data on the radius of gyration are not as plentiful, but for the copolymerization of MMA and EGDMA in dioxane the striking feature of decreasing radius of gyration with increasing molecular weight during a polymerization has been noted by Matsumoto et al.[31] From Figures 4–7 it is clear that those data manifest no such extreme effect.

Strong Decrease in Second Virial Coefficient with a_4. The second virial coefficient for these polymers in MEK at 25 °C decreases with increasing a_4, as seen in Figure 15, in which the initial second virial coefficient $A_2(0)$ is plotted versus a_4. Note only does the second virial coefficient diminish with a_4, but it also decreases more strongly with molecular weight than it would for a linear polymer. For polydisperse PMMA, we find[5] that A_2 scales as $M_\mathrm{w}^{-0.24\pm0.02}$, nearly the scaling predicted by theory ($N^{-1/5}$).[6] The branched copolymers, on the other hand, exhibit a more drastic dependence. In Figure 16, we see that A_2 scales as $M_\mathrm{w}^{-0.69\pm0.09}$ for polymers made from recipe b, $a_4 = 0.111$. This stronger dependence, however, is in good agreement with the scaling prediction of Daoud and Leibler[65] for branched polymers, in which $A_2 \propto M_\mathrm{w}^{-5/8}$. Similarly, strong dependences are observed for polymers made from recipe a; for $a_4 = 0.111$, the exponent is 0.50 ± 0.11; for $a_4 = 0.218$, the exponent is 0.64 ± 0.15; and for $a_4 = 0.629$, the exponent is 0.66 ± 0.10. (Data for $a_4 = 0.427$ and 0.819 are too noisy to allow for reliable calculation of this exponent.) Such a strong decrease in the second virial coefficient has also been seen in other experimental works. For MMA/EGDMA copolymers, this effect has been noted by three different groups.[31,66,67] It has also been seen in stepwise systems[43,45] and in sol–gel systems.[68] Thus, this is expected both from past experience and from theory and does not necessarily indicate any preculiarity as the decrease with a_4 might.

Discussion

The experimental results contradict the predictions of the ideal network theory on all four points: the absolute location of the gel point, the dependences thereof on both the amount of cross-linker and the primary chain length, and the divergence of M_w. These four points of disagreement, taken together, can only mean that the assumptions of ideality do not hold or, equivalently, that the pendant unsaturations do not behave like their monomeric counterparts. This conclusion could not be reached from the first two deviations alone. For those, an explanation can be constructed within the framework of the ideal theory itself—an explanation neither satisfactory nor credible, though, but still best mentioned and discarded at the outset.

Misapplication of the ideal theory in narrow conversion intervals could only come from two sources: use of improper chain length or unequal reactivity. The primary chain length, though, has been measured from $M_w(0)$, and there is no basis for suspecting a rapid diminution of the primary chain length by orders of magnitude, which is what would be required from a delay in gel point and observation of an apparent $\gamma > 1$. (It is also difficult to think of a mechanism for this at such low conversions.) Hence, the only remaining source is a false assumption of equal reactivity, which indeed has not been substantiated in any way (e.g., by measurement of the copolymer composition).

If unequal reactivity were the explanation, it would require that the copolymer composition F_B be constant or decrease somewhat as a_4 increases in the range $0.111 < a_4 < 0.819$ and that MMA be essentially homopolymerizing ($F_B \approx 0$) with no reaction of EGDMA even up to $a_4 = 0.819$. This would be an extreme case of unequal reactivity, strange for a system often considered to be equally reactive.[12,69] Experimental data suggest that the reactivity ratios for this system at 70 °C are not so extreme:[50] $r_A = 1.34 \pm 0.14$, $r_B = 0.75 \pm 0.11$ (based on double bonds or equivalents). Thus radicals of both monomers do prefer to react with MMA, but to a much lesser extent than this explanation demands. Moreover, ^{1}H and ^{13}C NMR spectra insist that a large amount of EGDMA is present in the copolymer. For reasons to be discussed below, these NMR results are not quantitative, but still do not allow $F_B \approx 0$. This explanation is thus rejected.

Thus, all four deviations, together or apart, insist that the basic assumptions of the theory are disobeyed. The pendants either differ in reactivity or engage in other reactions; more specifically, the reactivity of the pendant is reduced[23,70] or pendants are wasted in cyclization[71–74] (or both).[12] Either would delay gelation. Either might lead to an invariant gel point, depending upon how the reduction in reactivity or extent of cyclization depends on a_4. Either might yield an anomalous dependence on the primary chain length, although a size-dependent reactivity (i.e., a physical "substitution effect") is more believable here. Either might be an expression of non-mean-field behavior, cyclization obviously so and reduced reactivity if it were size-dependent[75] (and there is evidence for this[39]). How do the other features of this polymerization fit with these suggestions?

That cyclization is occurring is consistent with both the evidence for denser coils seen from the radius of gyration data of Figure 14 and the decrease in the second virial coefficient seen in Figure 15. It is well-known that cycles or branching leads to decreased radius of gyration at the same molecular weight,[76] and since here the zero-conversion polymer is being examined, the possibility of branching is nearly eliminated. Thus, cycles would be implicated as the cause of this slight densification, which is not so extreme, however, as to warrant the term "microgel".[77,78] The second virial coefficient is also known to diminish in the presence of cycles,[76] but it must be stress that neither of these proves cyclization. The decrease in coil size, as well as the decrease in second virial coefficient, could result from MEK simply being a poorer solvent for the copolymer; light scattering from an analogous polymer without cycles, such as poly(MMA-*co*-ethylene glycol methacrylate trimethylacetate), could answer this question.

The increase in the rate of polymerization with a_4 suggests a possible effect of the polymer structure on the kinetics. This could, however, merely be through composition, in one of two ways. First, it may be the result of unequal reactivity, so that the pseudo-kinetic rate constant k_p is a function of composition. That this would be the *sole* cause of such an extreme effect is not believable, however, for systems nearly equally reactive, such as this or acrylamide/methylenebisacrylamide[53] and for another reason to be mentioned below. The second possibility is that because the termination reaction is diffusion-controlled,[79] the initial termination rate constant should depend on the inverse of the viscosity of the comonomer solution, μ^{-1}, thus increasing the rate of polymerization as $\mu^{1/2}$. An increase in viscosity of a factor of ~ 3 is seen from $a_4 = 0$ to $a_4 = 0.819$ at 40 °C, giving a factor of $\sim 3^{1/2}$, which even with the factor of 2 resulting from the inequality of x and p cannot account for the sixfold increase in the rate of polymerization. Most importantly, the increase in rate of polymerization is a function of chain length, which eliminates both the unequal reactivity explanation and the simple explanation of a changing k_t through the viscosity.

The chain length dependence of the rate of polymerization at $a_4 = 0.111$ appears to be peculiar to the cross-linking system. Our results for MMA polymerizations with different amounts of transfer agent (which lead to differences in molecular weight of well over an order of magnitude) show no discernible effect of chain length on rate of polymerization,[5] while the polymerizations at $a_4 = 0.111$ do. Thus, the difference above must be specific to the copolymerization (or the cross-linking), and most probably through k_t, since only this should be strongly chain length dependent. The usual explanation for this is that the presence of the cross-linker allows cyclization to occur and a heterogeneous structure to develop, which discourages termination. For some modeling purposes, authors have even completely neglected termination.[80–82] While this is too extreme a point of view,[83] the accumulation of radicals which it implies has been seen experimentally for the system MMA/EGDMA.[84,85]

The suggestion that the cross-linking sterically suppresses termination cannot be the the cause of the chain length enhancement, since these systems are transfer-dominated and thus termination is a relatively insignificant route by which chains are ended. This line of reasoning also disposes of the explanation that the increase might be due to a shift toward a "false combination" mechanism wherein cross-linking occurs between two growing chains before terminating. Similarly, a decrease in the transfer to monomer reaction cannot explain the enhancement, because even for MMA transfer to monomer is an insignificant reaction under these conditions; the fact that we could make 7380K PMMA indicates that C_M is probably much less than 2.7×10^{-5}. It is not as easy to dismiss the suggestion that the enhancement is caused by an increase in k_p with the amount of cross-linker. Figure 12 shows that if changing k_p were the cause of the enhancement in chain length (along with the increase in average monomer molar mass, related to the inequality of p and x), then the additional enhancement in the rate seen in the figure could be adequately explained by the viscosity increase. If this were the case, though, the enhancement in both for $a_4 = 0.111$ is due solely to the increase in k_p, which must therefore be chain length dependent since the rate was shown in the previous section to be chain length dependent. A strongly chain length dependent propagation constant, though, is difficult to imagine. The coincidence of the two reduced quantities at $a_4 = 0.111$ in Figure 12 must be coincidental in the other sense of the word.

An alternate explanation is that transfer to the thiol is discouraged with increasing a_4. This explanation is preferred, because it is easier to envision a mechanism for decreasing transfer than a mechanism for a chain length dependent propagation rate constant. Two mechanisms may be proposed. First, it may be that a radical residing on an EGDMA monomer abstracts a proton at a lower rate than that on an MMA (probably for very local steric reasons). Second, it may be that the heterogeneity allows for some larger steric hindrance or preferential solvation. Which of these is the case cannot be determined from these results, and furthermore it must be kept in mind that there is no direct evidence here for a decrease in k_{tr}. Further experiments would be needed to elucidate these two phenomena and determine whether the thiol indeed becomes a less efficient transfer agent as the fraction of EGDMA increases. Support for this explanation, though, can be found in the recent work of the Osaka group,[31] which suggests a lower value of C_S for EGDMA polymerizations (0.15–0.30) than found in this work (0.6–0.7).

That termination is discouraged because of inaccessibility may indicate an inaccessibility on the part of the pendants themselves, leading to an apparent reduced pendant reactivity. These together might also explain the other deviations from theory, for example the lack of dependence on a_4 and the much weaker dependence on DP_w^0. Two possibilities may be raised for these two weak dependences. First, what if the gel point were better correlated with coil overlap concentration c^*? In this case, one would expect a lack of dependence on a_4 and a weaker dependence on DP_w^0 than that of eq 5, e.g., an inverse square root dependence if the radius of gyration of the primary chains exhibited Θ-point scaling (which is consistent with our experimental data). Second, what if the gelation occurs by reaction of pendant vinyls on the surface of microgels, as has been suggested in the literature?[77,78] Contrary to the first suggestion, one would still expect a dependence on a_4, but again a weaker dependence on the primary chain length (e.g., an inverse square root dependence if the radius of gyration of the primary chains, even though called microgels, exhibited Θ-point scaling). Of these two, our data are more consistent with the first picture.

All of this discussion merely shows consistency with the ideas of cyclization or reduced pendant reactivity; what is more desirable is direct experimental evidence of one or the other. This essentially would involve an experimental test of eq 7. If only cyclization were to occur, then the pendant conversion p_p would be greater than that predicted by the theory ($\sim p/2$), whereas if only reduced pendant reactivity were to occur, then the pendant conversion p_p would be less than $\sim p/2$. A combination of the two may of course yield intermediate results. A measurement of the composition of the polymers (both the copolymer composition and the pendant conversion) would shed light on this, even though it cannot strictly separate the two.

Measurement of the composition and pendant conversion was attempted by NMR, first by ^{1}H as in the work of Landin.[12,86] (For a more complete discussion of all NMR work, see ref 5.) These measurements consistently revealed a polymer with an apparent negative pendant conversion. ^{1}H spectra did not exhibit the sharp monomeric peaks indicative of unreacted EGDMA impurity,[5,12] confirming that the technique for purifying the polymer was sound and that impurity could not be the source of this error. Similarly, the negative pendant conversion cannot be explained by inadequate interpulse delay, and so forth. This suggested that some nuclei possess such small T_2 values (caused by immobility) that the resulting broad lines escape detection. In fact, this has been for styrene/EGDMA copolymers,[87] and in that case ^{13}C NMR proved to be quantitative. Thus ^{13}C NMR was tried, but again apparent negative pendant conversions were measured.[88] Although quantification is more difficult in this case, it appeared that the restrictions of uniform irradiation profile and sufficient interpulse delay were met. Again we speculate that the explanation for these anomalies is immobile regions yielding specific nuclei with very short T_2 values. We emphasize, though, that in no way have we demonstrated this; it is merely consistent with our observations and not unexpected. Because of this, we cannot offer definite comments about the amount of cyclization other than following. The large amount of pendant double bonds indicated by both ^{1}H and ^{13}C NMR suggests that the pendant conversion is not terribly large, consuming perhaps 10 or 20% of the pendants, but certainly not the 90–99% required to explain the delay in gelation. Instead, we must conclude that a reduced reactivity of pendants, probably for steric reasons, is a major contributor as well.

Conclusions

The cross-linking copolymerization of MMA and EGDMA at 40 °C is very nonideal in the presence of large quantities of the cross-linker ($0.111 \leq a_4 \leq 0.819$), contradicting the ideal network theory on all points. The absolute gel point is 1–2 orders of magnitude later than that predicted by the ideal network theory, the difference becoming more severe as the amount of cross-linker increases. The gel point moreover is relatively insensitive to the amount of cross-linker, rather than exhibiting the inverse dependence expected, such that under the specific formulations used, gelation always occurred near 2% mass conversion. The gel point also exhibits a weaker dependence on the primary chain length DP_w^0 than the expected inverse dependence, perhaps more closely following an inverse square root dependence. Lastly, M_w diverges with an apparent critical exponent γ in the first decade of ϵ of approximately 1.5, while the ideal network theory for these polymerizations insists on an exponent of unity over the entire range $0 \leq \epsilon \leq 1$. This exponent is more in line with percolation theory than with classical theory. In addition, the scaling of the radius of gyration also supports a percolation viewpoint.

In addition to these contradictions of classical theory, a number of other unusual features were noted. Both the rate of polymerization and primary chain length increase with a_4, which together suggest a decrease in both the termination and the transfer rates with increasing a_4, perhaps due to steric reasons given a heterogeneous structure. While the primary chain length increases with a_4, the primary radius of gyration experiences no accompanying increase, so that the coils are becoming denser with increasing a_4. Cyclization could be the source of this. Finally, the solvent methyl ethyl ketone becomes a progressively worse solvent for chains with increasing cross-linker, as seen through the second virial coefficient.

These results point toward cyclization and reduced pendant reactivity as sources of the deviation. Measuring the extent of cyclization, however, was not possible due to nonquantitative spectra possibly resulting from broad, undetectable signals. However, given the large signals in both ^{1}H and ^{13}C NMR due to resonances associated with unsaturations, it has to be concluded that a large number of pendant double bonds remain in the polymer so that the delay in gel point cannot be solely attributed to cyclization. Thus, reduced pendant reactivity must also contribute, in agreement with past work.[12]

The most obvious gap in these experiments is the lack of knowledge as to the composition of the copolymers. The anomalous NMR results should be confirmed and studied, but given the difficulties encountered, it may be preferable for the purposes of determining composition to employ other analytical techniques not as sensitive to mobility. For example, the polymer composition could be found by gas chromatography on the remaining monomer, as is commonly done in copolymerization studies. It might also be advisable to choose a different monomer suited for a particular technique. Elemental analysis, for example, while useless for this system because of the similarity in elemental composition between the two monomers, could be used with monomers such as bis[4-(methacryloxy)benzylidene]-1,2-diaminoethane.[29,89] The fact that pendant conversion is determined by a difference is also the second difficulty encountered in the ^{1}H and ^{13}C NMR analysis, since the doubly reacted cross-linker has no distinguishable resonance of its own. It would be preferable, then, to find a cross-linker which, doubly reacted, exhibits a distinguishable resonance. A candidate would be methylene dimethacrylate, the synthesis of which is described by Hwa.[90] This monomer, like bis[4-(methacryloxy)benzylidene]-1,2-diaminoethane, also has the attractive feature of undergoing hydrolysis, so that the cross-links may be "cut" and the primary chain length and cyclization examined as done in other studies.[29,70,71,73,89]

In addition to elucidating the composition of these copolymers, this research strongly suggests other experiments. The dependence of the gel point on the primary chain length, weaker than expected, is an unexplored trait of these systems. Two points are hardly sufficient data to evaluate competing hypotheses, and so data over an order of magnitude would be preferable, and with changing a_4, so that the crossover to the expected behavior at small a_4 can be noted. Interpretation of these results, however, will be more complicated since the shorter the primary chains, the longer the pregel regime, and thus the more important the effects of conversion-dependent kinetics. Accounting for the possible compositional drift and the change in $DP_w{}^0$, which may have to be measured experimentally with a hydrolyzable cross-linker, would then be necessary. The use of a hydrolyzable cross-linker, though, may be advisable in any event, as it would eliminate the extrapolation to zero conversion made in this work. Experiments at smaller primary chain length would also allow for the determination of critical exponents over a larger range of ϵ than possible in this work in which the initial molecular weight itself was so high.

These more difficult experiments, over broader pregel regimes, are also necessary if by choosing conditions under which the predictions were simple, we necessarily chose conditions in which the situation is highly nonideal. When the ideal gel point is much lower than the coil overlap concentration c^*, the impenetrability of the polymer coils may be a main contributor to the apparent reduction in pendant reactivity and may explain the invariance of the gel point with a_4. This can be avoided by examining more extensive pregel regimes, with the requisite attention to the drifts in primary chain length and composition.

Acknowledgment. This research was supported through a grant from the Office of Naval Research.

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(2) Walling, C. *J. Am. Chem. Soc.* **1945**, *67*, 441.

(3) Dušek, K. In *Developments in Polymerization—3*; Haward, R. N., Ed.; Applied Science: London, 1982; pp 143–206.

(4) Dotson, N. A.; Galván, R.; Macosko, C. W. *Macromolecules* **1988**, *21*, 2560.

(5) Dotson, N. A. Ph.D. Thesis, University of Minnesota, 1991.

(6) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(7) This assumes that there are no chemical mechanisms which provide for a rapidly changing primary chain length in the first few percent of conversion, such as the case of a rapidly depleted transfer agent ($C_s \gg 1$) which results in a sharp increase in primary chain length at low conversions, a case discussed in the following: Dotson, N. A. *Macromolecules* **1992**, *25*, 308.

(8) Sorokina, L. I.; Radbil, T. I.; Sorokina, G. N.; Shtarkman, B. P. *Polym. Sci. USSR (Engl. Transl.)* **1983**, *25*, 2414 (*Vysokomol. Soedin., Ser. A* **1983**, *A25*, 2081).

(9) Podosenova, N. G.; Lachinov, M. B.; Revnov, B. V.; Cherep, Ye. I.; Zubov, V. P.; Budtov, V. P. *Polym. Sci. USSR (Engl. Transl.)* **1985**, *27*, 2822 (*Vysokomol. Soedin., Ser. A* **1985**, *A27*, 2513).

(10) Boutevin, B.; Parisi, J.-P.; Vaneeckhoutte, P. *Eur. Polym. J.* **1990**, *26*, 1027.

(11) Dvornić, P. R.; Jaćović, M. S. *Polym. Eng. Sci.* **1981**, *21*, 792.

(12) (a) Landin, D. T. Ph.D. Thesis, University of Minnesota, 1985. (b) Landin, D. T.; Macosko, C. W. *Macromolecules* **1988**, *21*, 846.

(13) Sawada, H. *Thermodynamics of Polymerization*; Marcel Dekker: New York, 1976.

(14) Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*; Wiley: New York, 1989.

(15) Kent, M. S. Ph.D. Thesis, University of Minnesota, 1990.

(16) Kaye, W.; McDaniel, J. B. *Appl. Opt.* **1974**, *13*, 1934.

(17) Huglin, M. B., Ed. *Light Scattering from Polymer Solutions*; Academic Press: London, 1972.

(18) Ochiai, H.; Kamata, K.; Murakami, I. *Polym. Commun.* **1984**, *25*, 158.

(19) Galina, H.; Dušek, K.; Tuzar, Z.; Bohdanecký, M.; Štokr, J. *Eur. Polym. J.* **1980**, *16*, 1043.

(20) Gel times and conversions for these sets of polymerizations were predicted from the molecular weight data, assuming an exponent of divergence $\gamma = 1.5 \pm 0.2$, as suggested by the apparent critical behavior for those polymerizations for which the gel point was known. Thus, the gel point was found by extrapolation to zero on a plot of $M_w{}^{-2/3}$ versus x.

(21) Storey, B. T. *J. Polym. Sci.* **1965**, *A3*, 265.

(22) Malinský, J.; Klaban, J.; Dušek, K. *J. Macromol. Sci., Chem.* **1971**, *A5*, 1071.

(23) Okasha, R.; Hild, G.; Rempp, P. *Eur. Polym. J.* **1979**, *15*, 975.

(24) Shah, A. C.; Parson, I. W.; Haward, R. N. *Polymer* **1980**, *21*, 825.

(25) Vijayakumar, C. T.; Fink, J. K. *Polym. Commun.* **1988**, *29*, 276.

(26) Baselga, J.; Llorente, M. A.; Herenández-Fuentes, I.; Piérola, I. F. *Eur. Polym. J.* **1989**, *25*, 471.

(27) Ulbrich, K.; Ilavský, M.; Dušek, K.; Kopeček, J. *Eur. Polym. J.* **1977**, *13*, 579.

(28) Ulbrich, K.; Dušek, K.; Ilavský, M.; Kopeček, J. *Eur. Polym. J.* **1978**, *14*, 45.

(29) Wesslau, H. *Angew. Makromol. Chem.* **1967**, *1*, 56.
(30) Ito, K.; Murase, Y.; Yamashita, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 87.
(31) Matsumoto, A.; Takahashi, S.; Oiwa, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (2), 149.
(32) Stauffer, D. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1354.
(33) Stauffer, D.; Coniglio, A.; Adam, M. *Adv. Polym. Sci.* **1982**, *44*, 103.
(34) Herrmann, H. J.; Landau, D. P.; Stauffer, D. *Phys. Rev. Lett.* **1982**, *49*, 412.
(35) Herrmann, H. J.; Stauffer, D.; Landau, D. P. *J. Phys. A* **1983**, *16*, 1221.
(36) Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 370.
(37) Adolf, D.; Martin, J. E. *Macromolecules* **1990**, *23*, 3700.
(38) Daoud, M. *J. Phys., Lett.* **1979**, *40*, L-201.
(39) Whitney, R. S.; Burchard, W. *Makromol. Chem.* **1980**, *181*, 869.
(40) Munch, J.-P.; Ankrim, M.; Hild, G.; Okasha, R.; Candau, S. *Macromolecules* **1984**, *17*, 110.
(41) Bacri, J.-C.; Courdille, J.-M.; Dumas, J.; Rajaonarison, R. *J. Phys., Lett.* **1980**, *41*, L-369.
(42) Adam, M.; Delsanti, M.; Munch, J. P.; Durand, D. *J. Phys.* **1987**, *48*, 1809.
(43) Patton, E. V.; Wesson, J. A.; Rubinstein, M.; Wilson, J. C.; Oppenheimer, L. E. *Macromolecules* **1989**, *22*, 1946.
(44) Adolf, D.; Martin, J. E.; Wilcoxon, J. P. *Macromolecules* **1990**, *23*, 527.
(45) Koňák, Č.; Tuzar, Z.; Jakeš, J.; Štěpánek, P.; Dušek, K. *Polym. Bull.* **1987**, *18*, 329.
(46) Kajiwara, K.; Burchard, W.; Kowalski, M.; Nerger, D.; Dušek, K.; Matějka, L.; Tuzar, Z. *Makromol. Chem.* **1984**, *185*, 2543.
(47) Martin, J. E.; Wilcoxon, J.; Adolf, D. *Phys. Rev. A* **1987**, *36*, 1803.
(48) Hayden, P.; Melville, H. *J. Polym. Sci.* **1960**, *43*, 215.
(49) Horie, K.; Otagawa, A.; Muraoka, M.; Mita, I. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 445.
(50) Li, W.-H.; Hamielec, A. E.; Crowe, C. M. *Polymer* **1989**, *30*, 1513, 1518.
(51) Shah, A. C.; Holdaway, I.; Parsons, I. W.; Haward, R. N. *Polymer* **1978**, *19*, 1067.
(52) Matsumoto, A.; Yonezawa, S.; Oiwa, M. *Eur. Polym. J.* **1988**, *24*, 703.
(53) Tobita, H.; Hamielec, A. E. *Polymer* **1990**, *31*, 1546.
(54) (a) Matsumoto, A.; Matsuo, H.; Oiwa, M. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 373. (b) Matsumoto, A.; Matsuo, H.; Oiwa, M. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 287.
(55) Matsumoto, A.; Yonezawa, S.; Oiwa, M. *Eur. Polym. J.* **1988**, *24*, 703.
(56) Matsumoto, A.; Ando, H.; Oiwa, M. *Eur. Polym. J.* **1989**, *25*, 385.
(57) Matsumoto, A.; Inoue, H.; Matsumoto, T.; Oiwa, M.; Kimura, T.; Saito, H. *J. Macromol. Sci., Chem.* **1989**, *A26*, 1279.
(58) Matsumoto, A.; Matsumoto, T.; Inoue, H.; Oiwa, M.; Saito, H. *Eur. Polym. J.* **1990**, *26*, 661.
(59) Matsumoto, A.; Kohama, Y.; Oiwa, M. *Polymer* **1990**, *21*, 2141.
(60) Zimm, B. H.; Price, F. P.; Bianchi, J. P. *J. Phys. Chem.* **1958**, *62*, 979.
(61) Soper, B.; Haward, R. N.; White, E. F. T. *J. Polym. Sci., Part A-1* **1972**, *10*, 2545.
(62) Holdaway, I.; Haward, R. N.; Parsons, I. W. *Makromol. Chem.* **1978**, *179*, 1939.
(63) Walczyński, B.; Kolarz, B. N.; Galina, H. *Polym. Commun.* **1985**, *26*, 276.
(64) Batzilla, T.; Funke, W. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 261.
(65) Daoud, M.; Leibler, L. *Macromolecules* **1988**, *21*, 1497.
(66) Červenka, A.; Kratochvíl, P. *Collect. Czech. Chem. Commun.* **1970**, *35*, 1695.
(67) Kamada, K.; Sato, H. *Polym. J.* **1971**, *2*, 489.
(68) Dubois, M.; Cabane, B. *Macromolecules* **1989**, *22*, 2526.
(69) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991.
(70) Minnema, L.; Staverman, A. J. *J. Polym. Sci.* **1958**, *29*, 281.
(71) Simpson, W.; Holt, T.; Zetie, R. J. *J. Polym. Sci.* **1953**, *10*, 489.
(72) Gordon, M. *J. Chem. Phys.* **1954**, *22*, 610.
(73) Simpson, W.; Holt, T. *J. Polym. Sci.* **1955**, *18*, 335.
(74) Gordon, M.; Roe, R.-J. *J. Polym. Sci.* **1956**, *21*, 27, 39, 57, 75.
(75) Hendriks, E. M.; Ernst, M. H.; Ziff, R. M. *J. Stat. Phys.* **1983**, *31*, 519.
(76) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(77) Kast, H.; Funke, W. *Makromol. Chem.* **1979**, *180*, 1335.
(78) Dušek, K.; Galina, H.; Mikeš, J. *Polym. Bull.* **1980**, *3*, 19.
(79) Tulig, T. J.; Tirrell, M. *Macromolecules* **1981**, *14*, 1501.
(80) Lee, L. J. *Polym. Eng. Sci.* **1981**, *21*, 483.
(81) (a) González, V. M. Ph.D. Thesis, University of Minnesota, 1983. (b) González-Romero, V. M.; Macosko, C. W. *J. Rheol.* **1985**, *29*, 259.
(82) (a) Batch, G. L. Ph.D. Thesis, University of Minnesota, 1989. (b) Batch, G. L.; Macosko, C. W. *J. Appl. Polym. Sci.* **1992**, *44*, 1711.
(83) Bamford, C. H.; Jenkins, A. D.; Ingram, D. J. E.; Symons, M. C. R. *Nature* **1955**, *175*, 894.
(84) Zhu, S.; Tian, Y.; Hamielec, A. E.; Eaton, D. R. *Polymer* **1990**, *31*, 154.
(85) Hill, D. J. T.; George, G. A.; Pomery, P. J.; Rogers, D. G.; Carswell, T. G. *Polym. Mater. Sci. Eng.* **1992**, *66*, 297.
(86) The overall copolymer composition was measured from a comparison of the ethylene glycol peaks at 4.19 and 4.34 ppm with the methoxy peak at 3.59 ppm, while the pendant conversion was measured by comparison with the pendant methylene peaks at 5.57 and 6.10 ppm. The equation for pendant conversion suggested by Landin[12] was not used; it relies on a comparison of the polymeric pendant methylene and the near-backbone α-methyl. The disadvantages of this approach are numerous. It depends on separation of the backbone methylene and α-methyl resonances in a region where the baseline is hard to determine. This can be alleviated somewhat by decreasing the polymer concentration, but only at the cost of an increasing contribution of the impurity water (which appears at $\sim$1.6 ppm). Moreover, the complexity of the equation makes it more sensitive to errors than the simpler equations which depend only on differences. Lastly, it does not eliminate the necessity for either assuming the copolymer composition or using the ethylene glycol resonances, which were argued to be not separable from impurity resonance. Landin did the former, apparently on the basis of NMR data claimed to be not interpretable. These objections, along with the near impossibility of measuring a pendant conversion of 0.1 at such low amounts of cross-linker even under conditions favorable to quantification, render Landin's data questionable.
(87) Spěváček, J.; Dušek, K. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2027.
(88) The overall copolymer composition was measured from a comparison of the ethylene glycol peaks at 62 and 63 ppm with the methoxy peak at 51.7 ppm, while the pendant conversion was measured by comparison with the pendant carbonyl peak at 167.1 ppm and pendant quaternary at 136 ppm.
(89) Mrkvičková, L.; Kratochvíl, P. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1675.
(90) Hwa, J. C. H. *J. Polym. Sci.* **1962**, *58*, 715.

Registry No. MMA, 80-62-6; EGDMA, 97-90-5; EGDMA/MMA (copolymer), 25777-71-3.