mL of PhCN under nitrogen and kept at a constant temperature in a sealed NMR sample tube. The reaction was monitored by ^{31}P FT NMR with a Hitachi R-900 (36.43 MHz) spectrometer with proton decoupling, and the kinetic analysis was performed by determining the instantaneous concentrations of the monomer, propagating ends, and polymer units. The ^{31}P NMR spectrum was recorded after 8 scans with a pulse interval of 2 s. The time (16 s) to record the spectrum was so short that it was not necessary to take it into account for the kinetic analysis. The concentrations of the respective species were obtained directly from the integral intensity of the spectrum. The reaction system was homogeneous throughout the kinetic run.

Spectral Measurements. ^{1}H and ^{19}F NMR spectra were recorded on a Hitachi R-20B NMR spectrometer (60 and 56.46 MHz, respectively).

Registry No. 1, 16324-17-7; MeOTf, 333-27-7; MeI, 74-88-4; benzyl bromide, 100-39-0; benzyl chloride, 100-44-7.

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Dynamic Light Scattering Study of Copolymers Prepared in the Pregel State by the Radical Copolymerization of Styrene–*m*-Divinylbenzene

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ABSTRACT: Dynamic light scattering experiments have been performed on benzene solutions of macromolecular clusters prepared by radical copolymerization of styrene with *m*-divinylbenzene. The hydrodynamic radius of the clusters was found to diverge at the gel point. The law of variation of the cluster size with the monomer consumption indicates a critical behavior of the system.

Introduction

Gelation mechanisms have been apprehended over the past 30 years through the fundamental theory introduced by Flory[1-3] and Stockmayer[4,5] or, more recently, through the cascade model developed by Gordon and co-workers.[6-10] These theories allow one to predict for an irreversible gelation both the gel point and the evolution of some structural characteristics of the branched aggregates when the gel point is approached (from both the pregel and postgel sides). As a matter of fact, experience on *f*-functional random polycondensations has given strong support to the Flory–Stockmayer model. More specifically, both the gel point and the increase in the weight-average molecular weight with the extent of the reaction were found to be in satisfactory agreement with the theoretical predictions.[1,11] However, the Flory–Stockmayer model neglects excluded volume effects, steric hindrance, and cyclic bonds. The latter effect, which is known from the very early works to delay the gel point,[1,11] has given rise to a large number of studies.[12,23] Recently, percolation models have been applied to polymer gelling systems. As in the classical mean field models, the properties are defined by only one parameter, the conversion factor p, defined as the ratio of the actual number of bonds between monomers at a given time to the maximally possible number of such bonds. In the bond percolation model, which is the most widely used, the monomers occupy all the sites of a lattice, and between two nearest neighbors of lattice sites a bond is formed randomly with probability p. A cluster is defined as a group of lattice sites connected directly or indirectly by bonds. The infinite cluster that appears for p larger than the percolation threshold p_c is identified with the gel. Such a model takes into account excluded volume, cyclization, and possibly solvent effects.[24-28] It does not predict the gel point, as the p_c value depends on the choice of the lattice, but, on the other hand, it allows for a variation of p_c with the polymer volume fraction for gelations performed in the presence of a solvent.[24-28] However, the most important feature of the percolation models is that they predict critical exponents that differ drastically from those of the classical theories. As for the critical phenomena, the percolation model should apply only in the vicinity of the gel point, so that one expects to observe a crossover from classical to percolation behavior as p approaches to p_c. Up to now, there has been no clear experimental evidence for such a crossover but one must underline the paucity of experimental data (and there are far more theoretical papers

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Table I
Characteristics of Sample P9

init comp	41.7% styrene, 1.05% *m*-DVB, 1.27% AIBN
gel point t_c	8.5 h
conv factor p_m at reaction time	0.090 at 1 h, 0.176 at 2 h, 0.255 at 3 h, 0.329 at 4 h, 0.407 at 5 h, 0.457 at 6 h, 0.512 at 7 h

currently appearing than experimental ones). Furthermore, the analysis of the experimental results involves the following difficulties:

(i) It is not always obvious to relate the experimentally accessible parameters to the conversion factor p. Generally, the isoreactivity of all unsaturated chemical groups is assumed. However, there is experimental evidence of the contrary for several systems.[29-32] Recently, Cohen and Benedek reconsidered the Flory–Stockmayer model and presented a statistical mechanical treatment showing that the critical exponents are markedly dependent on the rules of chemical bonding between combining units.[32]

(ii) The exact determination of p_c is difficult and a small error on p_c can lead to large incertainties in $(p_c - p)/p_c$, which is the parameter relevant for the data analysis.

(iii) Except for a few systems,[33] there are no simple criteria allowing one to predict the range of $(p_c - p)/p_c$ in which the percolation behavior is expected to be observed. This range depends largely on the characteristics of the gelling system.

In this paper, we report a light spectroscopy investigation of benzene solutions of copolymers formed in the pregel state of a radical copolymerization process of styrene with *m*-divinylbenzene (*m*-DVB). The purpose of this study is to determine the variation of the average hydrodynamic radius of the clusters and the variance that gives a measure of the width of the radii distribution as a function of the overall conversion degree p_m of styrene and divinylbenzene. This factor is the most directly accessible parameter to characterize the extent of reaction.

Experimental Section

Sample Preparation. The radical copolymerization of styrene and *m*-DVB was performed in benzene solutions at $T = 60$ °C in the presence of 2,2′-azobis-isobutyronitrile (AIBN) as an initiator. The details of the polymerization procedure are given in previous papers.[29,30] The initial monomer solution was divided into a series of sealed tubes. The soluble copolymers obtained at periodic time intervals were separated, weighed, and redissolved at low concentration in benzene.

Two series of samples (designated in the following as P9 and P14) were prepared. They differ only slightly in their DVB content and thus in the time t_c required for gelation. The conversion factor p_m is the ratio of the consumed monomers (styrene + *m*-DVB) to the total number of monomers. In spite of the greater reaction probability of the divinylbenzene, p_m represents also to a good approximation the fraction of reacted double bonds, since the *m*-DVB/styrene ratio is very small. It was measured at various times t for the samples of series P9 by gas–liquid chromatography. The values of p_m are reported in Table I. For the series P14, p_m was not measured.

Correlation Time Measurements. A Spectra-Physics He–Ne laser ($\lambda = 632.8$ nm) was used in conjunction with a 96-channel clipped digital autocorrelator (Precision Devices and Systems Ltd Malvern) for measuring the autocorrelation function of the scattered light intensity. The scattering angle was varied from 20° to 90°. The experiments were performed at a temperature of 25 °C, which was held constant to within ±0.01 °C.

Intensity correlation data were routinely processed by using the method of cumulants[35-37] to provide the average decay rate $\bar{\Gamma}$ and the variance v. The latter parameter is a measure of the width of the distribution of decay rates and is given by

$$v = (\overline{\Gamma^2} - \bar{\Gamma}^2)/\bar{\Gamma}^2 \qquad (1)$$

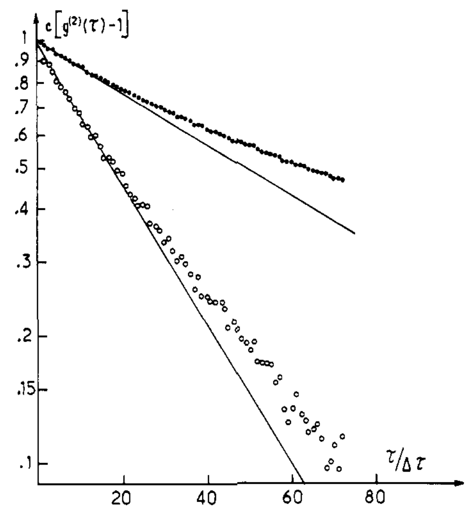

Figure 1. Semilogarithmic plots of $C[g^{(2)}(\tau) - 1]$ as a function of $\tau/\Delta\tau$ for sample P14 ($\theta = 30°$; $c = 0.01$ g cm^{-3}): (●) $\Delta t/t_c = 0.11$, $\Delta\tau = 10$ μs; (○) $\Delta t/t_c = 0.56$, $\Delta\tau = 5.5$ μs. The straight lines have slope $2D_0K^2$.

where $\overline{\Gamma^2}$ is the second moment of the distribution.

The diffusion coefficient D was determined from the average decay rate $\bar{\Gamma}$ according to

$$\bar{\Gamma} = 2K^2D \qquad (2)$$

The magnitude of the scattering vector K is given by

$$K = (4\pi n \sin(\theta/2))/\lambda \qquad (3)$$

where θ is the scattering angle, λ is the wavelength of the incident light in vacuo, and n is the index of refraction of the scattering medium.

Results

The autocorrelation function of light scattered from the copolymer solutions was significantly nonexponential, as could be expected from the polydispersity of the samples, which becomes very large near the gel point. However, for all the samples investigated in this study the data could be analyzed by Pusey's procedure.[37] More specifically, the average decay rate $\bar{\Gamma}$ as determined from a quadratic cumulant fit was found to be independent of the sampling time $\Delta\tau$ for $\bar{\Gamma}\Delta\tau < 0.04$. Figure 1 shows semilog representations of two typical time dependences of $C[g^{(2)}(\tau) - 1]$, where $g^{(2)}(\tau)$ is the normalized autocorrelation function for the scattered intensity and C is a constant depending on the experimental geometry. The background associated with the dc component was measured from time-delayed channels. The top portion of Figure 1 corresponds to a sample obtained at a time relatively close to the gel point ($\Delta t/t_c = 0.11$). The autocorrelation function of the bottom part of Figure 1 is for $\Delta t/t_c = 0.56$. Figure 2 illustrates the dependence of the average decay time on the scattering vector K for two samples. It can be observed that for the sample prepared far from the gel point $\bar{\Gamma}/2K^2$ is independent of K whereas $\bar{\Gamma}/2K^2$ decreases with K for the copolymer corresponding to the vicinity of the gel point. In the following, the average diffusion constant D will be taken as the limit when $K \to 0$ of $\bar{\Gamma}/2K^2$.

The concentration dependence of D for several samples is reported in Figure 3. The extrapolation of $D(c)$ to zero concentration gives the self-diffusion constant D_0.

The variations of D_0 with the time elapsed from the beginning of the copolymerization reaction for both P9 and P14 are given in Figure 4. The diffusion coefficient decreases rapidly at t increases and extrapolates to zero at t values in rather good agreement with the t_c values obtained from visual observation, which are $t_c = 6.75$ h (P14)

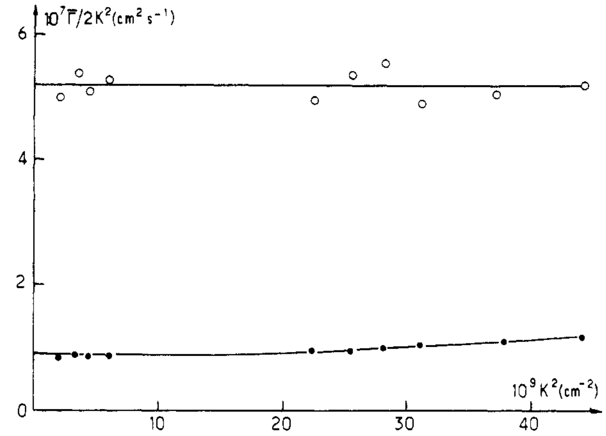

Figure 2. Variations of $\bar{\Gamma}/2K^2$ with K^2 for sample P14: (●) $t = 6$ h ($\Delta t/t_c = 0.11$), $c = 0.0025$ g cm^{-3}; (○) $t = 3$ h ($\Delta t/t_c = 0.56$), $c = 0.01$ g cm^{-3}.

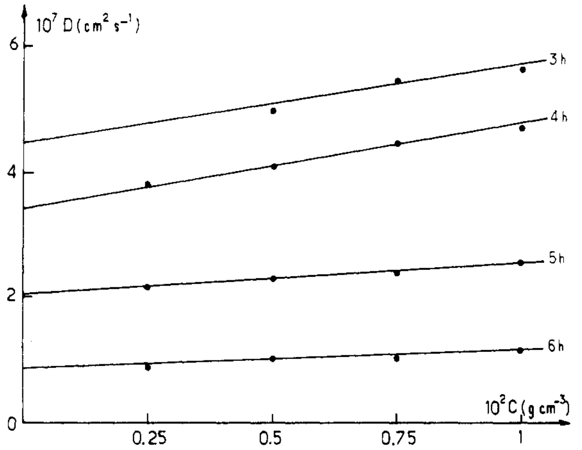

Figure 3. Concentration dependences of D for sample P14.

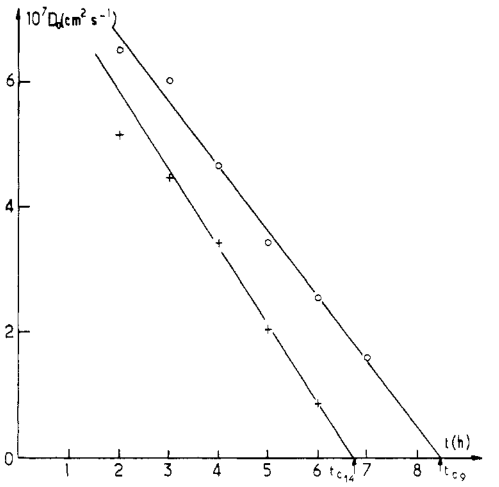

Figure 4. Variations of D_0 with the time elapsed from the beginning of the reaction: (+) P14; (○) P9.

and $t_c = 8.5$ h (P9), respectively.

The increase of particle size polydispersity when the gel point is approached is illustrated by Figure 5 where the variance v of the distribution function of decay rates is plotted vs. t.

Discussion

The ensemble of results reported here yields some information on the growth of the polymer particles as the copolymerization reaction proceeds. More specifically, the self-diffusion coefficient D_0 is a measure of the average hydrodynamic radius R_H of the particles defined through the Stokes-Einstein relationship:

$$D_0 = k_B T/6\pi\eta_0 R_H \qquad (4)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η_0 the viscosity of the solvent. For linear chains, the hydrodynamic radius is smaller than the radius of gyration as both theoretically predicted[38,39] and experimentally observed.[40-43] Generally, $R_H/R_G \sim 0.5$–0.7. The same conclusion can be inferred here from the K dependence of $\bar{\Gamma}/2K^2$ for samples obtained in the vicinity of the gel point (cf. Figure 2). The observed increase of $\bar{\Gamma}/2K^2$ with K can be assigned to the onset of internal deformation modes in the polymer particles. The contribution of these modes to the correlation functions becomes significant only when $KR_G \gtrsim 1$.[40] From the results reported in Figure 2 one can estimate that the internal-mode contribution occurs for approximately $K \gtrsim (1$–$1.4) \times 10^5$ cm^{-1}, which gives as an order of magnitude $R_G \sim 700$–1000 Å. The value of R_H determined from D_0 is $R_H = 380$ Å. As a matter of fact, both R_G and R_H represent averaged values since the samples are polydisperse. The radius of gyration is given by a z average; that is

$$R_G = \sum s^2 n_s R_s^2 / \sum s^2 n_s \qquad (5)$$

where s is the number of monomers in a so-called "s cluster" and n_s and R_s are the number and the radius of gyration of s clusters.

The hydrodynamic radius, as obtained from the cumulant analysis of the autocorrelation function of scattered light is defined through a z average of R_{Hs}^{-1}; that is[35-37]

$$R_H^{-1} = \sum s^2 n_s R_{Hs}^{-1} / \sum s^2 n_s \qquad (6)$$

where R_{Hs} is the hydrodynamic radius of the s cluster. Because of the different averages involved in the determination of R_G and R_H, the inequality between these two parameters will be enhanced by the polydispersity of the particle sizes.

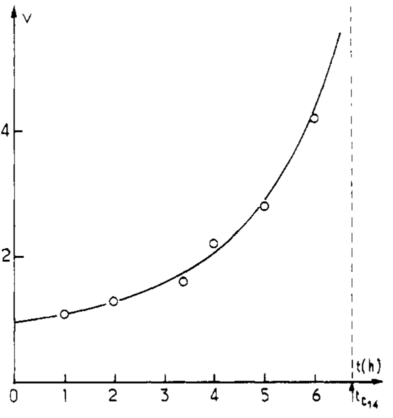

Figure 5. Variance vs. the time elapsed from the beginning of the reaction for sample P14 ($c = 0.01$ g cm^{-3}).

However, we are mainly interested in this study in the variation of R_H or equivalently of D with the bond probability p, or more specifically

$$\Delta p/p_c = p(t)/p_c$$

In previous studies,[40,45] $\Delta p/p_c$ was assimilated to $\Delta t/t_c$ in the vicinity of t_c. Figure 6 shows log–log plots of D_0 vs. $\Delta t/t_c$ for both P9 and P14 samples. The results are well represented by two straight lines with approximately the same slope of about 1.

A more relevant parameter to characterize the extent of the reaction is given by the monomer conversion factor p_m. This parameter has been shown previously to vary with time according to a first-order law.[29,30] The time

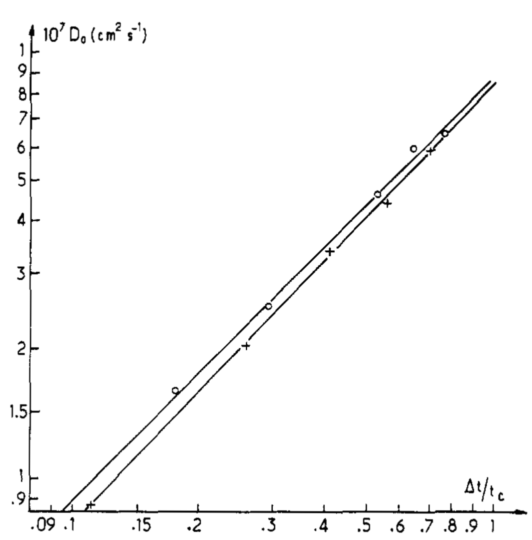

Figure 6. log–log plots of D_0 vs. $\Delta t/t_c$: (+) P14; (O) P9.

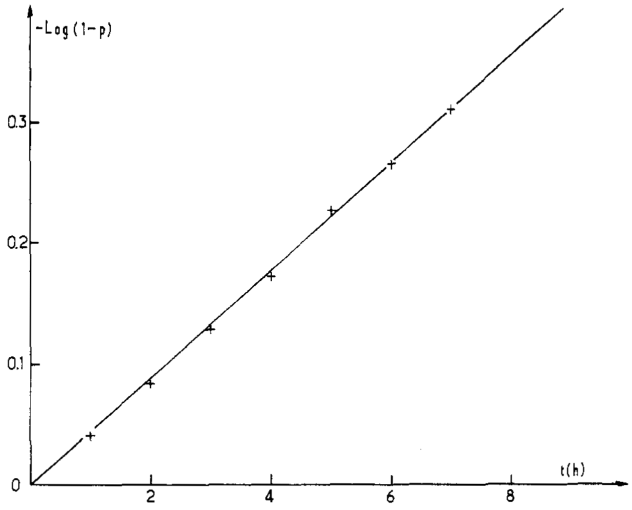

Figure 7. Time dependence of the monomeric conversion factor p_m for sample P9 ($p_{mc} = 0.59$).

dependence of p_m for sample P9 is presented in Figure 7. The extrapolation of $p_m(t)$ to t_c provides a determination of p_{mc}. The accuracy in p_{mc} is not very good because of the errors involved in both the extrapolation procedure and the determination of t_c. However, since no measurements were performed in the close vicinity of t_c, an error in p_{mc} does not affect the results very much. The variation of $\Delta p_m/p_{mc}$ with $\Delta t/t_c$ is given in Figure 8. Figure 9 presents a log–log plot of D_0 vs. $\Delta p_m/p_{mc}$ for samples P14 and P9. We have assumed here that the variation of $\Delta p_m/p_{mc}$ was the same for the two systems, which differ only slightly in their DVB content. Figure 9 shows that the variation of D_0 with $\Delta p_m/p_{mc}$ is well described by the law

$$D_0 \propto (\Delta p_m/p_{mc})^{\nu'}$$

with $\nu' = 0.88$ and $\nu' = 0.95$ for samples P9 and P14, respectively.

Let us discuss this result in the framework of the current theories. The variation of the z-average radius of gyration with $\Delta p/p_c$ has been shown to be given by the following power law:[24]

$$R_G \propto (\Delta p/p_c)^{\nu}$$

If one assumes that both the radius of gyration and the hydrodynamic radius of an s cluster obey the same scaling law, that is

$$R_s \propto R_{Hs} \propto s^{\rho}$$

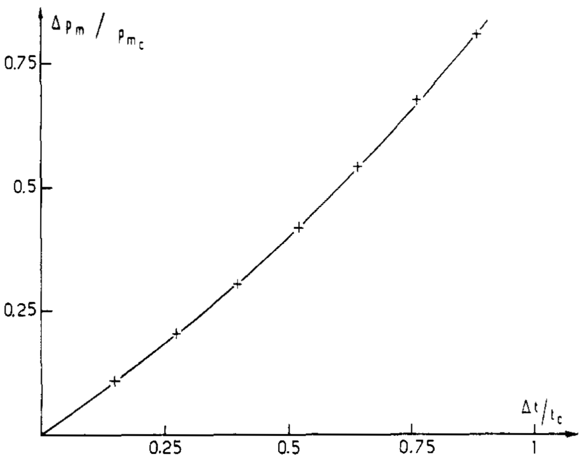

Figure 8. Variation of $\Delta p_m/p_{mc}$ with $\Delta t/t_c$ for sample P9.

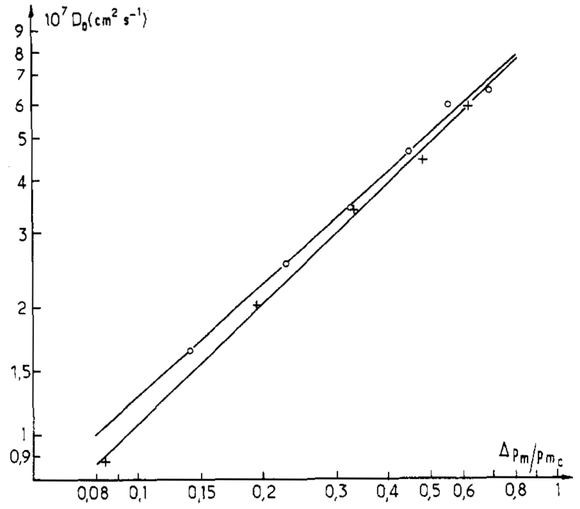

Figure 9. Variation of D_0 vs. $\Delta p_m/p_{mc}$: (+) P14; (O) P9.

then R_H and R_G will also follow the same scaling law as a function of $\Delta p/p_c$:

$$R_G \propto R_H \propto (\Delta p/p_c)^{\nu}$$

In the percolation theory $\nu = 0.88$[24]

At first sight, the experimental results seem to favor the percolation model if one identifies p and p_m. Let us, however, discuss the different assumptions that have been postulated to reach this conclusion.

(a) It has been assumed that the size of the clusters was the same in dilute solutions as in situ. This is a reasonable assumption since the reaction is performed in the presence of a good solvent and at moderate concentration ($c = 0.16$ g cm^{-3} for the most concentrated sample).

(b) It is likely that the ratio R_H/R_G varies somewhat with the branching of the species formed during the reaction. However, this effect should be pronounced only in the close vicinity of the gel point. Furthermore, the critical growth of the cluster as the reaction proceeds can be independently inferred from the particle molecular weight behavior. Light scattering measurements of weight-average molecular weight have been performed by Okasha[29] and by Hild and Rempp[30] on a system of composition very close to that of P9 or P14 (2% DVB instead of 1.9% and 2.13%, respectively). The variation of M_w with $\Delta p_m/p_{mc}$ as deduced from their results is reported in Figure 10. Not too far from the gel point the results are described by the law

$$M_w \propto (\Delta p_m/p_{mc})^{1.8}$$

Again the value of the exponent is rather close to that

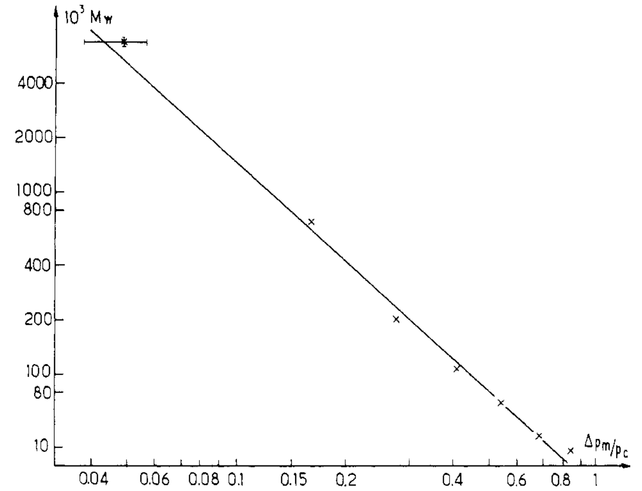

Figure 10. log–log plot of M_w vs. $\Delta p_m/p_{mc}$. The data are taken from ref 30.

predicted by the percolation theory, $\gamma = 1.7$, the classical value being $\gamma = 1$.

(c) The major difficulty concerns the relation between the chemical conversion factor p_m and the probability p. These two parameters can be identified with each other only if all chemical groups have the same reactivity. Recent studies of Okasha et al.[29,30] show that in the reaction considered here, the consumption of DVB is much faster than that of styrene. There is also strong experimental evidence that the first double bond of DVB is much more reactive than the second one. As a consequence, in the early stage of the reaction, linear or slightly branched chains containing pendant double bonds are formed. In a later stage these double bonds would react and connect the "primary chains" to form highly branched objects. This process would then resemble the vulcanization reaction in solution, for which critical exponents have been predicted.[34]

Finally, it is worth noting the results obtained by Schmidt and Burchard on a similar chemical system.[23] In these experiments, styrene and technical divinylbenzene were anionically copolymerized at complete conversion. Samples at varying distance from the gel point were obtained by changing the initiator concentration. Using as a reaction variable the [DVB]/[initiator] ratio, Schmidt and Burchard found classical values of the exponents near the gel point whereas in the region far away from the gel point, a behavior compatible with the percolation models was observed. The latter result is in agreement with our observations, although the two studies are not directly comparable in view of the totally different experimental conditions.

Conclusion

In this study, it has been shown that the self-diffusion coefficient of clusters increases with the monomeric conversion factor according to a power law $D_0 \propto (\Delta p_m/p_{mc})^{\sim 0.9}$. In the range of investigated p_m, there is no evidence of a crossover between two different regimes. The rapid growth of the clusters is a typical behavior of a critical system and the value of about 0.9 for the exponent favors a percolation model. It is also worth noting that in the reaction considered here, the primary chains formed in the early stage of the reaction are rather short; this and also the presence of solvent are favorable for the occurrence of a percolation mechanism over a large domain of $(\Delta p_m/p_{mc})$.[33,34] However, it is difficult to conclude whether the observed behavior is a result of the difference of reactivity between the different chemical groups involved in the reaction or a manifestation of the universality of the percolation models. Obviously, the answer could only be obtained by collecting many experimental data on different systems.

Registry No. (*m*-Divinylbenzene)·(styrene) (copolymer), 25703-32-6.

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