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Critical Exponents in Polymers: A Sol–Gel Study of Anionically Prepared Styrene–Divinylbenzene Copolymers

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ABSTRACT: Anionic copolymerization of divinylbenzene (DVB) with styrene (St) leads at low ratios of R ([DVB]/[initiator]) to branched polymers which beyond $R_c = 15.1$ form macroscopic gels. A sol–gel separation has been carried out. Molecular weights M_w and M_n and radii of gyration $\langle S^2\rangle_z^{1/2}$ of samples from the pregel and postgel have been measured by light scattering and plotted as functions of $\epsilon = |1 - (1 - r)R/(1 - r_c)R_c|$, where r, which could be determined from measurement of M_n, is the extent of ring formation of the second double bonds from the DVB units. The critical exponents so far determinable by experiment tend to support the Flory–Stockmayer (FS) theory rather than percolation theory. Because of the large extent of ring formation, full agreement is not obtained with the classical FS theory, as expected, since this theory neglects the long-range correlation effects associated with ring formation.

Introduction

Critical phenomena have been known since 1869 when Andrews[1] reported a phase diagram of carbon dioxide. Since then, a large number of critical systems have been discovered in physics and in physical chemistry, and much effort has been invested in a theoretical description of these phenomena. Mainly two controversial concepts have been developed. First and powerful success was achieved by theories which are now called mean-field theories (e.g., the van der Waals equation for the gas–liquid phase transition,[2] Weiss treatment of ferromagnetism,[3] and Flory–Huggins theory for liquid–liquid phase transitions mainly in polymers[4,5]). With Ising's famous treatment of one-dimensional ferromagnetism[6] by a first-order Markovian process, it has become more and more common to take into consideration nearest-neighbor interactions and the resulting cooperative nature of the critical phenomena. Extension of Ising's calculation to three-dimensional lattices has challenged many scientists, but so far an exact solution has only been found for the two-dimensional case by Onsager.[7] Computer simulations and approximate theories,[8–11] for instance, the scaling theory[12] and, more recently, the renormalization group theory,[13,14] have revealed, however, some relationships between the so-called critical exponents. According to these developments the properties of a system depend, in the vicinity of the critical point, on a function $\epsilon = (1 - T/T_c)$ with exponents which substantially deviate from the mean-field exponents (T and T_c are the temperatures at a given and at the critical point). A large number of measurements give strong evidence for these non-mean-field exponents.[9–11,15]

The astounding similarity of these exponents in quite different critical systems has led theoreticians to the hypothesis of universality for all critical phenomena. With this background, the recent interest of theoretical physicists in gelation processes becomes understandable, because this process is now considered unanimously as a critical phenomenon. It is useful, however, to stress the difference of this gelation phenomenon from the critical phenomena mentioned above.

(i) Most gelation processes in polymer science are, in practice, irreversible; i.e., once formed, the gel cannot simply be transformed into a solution by changing the temperature within a short interval of ϵ.

(ii) Gelation is not influenced by thermodynamic interaction of nearest-neighbor monomeric units. Instead, the process is controlled by kinetic equations and the resulting probabilities or extents of reaction, α.

(iii) The behavior of measurable quantities is determined by a reduced parameter $1 - \alpha/\alpha_c$ which takes the role of ϵ in the thermodynamic reversible critical phenomena.

Between 1941 and 1945 a theory of branching and gelation of polymers was developed by Flory and by Stockmayer.[16–20] This classical theory (hereafter FS) gives for the f-functional *random* polycondensation a very satisfactory prediction of the gel point and of the increase in

Table I
Critical Exponents and Relation between Order Parameter, Susceptibility, and Correlation Length for Various Systems[25] [a]

	exponent			
	expt (fluids)	mean-field theory	3-D Ising model	percolation theory[24]
order parameter	0.33-36	0.5	0.31	0.4
susceptibility	1.18-1.27	1.0	1.25	1.7
correlation length	0.59-0.67	0.5	0.64	0.8

system	order parameter	susceptibility	correlation length	ϵ
magnetism	M	χ_M	ξ	$1 - T/T_c$
gas-fluid	$\rho_L - \rho_G$	$\kappa_t = [p(\partial p/\partial \rho)_T]^{-1}$	ξ	$1 - T/T_c$
fluid-fluid	$c'' - c'$	$[c(\partial \Delta\mu/\partial c)_{p,T}]^{-1}$	ξ	$1 - T/T_c$
sol-gel	m_{gel}	M_w	$(\langle S^2 \rangle_z)^{1/2}$	$1 - \alpha/\alpha_c$
$\epsilon^{\text{exponent}}$	β	$-\gamma$	$-\nu$	—

[a] ρ_L and ρ_G are the densities of the liquid and gas phases, c'' and c' are the concentrations in the concentrated and dilute fluid phases, κ_t is the isothermal compressibility, p is the pressure, $\Delta\mu$ is the chemical potential, m_{gel} is the mass fraction of gel, M_w is the weight-average molecular weight, and $\langle S^2 \rangle_z^{1/2}$ is the radius of gyration (root of the z-average mean-square radius of gyration).

the weight-average molecular weight with the extent of reaction.[20,26,27] The FS treatment contains no mathematical approximations or premature averages, but it completely forbids ring formation in finite molecules and thus avoids all long-range correlations. It, therefore, enjoys the simplicity of a typical mean-field theory, to which it may be considered equivalent in this respect.

Recently, a model of percolation on a lattice in *space* has been applied to polymeric gelling systems.[21-24] Again, the properties are defined by only one parameter, p, the probability that two monomeric units come to lie on two adjacent lattice sites, whereupon a bond is formed. The percolation theory is considered to be equivalent to a non-mean-field theory, although no special parameter is introduced explicitly which could be related to the nearest-neighbor interaction or to long-range correlation between monomeric units as in the Ising model. The equivalence to a non-mean-field theory is based on results for the critical exponents which significantly deviate from those of the FS theory.[24] A list of the various critical exponents for phase separation and gelling systems is given in Table I.

The purpose of the present paper is to present some experimental data on critical exponents for a special polymer system, which may help to bring to the controversy a certain degree of clarification.

The Polymeric System

Critically branched polymers can be prepared by various techniques. Unfortunately, those systems which can be brought to gelation with ease are usually quite complex in their formation mechanism and are not appropriate for a crucial check of theories. On the other extreme we have the simple polycondensation;[20] but this process is not easily controlled in the vicinity of the gel point. The critical point occurs at fairly large extents of reaction, where, because of the high viscosity and the onset of a glass transition, the reaction can become diffusion controlled. Thus, the desired information from these theoretically simple systems can often be obtained only by extrapolation of data, obtained in a more or less dilute solution, to zero dilution.[20,26,27]

In the present study we have chosen anionically polymerized copolymers of styrene (St) with technical divinylbenzene (DVB). The polymerization was carried out in 5% solution in a good solvent (toluene) and was driven to complete reaction of all double bonds. Uncontrolled reaction of double bonds after isolation of the polymers, a serious problem in common St/DVB copolymers prepared by free radical polymerization, is here reduced to a minimum.[28-30]

The size of the molecules, i.e., M_w and $\langle S^2 \rangle_z$, is controlled by the molar ratio of DVB to the initiator concentration (eq 1) which takes the role of a link probability, as will be

$$R = [\text{DVB}]/[\text{initiator}] \qquad (1)$$

shown below. The molecular weight increases with increasing R ratio and tends to infinity at a critical value R_c. On the other hand, the high dilution and the fairly large amount of monovinyl monomers (87%) favor intramolecular reaction between pendant double bonds of the same macromolecule. This ring formation causes a shift of the gel point toward higher conversions of the monomer, and it is certainly the reason why undercritically branched polymers are obtained at low R ratios.

Results

The technique of polymerization has been described in previous papers.[29-31] Details of preparation for the present special system will be given in a separate paper, where also the hydrodynamic behavior and the influence of polydispersity are discussed. The present paper is confined to measurement of M_w, $\langle S^2 \rangle_z$, and the mass fraction of gel after a sol-gel separation.

The molecular weights and mean-square radii of gyration were measured by light scattering with a Sofica 4200 photogoniometer. Measurement was carried out in toluene at four or five concentrations and over an angular range of 20-150° in steps of 5°, and the results were extrapolated to zero concentration. The solutions were clarified by centrifugation for the lower molecular weight samples and by filtration through Millipore filters of 4.5-μm pore size for the high molecular weights. Figure 1 shows the dependence of M_w on R for the samples from the pregel stage and for the sol fraction from the postgel samples. As expected, M_w increases strongly when R_c is approached and decreases sharply beyond the gel point. The critical point is indicated by the vertical line in the figure but cannot be determined sufficiently precisely in this plot. Much better accuracy is achieved from a plot of $1/M_w$ against R, which is seen in Figure 2. The two curves from the pregel and the postgel can be accurately extrapolated to a zero value of $1/M_w$ and yield

$$R_c = 15.1 \begin{matrix} +\ 0.1 \\ -\ 0.04 \end{matrix}$$

where the upper limit of the error refers to the extrapo-

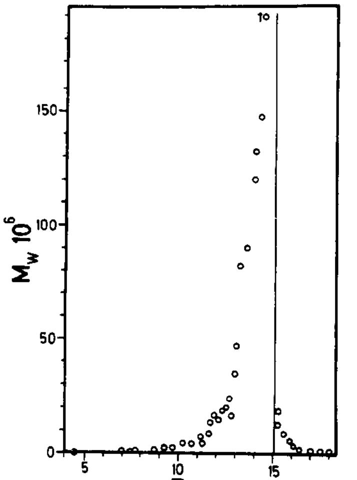

Figure 1. Molecular weight as a function of R (=[DVB]/[initiator]) for anionically prepared DVB/St copolymers: (○) samples before gelation (pregel); (●) from sol fraction (postgel).

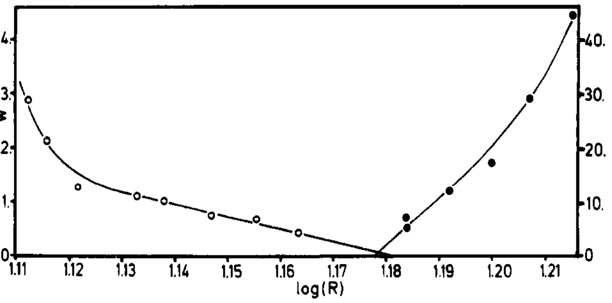

Figure 2. Plot of reciprocal molecular weight against log R for pregel (○) and postgel (●) samples. The two curves should intersect the abscissa at the same R_c. Note: the right scale (postgel) differs from the left scale (pregel).

lation of M_w from the pregel and the lower from the postgel.

Figure 3 shows the dependence of $\langle S^2\rangle_z$ on M_w. Even after allowance for some scatter, the curves for the pregel and the postgel samples show significantly different slopes. Apparently the postgel polymers differ slightly in their properties from the pregel materials. The two straight lines in Figure 3 can be represented by the empirical relationships

$$\text{pregel:} \quad \langle S^2\rangle_z = 5.5 \times 10^{-18} M_w^{1.025}\ \text{cm}^2$$

$$\text{postgel:} \quad \langle S^2\rangle_z = 0.74 \times 10^{-18} M_w^{1.17}\ \text{cm}^2$$

Finally, Figure 4 gives the mass fraction of gel after a sol–gel separtion as a function of R. This sol–gel separation is a delicate experimental problem. Reproducible results were obtained by the following technique. The gel was pressed through a filter (potato mash press) of about 2-mm pore diameter, which gave shreds of about 10 mm^3 in size. The shreds were left for about 12 h in a good solvent, toluene, and then filtered, and fresh toluene was added again to the shreds. The same procedure was repeated 5–7 times. The polymer was precipitated from the solution, and sol fraction and gel were dried under vacuum.

Discussion

As already mentioned, the St/DVB system does not gel below a critical R ratio or above a certain initiator concentration. The question now arises how this molar ratio is related to a branching probability and to the corresponding ϵ parameter. For *random* free radical copolymerization of a monovinyl with a divinyl monomer, cascade theory[32] gives

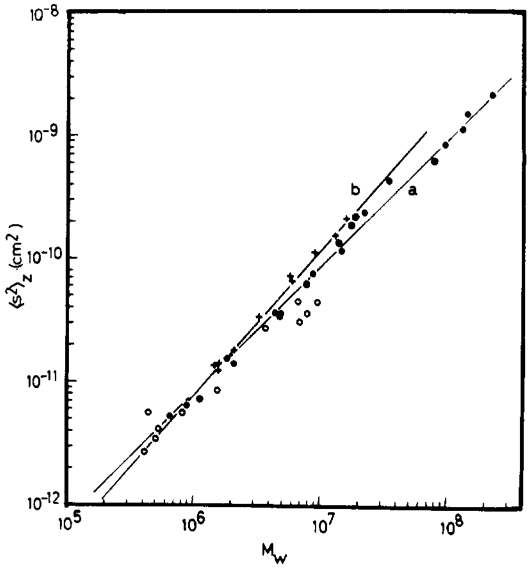

Figure 3. Molecular weight dependence of the mean-square radius of gyration $\langle S^2\rangle_z$ for pregel (curve a) and postgel (curve b) samples (○, ●, this work; +, Ullisch[45]).

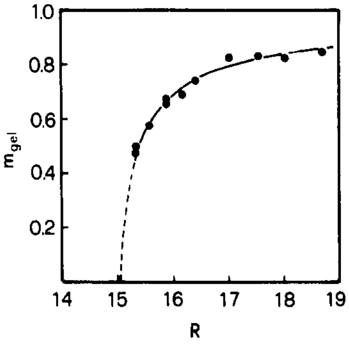

Figure 4. Mass fraction of gel after sol–gel separation as a function of R.

$$P_w/P_{wp} = (1 - (P_{wp} - 1)x\alpha)^{-1} = (1 - \alpha/\alpha_c)^{-1} \equiv \epsilon^{-1} \qquad (2)$$

and

$$\langle S^2\rangle_z/\langle S^2\rangle_{zp} = (1 + \alpha x)/(1 - (P_{wp} - 1)x\alpha) \sim \epsilon^{-1} \qquad (3)$$

where

$$\alpha_c = 1/((P_{wp} - 1)x) \qquad (4)$$

with the mole fraction of DVB in the polymer (the composition)

$$x = [\text{DVB}]/([\text{DVB}] + [\text{St}]) \qquad (5)$$

In these equations α is the probability of reaction of a pendant double bond or, in other words, the conditional probability for the reaction of the second double bond if the first has already reacted. The reaction of the first double bond together with the double bonds of the monovinyl monomers defines the primary chain degree of polymerization P_{wp}. Since x is the DVB composition in the polymer, αx is the cross-linking probability of primary chains. The number of pendant double bonds, i.e., the functionality f of a primary chain is thus given by

$$f = P_{wp}x \qquad (6)$$

The mean-square radii of gyration of the branched and the primary chain molecules are denoted by $\langle S^2\rangle_z$ and $\langle S^2\rangle_{zp}$, where under Θ conditions

$$\langle S^2\rangle_{zp} = b^2P_{wp}/4 \qquad (7)$$

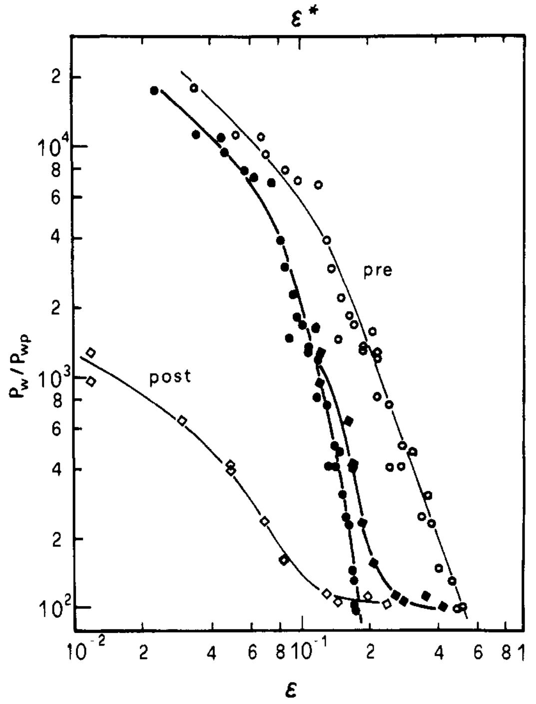

Figure 5. Plot of the reduced degree of polymerization P_w/P_{wp} for samples from the pregel (○, ●) and postgel (◇, ◆), respectively, as a function of $\epsilon = |1 - (1 - r)R/(1 - r_c)R_c|$ and $\epsilon^* = |1 - R/R_c|$. Circles, pregel; diamonds, postgel. The two well-separated curves of the pregel and postgel in the ϵ^* plot form an almost common curve in the ϵ plot. The open symbols refer to ϵ^* and the filled ones to ϵ.

with b being the effective bond length of a chain. An equation similar to eq 2 but with an extra factor $1 + \alpha$ was derived by Stockmayer[19] and later by Gordon.[33] This extra factor arises from a slight difference in the model. Stockmayer and Gordon considered cross-linking of previously formed chains, while in the present model the formation and cross-linking of primary chains takes place simultaneously.

Equations 2 and 3 cannot be applied directly to the present problem for two reasons: (i) The primary chain is not constant but increases with the R ratio. (ii) The reaction is taken always to complete reaction of *all* double bonds. Thus α is not longer the fraction of the second double bonds from DVB which have reacted; rather, it is the fraction of double bonds which is involved in a cross-linking reaction.

Let us denote by r the fraction of second double bonds which are wasted in intramolecular ring formation; then $\alpha = 1 - r$. In anionic polymerization the primary chains have a Poisson length distribution, where $P_{wp} - 1 = P_{np}$, and the number-average degree of polymerization is given by

$$P_{np} = (2[\mathrm{DVB}] + [\mathrm{St}])/[\mathrm{initiator}] = R(2 + A) = P_{wp} - 1 \quad (8)$$

with [initiator] the molar initiator concentration and A the molar ratio of styrene to divinylbenzene. Thus, instead of eq 2 we have

$$P_w/P_{wp} = (1 - (2 + A)xR(1 - r))^{-1} = (1 - R(1 - r)/R_c(1 - r_c))^{-1} = \epsilon^{-1} \quad (9)$$

with

$$R_c(1 - r_c) = 1/((2 + A)x) \quad (10)$$

Table II
Conditions of Anionic Styrene (St)-Divinylbenzene (DVB) Copolymerization[31 a]

solvent	toluene + 0.54 vol % THF
total volume	500 mL
total concentration of monomer	c = 5 vol %
DVB volume fraction (in the monomer mixture)	$\phi = 0.15$
DVB mole fraction	$x = 0.13$
St/DVB mole ratio	$A = 6.7$
mole ratio of initiator (n-butyllithium)	R = 6-18, $R_c = 15.1$
initiating temperature	−78 °C
polymerization temperature	25 °C

[a] $\phi = v_{\mathrm{DVB}}/(v_{\mathrm{DVB}} + v_{\mathrm{St}})$, $x = [\mathrm{DVB}]/([\mathrm{DVB}] + [\mathrm{St}])$, $A = [\mathrm{St}]/[\mathrm{DVB}]$, $R = [\mathrm{DVB}]/[\mathrm{initiator}]$.

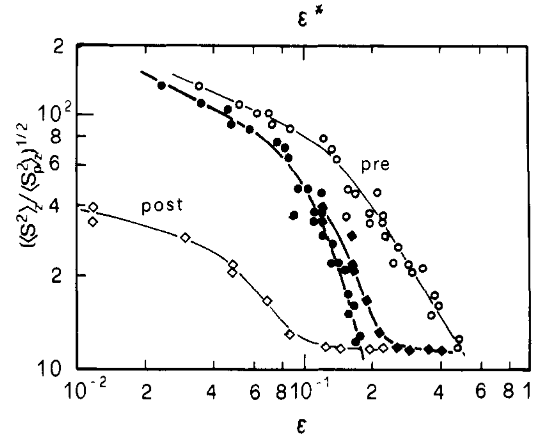

Figure 6. Plot of the reduced radius of gyration $(\langle S^2\rangle_z/\langle S_p^2\rangle)^{1/2}$ as a function of ϵ and ϵ^*, respectively. Notation is as in Figure 5.

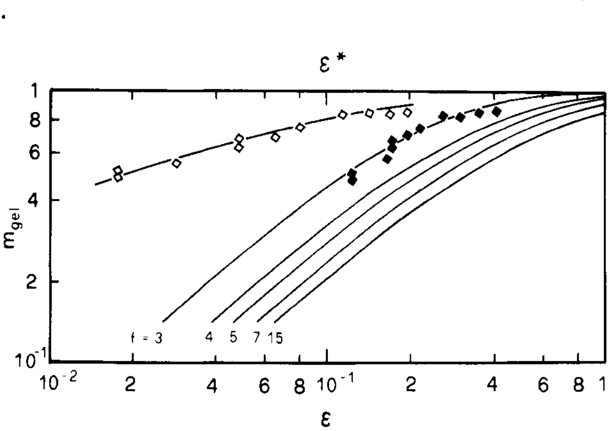

Figure 7. Mass fraction of gel, m_{gel}, as a function of ϵ (◆) and ϵ^* (◇), respectively. The curves indicated by f = 3, 4, 5, 7, and 15 are theoretical curves for f-functional random polycondensates calculated on the basis of cascade theory.[33,35]

The data for x and A used in this experimental study are listed in Table II; with $R_c = 15.1$ we find $1 - r_c = 0.059$; i.e., at the gel point only 5.9% of the second double bonds are involved in cross-links. Under the assumption that ring formation is independent of R, we have according to the cascade theory, eq 9

$$P_w/P_{wp} = 1/(1 - R/R_c) \equiv \epsilon^{*-1} \quad (11)$$

Figures 5–7 show the results of P_w/P_{wp}, $\langle S^2\rangle_z/\langle S^2\rangle_{zp}$, and the mass fraction of gel, m_{gel}, as functions of ϵ^*, where instead of eq 7 we have used

$$\langle S^2\rangle_z^{1/2} = 1.43 \times 10^{-9} M_w^{0.580}\ \mathrm{cm} \quad (12)$$

a relationship that was found by Yamamoto et al.[34] for anionically polymerized polystyrene in toluene. Equation 7 has not been used for two reasons. First, it refers to

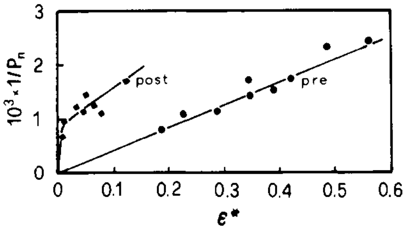

Figure 8. Dependence of the reciprocal number-average degree of polymerization on $\epsilon^* = |1 - R/R_c|$ for pregel (●) and postgel (♦) samples.

polymers at Θ conditions, but toluene is a very good solvent for polystyrene with a pronounced excluded-volume effect. Second, eq 7 describes polydisperse chains ($M_{wp}/M_{np} = 2$) while in anionic polymerization a Poisson length distribution with $M_{wp}/M_{np} \cong 1$ is observed,[20] where $\langle S^2 \rangle = b^2 P_{wp}/6$.

In all cases, curves are obtained from the double-logarithmic plot, rather than straight lines. This result contradicts both eq 11 and percolation theory, as the predicted high exponents are obtained in the noncritical region only.

The assumption of a constant average ring formation, underlying eq 11, is, however, doubtful and in fact need not be made. Average values for $1 - r$ can be obtained from measurements of the number-average degree of polymerization P_n of the branched polymer as follows. By simple stoichiometric arguments it can be shown[30] (see Appendix) that

$$P_n = pP_{np} \tag{13}$$

and

$$r = (R - 1)/R + 1/pR \tag{14}$$

where p is the number of primary chains per branched macromolecule. Combination of eq 10, 11, and 8 yields

$$(1 - r)R = 1 - R(2 + A)/P_n \tag{15}$$

We have carried out osmotic pressure measurements for ten samples in the pregel and eight in the postgel state. The dependence of $1/P_n$ on ϵ^* is shown in Figure 8. The two curves can be represented by the empirical relationships

$$\text{pregel:} \quad 1/P_n = 3.9 \times 10^{-3}\epsilon^* \tag{16a}$$

$$\text{postgel:} \quad 1/P_n = 7.0 \times 10^{-3}\epsilon^*(1 + 128/(1 + 1000\epsilon^*)) \tag{16b}$$

The correct ϵ parameter can now be expressed in terms of $\epsilon^* = |1 - R/R_c|$ (see eq 9, 15, 16)

$$\text{pregel:} \quad \epsilon = 0.511(1 - \epsilon^*)\epsilon^* \tag{17a}$$

$$\text{postgel:} \quad \epsilon = 0.920(1 - \epsilon^*)\epsilon^*(1 + 128/1000\epsilon^*) \tag{17b}$$

The influence of the R-dependent ring formation is substantial. The two well-separated curves of the pregel and postgel properties in the ϵ^* plot now appear to form almost one common relationship when plotted against ϵ. This suggests an amplitude ratio of $C^+/C^- \cong 1$ describing the degree of polymerization above (+) and below (−) the percolation threshold, which is in line with the FS theory. Percolation theory predicts[46] a ratio of about 10. It may be noticed that because of the variation of ring formation the points from the sol fraction are not as close to the gel point as it may appear from the plot of M_w against R (Figure 1). It is not R which is proportional to the probability of relation but $(1 - r)R$. As a consequence, M_w as a function of $(1 - r)R$ is far less asymmetric with respect to the gel point than in Figure 1. Also, after correction of ϵ^* for the R-dependent ring formation, bent lines in the double-logarithmic plots (Figures 5 and 6) are still observed. The exponents for P_w and $\langle S^2 \rangle_z^{1/2}$ seem to approach asymptotic values of $\gamma_c = 0.96$ and $\nu_c = 0.5$, which are close to the critical FS exponents, while the exponents of the percolation theory deviate strongly from experiment, with $\lambda_c^{perc} = 1.7$ and $\nu_c^{perc} = 0.8$.[24] The exponents at larger ϵ are $\gamma = 3.8$ and $\nu = 3.5$, which would be closer to the prediction of percolation theory, but here we are in the noncritical region, where to date no prediction exists from percolation theory. Similar behavior has previously been observed with branched PMMA copolymers,[32] where a curve was also obtained for P_w/P_{wp} in a plot against ϵ with $\gamma_c = 1.0$ in the critical region but $\gamma = 1.5$ in the noncritical region. The critical exponents are listed in Table III.

Table III
Critical and Noncritical Exponents from Experiment, Classical Flory–Stockmayer Theory, and Percolation Theory

	expt	classical theory	percolation theory[24]	Figure
γ	3.8	1.0		5
γ_c	0.96	1.0	1.7	5
ν	3.5	0.5		6
ν_c	0.5	0.5–0.6[a]	0.8	6
γ/β	4.5			10a
γ_c/β_c	<3.6	1.0	4.25	10a
ν/β	3.3			10b
ν_c/β_c	<1.65	0.5–0.6[a]	2.0	10b
ν/γ	0.54	0.5–0.6[a]		9
ν_c/γ_c	~0.50	0.5–0.6[a]	0.47	9

[a] Depends on excluded volume.

The question arises here whether the critical region for the percolation exponents is really covered by the measurements. As pointed out by Ginzburg, a non-mean-field behavior can be expected only if the fluctuation of the number of clusters (branched molecules of definite size) within a volume becomes significant; otherwise, a mean-field behavior will result.[47] In recent papers by de Gennes[48] and Daoud[49] formulas are derived for estimating the width of the critical region within which non-mean-field behavior should be observable. The de Gennes calculation is confined to the undiluted bulk state, for which the critical region is concluded to be too small to observe. Daoud's paper involves a number of restrictive assumptions which make its application doubtful for our experiments and in any case offers only scaling laws and not actual magnitudes. The Daoud model or any alternatives must surely agree that the width of the critical region increases with decreasing concentration of the polymerizing system. It must thus be conceded that the bounds of the critical region might fall within our experimental range, but it would at present be speculative to attribute the changes of slope in Figures 5 and 6 to this cause.

For another comparison we have calculated the dependence of m_{gel} on ϵ from Gordon's cascade theory,[33,35] which in this case corresponds to the FS theory. Again the mass fractions fall now in the region of the mean-field theory (Figure 7). The average functionality of the gelled samples according to eq 6 ranges from 35 to 42 and the results are thus not in complete agreement with the FS theory for random cross-linking. Such agreement indeed was not expected; the extraordinary large extent of ring formation of the second double bonds of the DVB units, of the order of 0.852–0.941 for the pregel state and of 0.941–0.968 for the postgel samples, makes a correction to the random theory necessary because of the non-Markovian character of ring formation in a branched or gelled material. Note

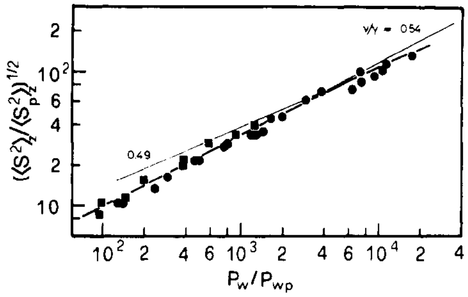

Figure 9. Dependence of reduced radius of gyration on reduced degree of polymerization: (●) pregel; (■) postgel.

that because of this high ring formation the effective functionality of the primary chains is reduced from 14–42 to 2.1–1.3. Hence the present polymerization process can certainly be described only imperfectly by a mean-field theory.

Finally, we must recall the complexity of the technical DVB system since this monomer consists of two isomers, *p*- and *m*-DVBs, which exhibit different reactivities. Experiments with the pure isomers, however, gave the same qualitative picture, although the gel point occurred[30] at different *R*.

We are aware that even after correction for rings, the ϵ parameter may still not be correctly determined, as we have used a mean-field approximation for the calculation of the ring formation. The parameter ϵ can, however, be eliminated by combining the P_w/P_{wp}, $(\langle S^2\rangle_z/\langle S^2\rangle_{zp})^{1/2}$, and m_{gel} relationships. This is done in Figure 9 for the degree of polymerization and the radius of gyration. A common line is found in the double-logarithmic plot with an exponent of $\nu/\gamma = 0.54$ which seems to decay slightly toward 0.50. Percolation theory predicts[24] $(\nu_c/\gamma_c)^{perc} = 0.47$ and the classical theory 0.5–0.6, depending on the excluded-volume effect. These exponents cannot be taken as a proof of one theory or the other because of the small difference between them. The pregel and postgel curves do not coincide in Figure 3. This is the result of the increase of the primary chain length with the *R* parameter which is corrected in the plot of the reduced parameters.

The result of combining the degree of polymerization or the radius of gyration with the mass fraction of gel is shown in Figure 10, parts a and b, respectively. The exponent in Figure 10a is in good agreement with that from the percolation theory and certainly much larger than the classical exponent. Figure 10b is more difficult to interpret. Near the critical point we have $\nu/\beta = 1.65$, which again is close to the percolation value of 2.0; the mean-field theory gives 1.0.

Figure 7 reveals, however, that an asymptotic region has not yet been reached by experiment when compared with the mean-field theory. In fact, the experimental data indicate a decay of the slope at larger molecular weights, and values closer to the mean-field theory might be obtained at the critical point if reliable measurements could be performed. Finally, we have to recall that the extraction of the soluble molecules from a gel is difficult, and it will be more incomplete the more closely the gel point is approached. In this region the large macromolecules will be held back in the gel by strong entanglements. Thus, the experimentally determined m_{gel}, though reproducible, is certainly too large, and a lower exponent will result. A list of the critical and noncritical exponents is given in Table III.

Conclusions

This experimental study reveals several points of relevance.

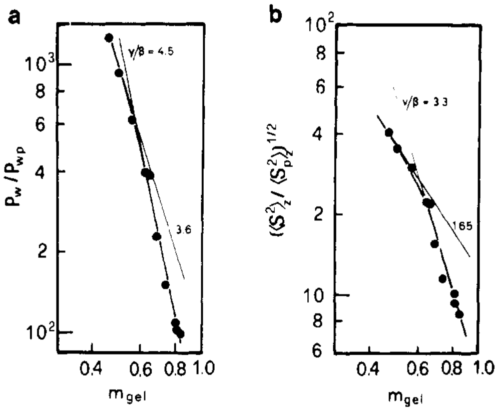

Figure 10. Reduced degree of polymerization (a) and reduced radius of gyration (b) as functions of m_{gel}.

(1) It is hazardous to draw conclusions on the validity of a theory without having experimental data on the extent of ring formation and its change in the course of reaction.

(2) In no case are simple exponential laws obtained. The critical exponents so far determinable appear to agree more with a mean-field theory, while in the region far away from the gel point a non-mean-field behavior is observed, which stands in contradiction to prediction by present percolation models.

(3) Only when the relevant ϵ parameter is eliminated and the structural properties P_w/P_{wp} or $(\langle S^2\rangle_z/\langle S^2\rangle_{zp})^{1/2}$ are plotted against m_{gel} does percolation theory give a better description.

Clearly a system with a conversion-dependent formation of loops cannot be described exhaustively by a mean-field approach. A refinement of the FS theory appears to be possible within the framework of the cascade theory because this general branching theory is essentially a first-order Markovian theory[36–39] and can deal to some extent with long-range correlations.[40–42] The branching theory by Good and Gordon[43,44] is thus more complete than a simple mean-field theory and more nearly resembles the linear Ising model,[51] but no Markov process of finite order can be expected to yield the true critical exponents. On the other hand, a refinement via percolation theory will probably lead to a better description of the present gelling process. To this end, however, physicists will probably have to relax the hypothesis of universality and take the pecularities of the individual system into consideration.

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Appendix. Determination of the Extent of Ring Formation from M_n Measurements

Let P_n and P_{np} be the number-average degrees of polymerization of the branched macromolecule and the primary chains, respectively; then

$$P_n = pP_{np} \qquad \text{(A1)}$$

where *p* is the number of primary chains per branched molecule. Furthermore, since $R = [\text{DVB}]/[\text{initiator}]$, we have *Rp* second double bonds of DVB units per macromolecule; $p - 1$ of these are cross-links and the rest must be involved in ring formation, since no unreacted double bonds were found after reaction. Thus

$$r = \frac{Rp - (p - 1)}{Rp} = (R - 1)/R + 1/pR \qquad \text{(A2)}$$

which is the relationship when p is replaced by P_n/P_{np}.

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Pressure Dependence of Secondary Transitions in Amorphous Polymers. 1. T_{ll} for Polystyrene, Poly(vinyl acetate), and Polyisobutylene

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ABSTRACT: Wood's variation of the Tait equation and several approximations to the Tait equation developed herein have been employed to analyze isothermal volume–pressure data from the literature. Evidence for the T_{ll} transition and its pressure coefficient, $\mathrm{d}T_{ll}/\mathrm{d}P$, is given in detail for atactic polystyrene, poly(vinyl acetate), and polyisobutylene. Similar values obtained elsewhere by us on several methacrylates (atactic, isotactic, and cyclohexyl) are cited. Values of T_{ll}/T_g range from 1.15 to 1.20 except for a value of 1.32 for PIB. Application of these techniques to the determination of pressure coefficients for other transitions in the liquid and glassy states (but not T_g) is suggested. $\mathrm{d}T_g/\mathrm{d}P$ values for the polymers cited, as given by the original authors or in the literature, vary from 20 to 30 K/kbar; values of $\mathrm{d}T_{ll}/\mathrm{d}P$ are 2–5 times higher, or in the range 50–120 K/kbar. $\mathrm{d}T_{ll}/\mathrm{d}P$ varies as $28000/T_g$. We suggest that T_{ll} determined from quasi-static P–V–T data has a thermodynamic basis to the same extent that T_g does. We propose tentatively that isothermal values of $1 - V/V_0$ may change for some polymers in an essentially linear fashion as a function of pressure, with slope changes at each pressure-induced transition, and that the entire isotherm may be approximated in such cases by a Tait equation with a single value of b, so long as T is not too far above T_g.

Introduction

This is the first of a series of studies devoted to an analysis of published P–V–T data on amorphous polymers, primarily to determine T_{ll} (at or near $1.2T_g$) and other transitions which may appear in the liquid state as well as their pressure coefficients and, on occasion, liquid-state compressibilities. When data permitted, glassy state transitions, T_β, T_γ, etc., and their pressure coefficients were also determined but will be reported in full in a later paper in this series.

P–V–T data examined include those of Quach and Simha[1,2] and Öels and Rehage[3] for polystyrene (PS), Beret

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