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# Critical Exponents for Off-Lattice Gelation of Polymer Chains

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ABSTRACT: The random polycondensation of telechelic linear chains cured with tri- and tetrafunctional cross-linkers has been simulated. Calculations are done for both bulk and solution reactions; critical points are located by different methods, with results in good agreement with experiment. Critical exponents $\beta$ and $\gamma$ vary from system to system, with average values $\beta = 0.300 \pm 0.024$ and $\gamma = 1.77 \pm 0.16$. The average value $C_-/C_+ = 13.58 \pm 3.50$ is slightly larger than that from standard percolation.

The statement[1] that "random gelation is nothing but bond percolation on a continuum" characterizes efforts[2-5] to determine the universality class for gelation. Most of the simulations have been done on lattices, which leaves unanswered several questions related to the influence of underlying order on an inherently disordered phenomenon. Continuum percolation of noninteracting disks[6] in two dimensions appears to be in the same universality class as lattice percolation, but this is not a realistic physical model for polymer gelation.

In our model, prepolymer chains and cross-linkers are randomly distributed in a cubical box. Simulations (not described here) show that intermolecular correlations are relatively unimportant for polymer gelation if the chain concentration is above about 30% by weight. (Equilibrium correlations are short-range, but gelation is primarily dependent on long-range correlations. Furthermore, the transition-state intermediates that inevitably accompany bond formation are not at thermodynamic equilibrium.) One end of each chain is located with uniformly distributed random numbers, and the other end has a Gaussian distribution with one-dimensional variance given[7] by $\sigma^2 = C_n n l^2/3$. Here $n$ is the number of skeletal bonds in the prepolymer, $l$ is the length of one bond, and $C_n$ is the characteristic ratio.[8] The details of the model and program have been described in previous work.[9,10] In this paper, the influence of cyclization on the critical point is investigated by varying the concentration and molecular weight of the prepolymers. The purpose is twofold: (1) to examine the model near the critical region, where some experimental data are available for comparison, and (2) to estimate critical exponents for realistic off-lattice simulations.

**Table I**
**Estimates of Critical Extent of Reaction**

| system | mol wt | concn, vol % | $P_c^a$ | $P_c^b$ | $P_c^c$ | $\eta^d$ |
|---|---|---|---|---|---|---|
| | | $A_2 + B_4$ | | | | |
| 1 | 1850 | 100 | 0.583 | 0.590 | 0.591 | 5.20 |
| 2 | 1850 | 62 | 0.603 | 0.613 | 0.614 | 6.74 |
| 3 | 1850 | 26 | 0.652 | 0.661 | 0.658 | 12.22 |
| 4 | 11600[e] | 100 | 0.573 | 0.578 | 0.576 | 2.85 |
| 5 | 11600 | 100 | 0.560 | 0.574 | 0.575 | 2.18 |
| 6 | 18500 | 100 | 0.556 | 0.568 | 0.569 | 1.92 |
| | | $A_2 + B_3$ | | | | |
| 7 | 1850 | 100 | 0.700 | 0.718 | 0.712 | 4.15 |
| 8 | 11600[e] | 100 | 0.684 | 0.710 | 0.706 | 3.85 |

[a] From $DP_w$ extrapolation. [b] From upper–lower bound. [c] From scaling equation. [d] Percentage of intramolecular reactions at $P_c^b$. [e] Log-normal distribution.

The systems investigated are described chemically as $A_2 + B_i$, where $A_2$ is a telechelic prepolymer, and $B_i$ ($i = 3$, 4) is a low molecular weight cross-linker with functionality equal to $i$. A and B groups are in equal numbers; 10 000 $A_2$ molecules are generated for each configuration, and results are averages of at least four configurations for each set of parameters. Bond formation between A and B groups in static configurations is controlled by varying a capture radius centered on the randomly distributed cross-linkers. Ends that fall outside the capture sphere

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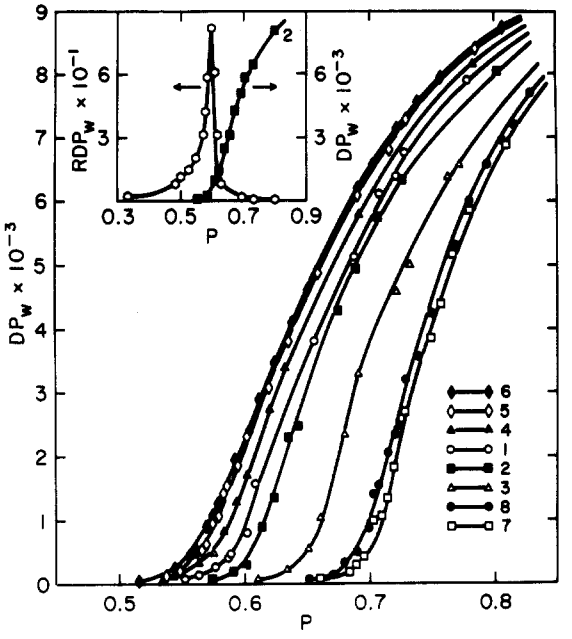


**Figure 1.** $DP_w$ distribution for tri- and tetrafunctional systems. Curve $i$ is identified with system $i$ in Table I. The inset shows the variation of $RDP_w$ with $P$ for system 2.

cannot react; those that are within it react in succession from the nearest to farthest, until the cross-linker is saturated. This device, which mimics the volume within which a cross-linker can diffuse in a given length of time, allows one to control the extent of reaction. Table I lists all systems investigated. The effect of dilution on intramolecular reactions has been examined at three different concentrations for molecular weight 1850. Experimental work[11] was done on commercial poly(dimethylsiloxane) (PDMS) with a molecular weight distribution characterized by $DP_w/DP_n = 2.21$: we have assumed a log-normal distribution[12] for some of the molecular weight 11 600 runs. Here, $DP_n$ and $DP_w$ are the number- and weight-average degree of polymerization, respectively.

Figure 1 shows the size distributions for tri- and tetrafunctional systems. Crude estimates (Table I, column 4) of the critical points were made by extrapolation of the curves to the abscissa; these will be compared with more refined estimates.

Various methods have previously been used to locate critical points: (1) the maximum slope of the modified second moment of the cluster distribution,[13] (2) the maximum reduced average cluster size[14] ($RDP_w$), and (3) log–log plots[15] of $DP_w$ vs. extent of reaction ($P$). Techniques 1 and 2 are illustrated in Figure 1. Since $RDP_w$ reaches a maximum whenever there are two or more large particles, it gives a lower bound to the true gel point. When these particles coalesce into a single large particle, the maximum slope in the $DP_w$ distribution is attained; this is an upper bound. The inflection point is found by Newton's interpolation method.[16] The average of the upper and lower bounds is given in column 5 of Table I.

In Figure 2, the critical extent of reaction ($P_c$) is varied so as to give the best-fit straight lines according to

$$DP_w = C_-[P_c - P]^{-\gamma} \quad \text{for } P \to P_c^- \tag{1}$$

$$RDP_w = C_+[P - P_c]^{-\gamma} \quad \text{for } P \to P_c^+ \tag{2}$$

where $C_\pm$ are critical amplitudes with respect to pre- and postgel regions. After the best $P_c$ is found, $\beta$ is determined from the gel fraction ($G$) by linear regression:

$$G = K[P - P_c]^{\beta} \quad \text{for } P \to P_c^+ \tag{3}$$

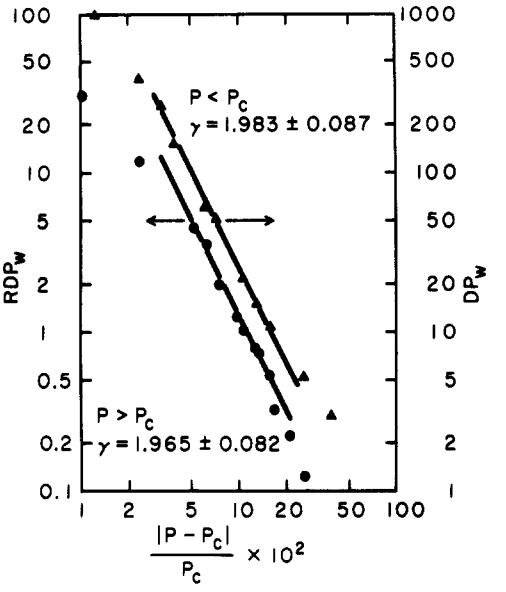


**Figure 2.** log–log plot of $RDP_w$ and $DP_w$ vs. $|P - P_c|/P_c$ for system 7. The best estimates for $P_c$ and $\gamma$ are obtained when the two lines have the same slopes. Since log $(C_-/C_+)$ is equal to the vertical distance between these two lines, the value $C_-/C_+$ is very sensitive to the choice of the $|P - P_c|$ range. All the data listed in Table II are calculated consistently with the same critical region, which is similar to the linear intermediate region used in ref 3. The leftmost points are not included in this fit because of the finite size effect.[3] If the rightmost points are included in the calculation, $C_-/C_+$ would increase to 38.14 with minor changes in $\gamma$ and $P_c$.

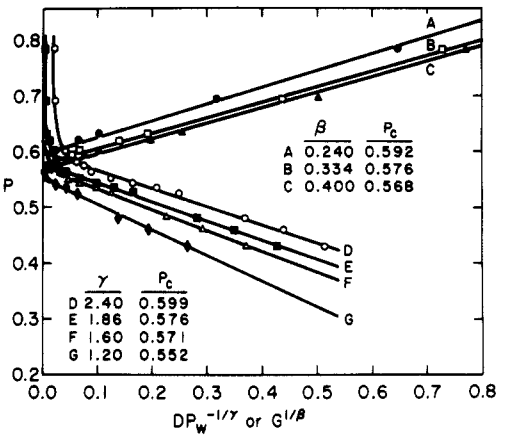


**Figure 3.** Sensitivity of $\beta$ and $\gamma$ to $P_c$ for system 4. The parameter values $\gamma = 1.86$ and $P_c = 0.576$ were derived from a log–log plot similar to Figure 2. The exponent $\beta = 0.334$ is determined by using this $P_c$ value to fit the gel fraction ($G$) data.

**Table II**
**Critical Exponents for All Systems**

| system | $\beta$ | $\gamma$ | $C_-/C_+$ |
|---|---|---|---|
| | $A_2 + B_4$ | | |
| 1 | 0.283 (0.014)[a] | 1.60 (0.14) | 13.27 (3.65) |
| 2 | 0.290 (0.016) | 1.53 (0.15) | 14.45 (1.87) |
| 3 | 0.275 (0.013) | 1.75 (0.26) | 14.72 (2.56) |
| 4 | 0.334 (0.018) | 1.86 (0.12) | 9.22 (2.90) |
| 5 | 0.294 (0.010) | 1.90 (0.25) | 12.09 (2.10) |
| 6 | 0.339 (0.006) | 1.73 (0.12) | 9.21 (1.50) |
| | $A_2 + B_3$ | | |
| 7 | 0.288 (0.009) | 1.97 (0.09) | 19.62 (2.40) |
| 8 | 0.293 (0.009) | 1.83 (0.18) | 16.08 (2.80) |

[a] Standard deviations are given in parentheses.

Figure 3 illustrates the fit for the tetrafunctional system 4. The critical points found in this way are close to those

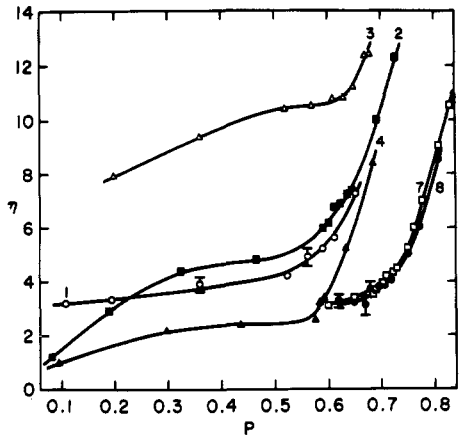


**Figure 4.** Dependence of the percentage of intramolecular reactions ($\eta$) on $P$. Curves for systems 5 and 6 have been omitted for clarity.

obtained by the upper–lower bound method. Table II lists all the critical exponents.

For a system with a prepolymer molecular weight of 11 600, experimental results[11] give $P_c = 0.581 \pm 0.01$, which is very close to that found by the upper–lower bound methods (0.578) and the scaling method (0.576). Similar agreement is also found for the trifunctional system, where experiment gives $P_c = 0.703 \pm 0.01$. For systems of long prepolymers, the two computational methods give critical points just slightly less than those of branching theory (0.577 and 0.707 for tetra- and trifunctional systems, respectively). The discrepancy is small and might arise from an edge effect for the finite simulations, from statistical uncertainty in the numerical calculations, and from uncertain critical point estimation methods used here. It appears that cyclization nearly compensates for the overestimate of $P_c$ by branching theory, as discussed more thoroughly below.

As the chain molecular weight varies from 18 500 to 1850, the critical extent of reaction should increase because of loop formation. Results in Table I confirm this prediction. Similarly, chains have a greater probability for forming single loops with increasing dilution. The observed trend (Table I) is $P_c$(bulk) < $P_c$(62 vol %) < $P_c$(26.23 vol %), in agreement with expectations. Figure 4 shows that the percentage of intramolecular reactions increases as the extent of reaction increases, with a large increase just beyond the critical point. The relative order of the extent of intramolecular reaction follows the expected pattern.

In Table II $\gamma$ varies from 1.53 to 1.97 with an average $\gamma = 1.77 \pm 0.16$, close to standard percolation results (1.7). Variations of $\beta$ from 0.275 to 0.339 are found. The average is $\beta = 0.300 \pm 0.024$, which is considerably smaller than percolation ($\beta = 0.40$). Values of $C_-/C_+$ deviate substantially from classical results (1.0); they average to $C_-/C_+ = 13.58 \pm 3.50$, which is slightly larger than percolation (8–11). Our results for this quantity differ from those of Herrmann et al.[2,3] and Gawlinsky and Stanley.[6]

As indicated by Stauffer[15] and Gordon,[17] a minor change in $P_c$ may result in large variations in critical exponents. Figure 3 also shows how $\beta$ and $\gamma$ vary with $P_c$.

Finite size scaling has recently been used extensively for lattice percolation. For our simulations that lack translational symmetry, it is necessary to calculate and order all pair distances; further increases in the size would entail tremendous computing times. Previous studies[9] show that if more than 5000 primary chains are sampled, edge effects are not observed. Simulations based on 10 000 primary chains give a fair estimate of critical parameters.

The classical branching theory is correct in six and higher dimensions.[18,19] If one were to attempt to construct space-filling models of trees that conform to branching theory statistics, they could not be built in 3D space. There is enough room in six dimensions to hold such highly ramified structures, but to imbed them in three dimensions they would have to be pruned. This implies that if one could somehow devise a polycondensation reaction that could be carried out in the laboratory to yield truly acyclic molecules, the critical extent of reaction would be below the branching theory result. The computer simulations always yield some fraction of cyclics, and this causes $P_c$ to increase. It appears that cyclization fortuitously compensates for the imbedding error of branching theory, at least for end-linked polymers, so that both the measured and the simulated gel points land very near to the branching theory prediction. This contention is not easily tested by going to higher dimensions with these off-lattice simulations. The problem is that we do not know of any *unique* way to specify the physical density in four and higher dimensions so as to ensure that the results would not be influenced by an unsuspected dilution effect. For lattices this is not a difficulty, since a one-dimensional length (the bond length) is effectively held constant on changing spatial dimensionality.

Renormalization group theory[20] demands that both critical exponents and amplitude ratios should be universal for random percolation. The model simulations reported here seem to be different from percolation and classical universality. Because spatial and topological neighbors are not well correlated in elastic networks, the rescaling operation of renormalization group theory is not obviously identical with that for crystals or liquids. This question deserves careful consideration, especially because a new universality class is found for kinetic percolation.[3] Still other evidence, i.e., experimental results[4] for anionically prepared styrene–divinylbenzene copolymers, tends to support the Flory–Stockmayer theory. Further experiments and simulations on various polymerization systems are needed to clarify these apparent departures from theory. For the present, the good agreement between critical points determined with the aid of this model and those measured experimentally tends to justify the model, as does the fact that it gives the right trend of cyclization with dilution. It provides a reliable means to study critical phenomena in addition to a number of other important features of polymer network formation.

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# Elastic Coherent Scattering from Multicomponent Systems. Applications to Homopolymer Mixtures and Copolymers

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ABSTRACT: A general equation giving the scattering intensity of a solution of polymers and copolymers at any concentration and angle is derived. Its relation with thermodynamics and its application to polydisperse systems are discussed. Small-angle neutron scattering experiments on a diblock copolymer of deuterated polystyrene–poly(methyl methacrylate) (PS–PMMA) were performed in bulk and in solution near the Θ point. The results are consistent with the theoretical predictions.

In recent publications[1,2] a new method for the evaluation of the scattering intensity of a solution of two homopolymers as a function of the concentration was presented. The idea was to assume that the interactions between two polymer molecules can be evaluated by taking into account not only the direct contact but also linear chains of contacts.

The results are identical in the bulk limit with the formula obtained by de Gennes[3] using the "random phase approximation" RPA method. In solution, at zero scattering angle one finds the classical results of the theory of scattering by multicomponent systems.[4,5] This calculation which is made in the framework of a mean-field approximation is a poor approximation in the vicinity of the critical concentration $c^*$ where the molecules begin to overlap but in concentrated solution it should be a reasonable approximation.

In this paper, we want first to generalize the method of ref 2 to the calculation of the scattering intensity of a solution containing an arbitrary number of polymers and copolymers, monodisperse and polydisperse.

This general formulation will be applied explicitly to the case of two or three constituents (one copolymer + one homopolymer of different natures and three homopolymers). The second part will describe experiments made by small-angle neutron scattering (SANS) on a diblock copolymer in bulk and in solution with a pure solvent. It will be shown how it is possible by applications of our theoretical results to interpret the data and to obtain from the measurements the values of the interaction parameters.

## Theoretical Section

**Mixture of Homopolymers.** Let us assume that we have $p$ species of polymers, each of them being characterized by its degree of polymerization $n_i'$, its structure factor $P_i(q,c)$ which can depend on concentration, or the number of molecules per unit volume $N_i$. The intensity scattered by the unit volume of solution can be written if we neglect or subtract the compressibility effects as[6]

$$I(q) = \sum_{i=1}^{p} a_i^2 N_i n_i'^2 P_i(q) + \sum_{ij} a_i a_j Q_{ij}(q) \qquad (1)$$

$I(q)$ is the scattering intensity (neglecting a normalization factor which depends on the kind of radiation used (neutrons, X-rays, or light) as a function of the parameter $q = 4\pi \sin(\theta/2)/\lambda$ ($\lambda$ is the wavelength of the incident beam and $\theta$ the scattering angle). The quantity $a_i$ is the contrast factor corresponding to the species $i$ in the solvent. For neutrons, it is the difference between the coherent scattering length of the monomeric unit $i$ and the corresponding value for the solvent, after correction for the difference in specific volumes. $Q_{ij}$ is the term due to interferences between waves scattered by molecules $i$ and $j$.

In the classical single contact Zimm's approximation, it is given by the relation

$$Q_{ij} = -v_{ij} N_i n_i'^2 P_i(q) N_j n_j'^2 P_j(q) \qquad (2)$$

where $v_{ij}$ is the excluded volume parameter for a contact between $i$ and $j$ molecules.

In the method developed in ref 1 and 2, one takes into account all the linear chains of contact between two molecules (Figure 1).

Let us call $C_{nij}$ the contribution of a diagram such as Figure 1 to the interaction term $Q_{ij}$. If we define $x_i$ by the relation

$$x_i = N_i n_i'^2 P_i(q)$$

we can write

$$C_{nij} = (-1)^{n+1} x_i^{n_1} \ldots x_k^{n_k} \ldots x_j^{n_j} v_{ik}^{n_{ik}} \ldots v_{kl}^{n_{kl}} \ldots v_{jm}^{n_{jm}} \qquad (3)$$

where $n_1, n_2, \ldots, n_j$ are the number of chains of each species. Since there are $n + 2$ chains in this diagram

$$\sum n_k = n + 2$$

remembering that the first chain in the series is of type $i$ and the last one of type $j$. $n_{ik}$ is the number of contacts between a chain of $i$ species and a chain of $k$ species such that

$$\sum n_{ij} = n + 1$$

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