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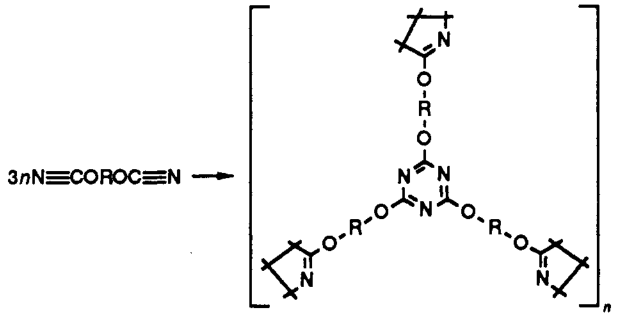
Communications to the Editor

Critical Behavior of a Trifunctional, Randomly Branched Polymer. Percolation versus Cascade Theory

Introduction. The simplest polymer for examining the validity of scaling exponents in gelling systems predicted by classical or percolation theory should be a trifunctionally branched homopolymer built up by a definite chemical reaction. Pure polycyanurates, synthesized through polycyclotrimerization of difunctional aromatic cyanic acid esters, meet these requirements:[1,2]



We polycyclotrimerized the dicyanate of Bisphenol A, in bulk at 453 K. Randomly trifunctionally branched polycyanurates with molecular weights M_w from 5×10^4 up to 5×10^6 g/mol were obtained by stopping the reaction before the critical conversion of the cyanato groups. Solutions of the polymers in tetrahydrofuran were characterized by static and dynamic light scattering and size-exclusion chromatography coupled with light scattering. In this way, the relations for the radius of gyration $R_g \equiv (\langle S^2 \rangle_z)^{1/2}$

$$R_g \sim M_w^{\nu} \tag{1}$$

the hydrodynamic radius $R_h \equiv (\langle 1/R \rangle_z)^{-1}$

$$R_h \sim M_w^{\nu} \tag{2}$$

and the weight fraction molecular weight distribution[3]

$$\Phi(M) \sim M^{1-\tau} f(M/M^*) \tag{3}$$

are obtained, where f is a cutoff function and τ an exponent to be discussed later. Furthermore, the validity of the theoretical scattering function

$$P_w P_z(q) = \frac{1 + 2\alpha \exp(-b^2q^2/6)}{1 - 2\alpha \exp(-b^2q^2/6)} \tag{4}$$

was examined, which was derived with the help of cascade theory,[4,5] where $q = (4\pi/\lambda) \sin \theta/2$ is the scattering vector and α the conversion of the cyanato groups. Equation 4 is based on Gaussian subchains between any two branching points, i.e., centers of cycles, and thus in this model b is the effective bond length between two such neighboring cycles.

Scaling Exponents. In Figure 1 the measured R_g–M_w and R_h–M_w relationships are illustrated. The regression lines follow the equations

$$R_g = 0.059 M_w^{0.52} \tag{5}$$

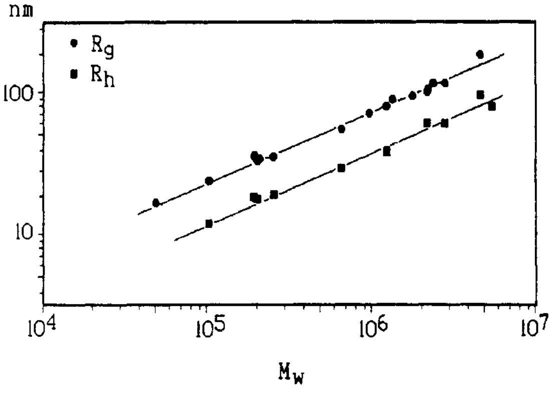


Figure 1. Radius of gyration R_g and hydrodynamic radius R_h versus molecular weight M_w for different polycyanurates.

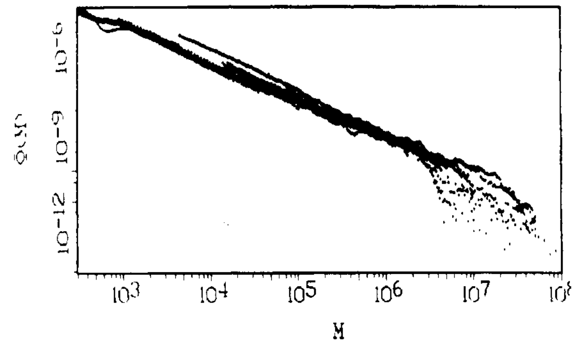


Figure 2. Double-logarithmic plot of the molecular weight distribution for different polycyanurates measured by SEC/LALLS.

and

$$R_h = 0.030 M_w^{0.52} \tag{6}$$

with correlations of 99.44% or 99.39%, respectively, and a 5% confidence interval of 0.03 for the two exponents.

The scaling exponent τ of the molecular weight distribution was calculated by a regression analysis of the linear part of log $\Phi(M)$ versus log M as shown in Figure 2. The SEC/LALLS data of the polymers with different M_w were analyzed separately so that a mean relation

$$\Phi(M) \sim M^{-1.22} f(M/M^*) \tag{7}$$

with a correlation of 99.53% and a 5% confidence interval of 0.02 results. The exponent $\tau = 2.22$ is in excellent agreement with the percolation prediction of 2.20 and deviates from the Flory–Stockmayer distribution[6,7] with a $\tau = 2.5$. Taking into account that the exponent ν in eq 1 contains information on both the solvent quality and the molecular weight distribution, it is related to ν^B through[8]

$$\nu^B = \nu(3 - \tau) \tag{8}$$

where ν^B now refers to the exponent of molecularly uniform branched clusters. With the exponent from eq 5, a value of $\nu^B = 0.41$ is obtained, which well agrees with the result of Schosseler et al.[9] for irradiated polystyrene but is slightly smaller than that found by Patton et al.[10] for branched polyesters.

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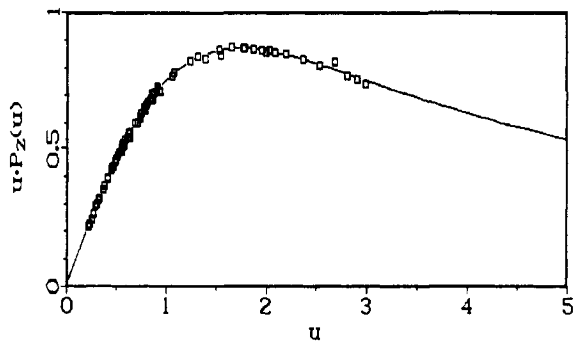

Figure 3. Plot of $uP_z(u)$ versus u for different polycyanurates; curve calculated with eq 4.

Unfortunately, a scaling of M_w or R_g against the distance to the gel point $|\alpha - \alpha_c|$ was not possible with the required reliability in order to decide between classical or percolation exponents. The conversion of the cyanato groups measured by FTIR lies in the range from 49.5% to 50.5%, which agrees with the theoretical critical conversion of 50%. However, to carry out a reliable check for classical or percolation exponents γ, an accuracy of conversion data better than 5×10^{-4} is needed, which would enable a clear distinction between α = 49.944% (M_w 5×10^5) and α = 49.994% ($M_w = 5 \times 10^6$); this is not possible with FTIR. If one calculates the regression line from the data with the high error level, any exponent between $\gamma = 1$ and $\gamma = 1.78$ can be calculated with very low significance.

Scattering Curve. A very good agreement between the measured scattering data of all polymers from $M_w = 5 \times 10^4$ up to 5×10^6 with the curve predicted by cascade theory (eq 4) is found and shown in Figure 3. The plot of $uP_z(u)$ versus $u = R_g q$ is preferred,[11] since the exploration of the maximum seems to be more revealing than the sigmoidal behavior of the corresponding Kratky plot. The effective bond length b needed for the normalized plot is calculated with the help of the formula for the radius of gyration derived from the theoretical scattering curve[4,5]

$$\langle S^2 \rangle_z = b^2 \frac{2\alpha}{1 - \alpha^2} \tag{9}$$

and has a mean of 2.4 nm. The actual bond length between two cyanurate ring centers is l = 1.409 nm[12] and corresponds to a characteristic ratio of $C_\infty = b^2/l^2 = 2.9$. The plot demonstrates that the cascade approximation works well for predicting the scattering behavior of these polymers.

Discussion. The work on this simple trifunctional, randomly branched homopolymer was started in the hope of reaching a clear choice between the percolation or the older Flory–Stockmayer predictions for the branching process. The advantage of the present example consists of the fact that all the measured quantities can be calculated by Gordon's cascade theory.[4,5,13]

In spite of all our efforts, the intended check could not be made as accurately as we wished. The main reason for this drawback is the inevitable experimental error in determining the extent of reaction and in recording the correct shape of the size distribution function at the high molar mass end. Thus we failed to estimate the critical exponent γ in $M_w \sim |\alpha_c - \alpha|^{-\gamma}$ and σ, which defines the cutoff function in eq 3 through $M^* \sim |\alpha_c - \alpha|^{-1/\sigma}$. The characteristic molar mass M^* was shown by Schosseler et al.[9] and Patton et al.[10] to be correlated to M_{max}, which is the molar mass of the maximum in the light scattering signal of the SEC/LALLS chromatogram. The exponent σ, nevertheless, cannot be determined without knowing α_c, which for the mentioned reasons could not be determined with the required accuracy.

The exponents γ and σ are related to τ by $\gamma = (3 - \tau)/\sigma$ where τ is the exponent that defines the width of the size distribution in eq 3. Its value was found to be $\tau = 2.22$, and from this we might conclude that percolation is indeed the better theory and that the cascade theory with its exponent of $\tau = 2.5$ should be discarded.[3,6]

However, there are two other results, which demonstrate that the ideal percolation concept does not offer the absolute universality that is sometimes expected.

Fractal dimension: Two limiting cases have been considered in detail in the past[3,8,14] by the use of hyperscaling arguments, i.e., a combination of percolation exponents with the cluster dimension in real space (e.g., $d = 3$). For the nonswollen cluster in the reaction bath a fractal dimension of $D_B = 2.5$ was predicted whereas the same clusters dissolved in a good solvent will swell and should have a $D_B = 2.0$. (The subscript B indicates a molecularly uniform branched cluster.) The experimentally observed value $D_B = 1/\nu_B = 2.44$ is close to that of a nonswollen cluster, although all measurements have been made in the good solvent THF, which gave high positive virial coefficients. This result appears at variance with the hyperscaling prediction. In fact, if we look more carefully at the chemical structure of this polymer, we notice that swelling of this macromolecule appears scarcely possible. Evidently the fractal structure of the nonswollen clusters, fixed during the reaction in the melt, remains essentially preserved in the good solvent.

Cascade theory versus percolation: The exponent $\tau = 2.22$ suggests that percolation is the better theory. One might conclude from this that cascade theory would give wrong results also for the calculated absolute values. However, excellent agreement with experimental data is obtained with this analytic theory, at least for the present polymer. This result clearly indicates that, in spite of the wrong prediction of the critical exponents, the Flory–Stockmayer theory in its extension by Gordon's cascade theory[4,5,13] is, nevertheless, often a very good approximation when measured quantities are concerned and not only exponents are considered.

The good fit of measured data by an apparently wrong model is puzzling, in particular, as the calculations of the mean-square radius of gyration and the particle scattering factor are based on Gaussian chain statistics, which ignores all volume effects. The result of this assumption is the unrealistic fractal dimension $D_a = 4.0$ of a single cluster and a very broad molar mass distribution.[15] However, after we average over the distribution, an apparent fractal dimension of $D_{app} = 2.0$ is obtained. Just the same value is derived from percolation theory for nonswollen clusters. The experimental value is very close to these data. Apparently the fractal dimension $D_a = 4.0$ is counterbalanced by the broad molar mass distribution and leads to the same result as that for the nonswollen cluster with D_a = 2.5 but the less broad molar mass distribution of the percolation theory (see eq 8). The polydispersity index M_z/M_w can be shown to be related to M_w as[14]

$$M_z/M_w \sim M_w^{\,q} \tag{10}$$

with

$$q = [1/(3 - \tau)] - 1 \tag{11}$$

Equation 11 again shows τ as the characteristic exponent that defines the width of the molar mass distribution given by eq 3.

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Note Added in Proof: Polycyclotrimerization was treated previously by Fukui and Yamabe,[19] who derived equations for the number- and weight-average degrees of polymerization. They also derived an asymptotic equation for the weight-fraction distribution of molar masses with an exponent $\tau = 2.5$. We are grateful to Professor Stockmayer for drawing our attention to this paper.

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