Size and mass of branched epoxy resins

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Branched polymers were prepared from the bifunctional 4,4′-diglycidyloxy-2,2-diphenylpropane (diglycidyl ether of bisphenol A) and hexafunctional poly(oxypropylene) diamine (Jeffamine T-403) at different distances from the gel point in the absence and presence of a diluent. Polymers with different amounts of intramolecular cycles were prepared by dilution during polymerization of the epoxide system with diglyme/butanol mixed solvent. The static and dynamic light scattering from dilute solutions of these epoxide samples was measured. The results are discussed in terms of existing gelation theories. The critical exponents of M_w lie between the values predicted by the Flory–Stockmayer and percolation theories and are shifted towards the percolation value with increasing fraction of intramolecular cycles. Polymer growth near the gelation threshold is discussed.

(Keywords: branched epoxy–amine polymers; static and dynamic light scattering; gelation processes; critical phenomena)

INTRODUCTION

Gelation is considered to be a critical phenomenon of connectivity. The laws that described changes in the characteristic quantities in the vicinity of the gel point are of the form $X \sim \varepsilon^g$, where X is a property of the critically branched system, ε is the relative distance from the critical (gel) point and g is the critical exponent.

The critical region may be dominated by long-range correlations and, therefore, different theories can yield different values of the critical exponents depending on whether and how they take these correlations into account. Among the network formation theories, the classic Flory–Stockmayer (FS) theory[1], belonging to the group of statistical theories, does not take any long-range correlations into account. The more modern versions of the statistical theories, like the theory of branching processes (cascade theory), can deal with some long-range correlations like cyclization, but all effects are reduced to the level of a monomer unit affecting the distribution of the number of bonds per unit effective in branching[2]. The spanning-tree approximation to cyclization can serve as an example[3]. The reacting functional groups of a unit are distinguished according to whether they participate in inter- and intramolecular bonds. These modifications can be quite successful in prediction of some structural parameters and the position of the critical point. However, classic critical exponents are always obtained because there is no effect of the size and symmetry of the reacting molecules on the apparent reactivity of a functional group.

The other group of theories — the kinetic or coagulation theories — although mean-field in nature, can simulate the size dependence of the apparent reactivity. The long-range time correlations in structural growth are taken into account rigorously[2]. These theories can yield non-classic critical exponents (see for example refs. 4 and 5).

The simulation of the network formation processes in space can take long-range spatial correlations into account. The most widely used is lattice percolation[6] in two variants: random percolation and initiated (kinetic) percolation. The simulation corresponds to full diffusion control since the lattice is stiff. The critical exponents, different from the classical ones as well as from the exponents of the coagulation theories, belong to the same universality class. However, an off-lattice network formation simulation in three-dimensional space yields critical exponents different from the percolation values[7]. Simulation of various aggregation processes (e.g. diffusion-limited aggregation (d.l.a.), ballistic model, etc.) also yields different critical exponents[8]. From the point of view of the reaction mechanism of network formation, one can expect the weakest long-range correlations for the step reaction (slow with respect to diffusion) between long strongly overlapping polymer molecules. The strongest long-range correlations were found for chain (free-radical) copolymerization with fast propagation, strong cyclization and the excluded-volume effect. Near the gel point, the reaction becomes diffusion-controlled and even the modified statistical theories do not yield any reasonable agreement with experiment[9]. Generally, dilution of the reacting system plays an important role. It increases the isolation of the reacting clusters, promotes cyclization and, as a consequence, limits interpenetration.

For comparison of the experimental critical exponents with those of the theories, the width of the critical region is important because some non-critical data can be involved in determination of the critical exponents. However, the width is generally not known.

Recent experimental development has been reviewed by Adam[10]. Three main groups of network formation processes have been discussed: (1) stepwise reaction such

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as polycondensation, (2) chain free-radical copolymerization, and (3) vulcanization of linear polymers by γ-rays. It has been concluded that the experimental results obtained in the last decade seem to indicate that the growth of polymers near the gelation threshold is a critical connectivity phenomenon, which belongs to the same class of universality as percolation[6] rather than to the class of the statistical (e.g. cascade) theory[2].

There have been indications that the critical exponents depend on dilution of the sample during network formation: the exponents for bulk-polymerized polyurethane and epoxy–amine samples were closer to the classic values[11,12] and were shifted towards the percolation values with increasing dilution[11]. This is consistent with a narrowing of the degree of polymerization distribution caused by increasing cyclization because of the increasing bulkiness of the large clusters. As a consequence, the critical region also becomes wider. To contribute to the solution of this problem, we have selected a polyepoxide system in which the chemical reaction is a stepwise polyaddition and where the cyclization can be substantially enhanced by the presence of solvent[13]. The distance from the gel point was varied by varying the initial molar ratio $r_A = 2[NH_2]_0/[epoxy]_0$ at conversions of the minority (epoxy) groups $\simeq 100\%$. Then, $\varepsilon = |1 - r_A/r_{Ac}|$, where r_{Ac} is the critical value of r_A. The objective of this work is to determine the critical exponents for quantities measured by static and dynamic light scattering methods as a function of the solvent content during network formation and to compare them with existing theories.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA) (Research Institute for Synthetic Resins and Lacquers, Pardubice) with number-average molecular weight $M_n = 350$, epoxy equivalent $\gamma_E = 174.5$ g/mol epoxy and functionality $f_n = 2.0$ was used. Jeffamine^R T-403 (Texaco) had $M_n = 439$, amino equivalent $\gamma_A = 78.0$ g/mol H in NH_2, which gives $f_n = 5.46$. Diethylene glycol dimethyl ether (diglyme) and 1-butanol of analytical-grade purity were dried and redistilled.

Sample preparation

DGEBA was dissolved in Jeffamine at 40°C, stirred for 5 min and diluted with a mixed solvent diglyme/butanol (1:1 by volume). All the samples were reacted at 120°C for 120 h in a nitrogen atmosphere. These conditions ensured practically complete conversion of the epoxy groups. The reacted samples were diluted for the light scattering experiments by mixed diglyme/butanol solvent. The diluted solutions were cleared using a centrifuge.

Determination of the critical molar ratio

The critical molar ratio r_{Ac} is equal to the highest value of r_A at which the gel appears at full conversion of the minority (epoxy) groups. Thus, the r_{Ac} value is usually determined by measuring the solubility of the reacted samples at a given r_A. The accuracy of determination of r_{Ac} is associated with the number of samples taken in the vicinity of the gel point. In order to increase the accuracy of the procedure, D_z^2, and possibly M_w^{-1} (where D_z and M_w are the z-average diffusion coefficient and weight-average molecular weight of branched macromolecules, respectively) were plotted in the proximity of the gel point as a function of r_A (see *Figure 1*). It can be seen from *Figure 1* that all experimental dependences can be reasonably fitted by straight lines. The value of r_{Ac} has been estimated as the mean value of both the intercepts on the horizontal axis. The r_{Ac} values have been determined with an accuracy of better than ±0.005.

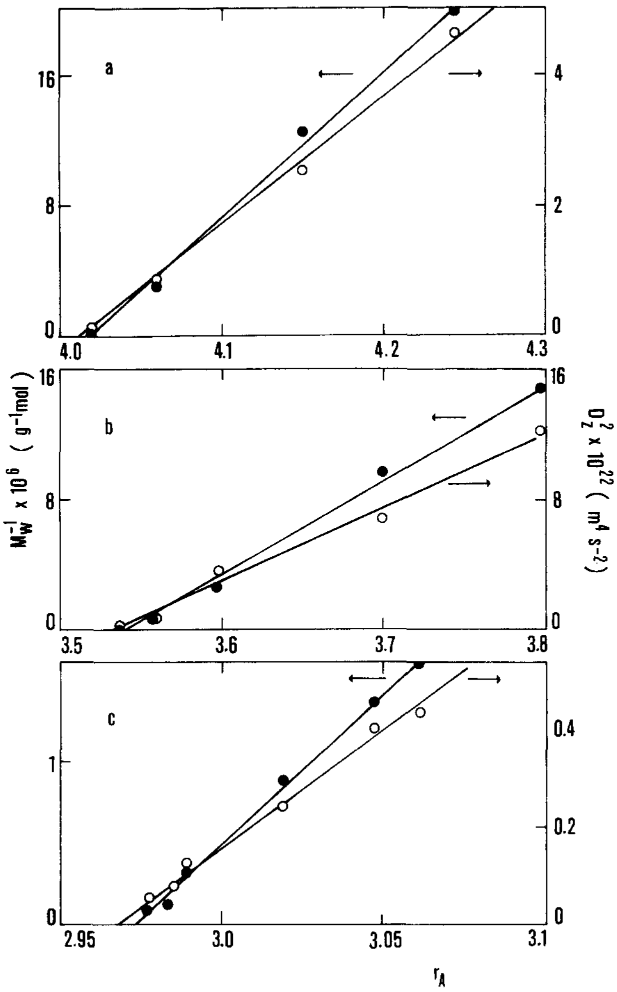

Figure 1 Dependence of D_z^2 and M_w^{-1} on the initial molar ratio of amine functional groups r_A in the proximity of the gel point: (a) bulk-polymerized samples, (b) solvent-polymerized (60%) samples, (c) solvent-polymerized (80%) samples

Static light scattering

The weight-average molecular weight M_w, the second virial coefficient A_2 and the z-average radius of gyration R_g were determined from the static light scattering of solutions of branched samples in a diglyme/butanol mixture. The measurements were performed with a Sofica instrument (angular range from 30° to 150°) at 25°C using a high-pressure mercury lamp (wavelength $\lambda_0 = 546$ nm) as the light source. The refractive index increment of the polymers in diglyme/butanol mixture (1:1), $dn/dc = 0.100$ cm^3 g^{-1}, was determined with Brice–Phoenix differential refractometer.

Dynamic light scattering

A homodyne spectrometer equipped with a 96-channel digital correlator was used for these measurements[14].

Time correlation functions were analysed using the method of cumulants and single-exponential forced fit. The *z*-average diffusion coefficient D_z was determined from the first cumulant Γ by extrapolating Γ/K^2, where K is the scattering vector, to zero concentration and scattering vector.

RESULTS AND DISCUSSION

The results obtained by analysis of light scattering data are presented in log–log scales in *Figures 2* and *3*. All experimental dependences can be fitted by straight lines, which means that, within experimental error, the power laws predicted by theory are adequate for the description of the system below the gel point. The critical exponents (slopes of the straight lines in *Figures 2* and *3*) are given in *Table 1*.

It can be seen from *Table 1* that the experimental critical exponents of M_w lie between the predictions of the FS ($\gamma = 1$) and percolation ($\gamma = 1.74$) theories. The exponents are higher for the solution-polymerized systems than for

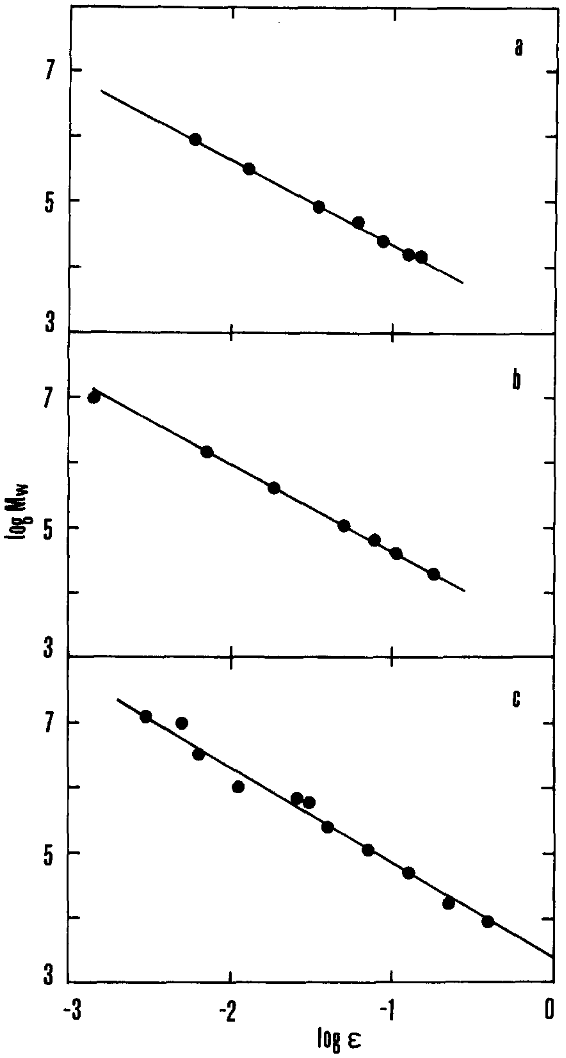

Figure 2 Dependence of the weight-average molecular weight M_w on ε: (a) bulk-polymerized samples, (b) solvent-polymerized (60%) samples, (c) solvent-polymerized (80%) samples; full lines represent the least-squares linear fits

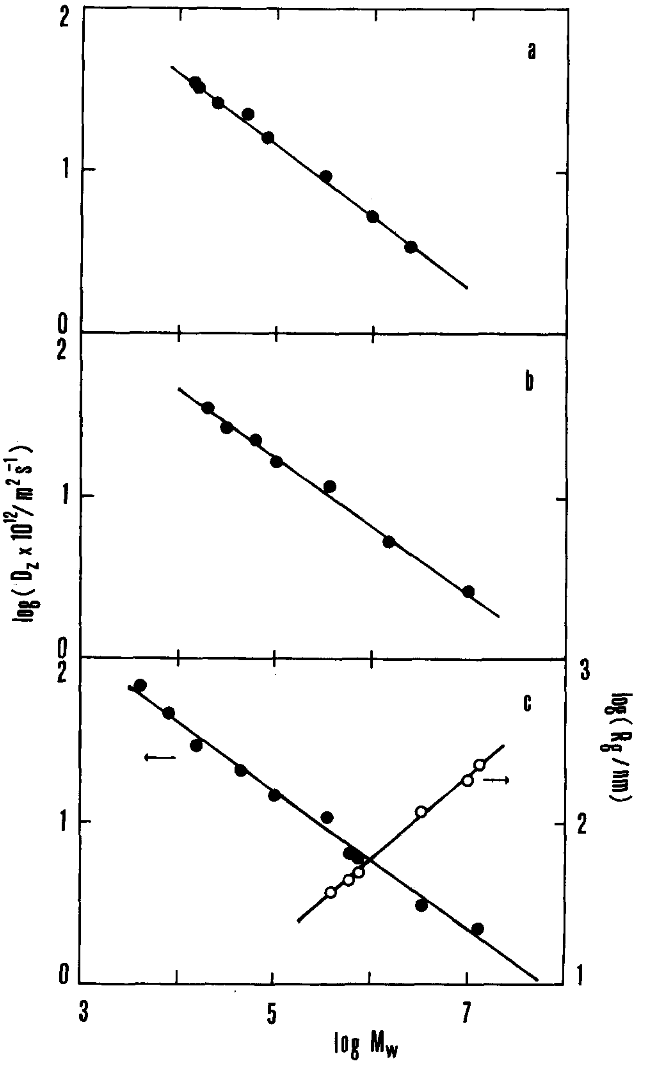

Figure 3 Dependence of the *z*-average radius of gyration R_g and diffusion coefficient D_z on M_w: (a) bulk-polymerized samples, (b) solvent-polymerized (60%) samples, (c) solvent-polymerized (80%) samples; full lines represent the least-squares linear fits

Table 1 Theoretical and experimental critical exponents

	ν'	γ	ν	γ/ν'	$x=(3-\tau)D$
Theoretical	–	–	–	–	–
FS	–	1	1/2	–	1.5
Percolation	–	1.74	0.88	–	2.4
Experimental	–	–	–	–	–
Bulk-polym.	0.57±0.03	1.29±0.05	–	2.27±0.08	–
Solvent-polym.[a]	0.59±0.02	1.35±0.04	–	2.27±0.08	–
Solvent-polym.[b]	0.64±0.04	1.44±0.06	0.74±0.06	2.33±0.05	1.94±0.09
Proportionality	$D_z \sim \varepsilon^{\nu'}$	$M_w \sim \varepsilon^{-\gamma}$	$R_g \sim \varepsilon^{-\nu}$	$M_w \sim D_z^{-\gamma/\nu'}$	$M_w \sim R_g^x$

[a] 60 wt%
[b] 80 wt%

the bulk-polymerized system and increase with dilution. This result indicates that dilution significantly increases the long-range correlations within the clusters, e.g. in the increasing degree of cyclization.

The fraction of bonds wasted in cycles can be estimated from the dependence of r_{Ac} on dilution of the reaction mixture with a solvent (see *Figure 4*). The quantity:

$$\Delta r = (1/r_{Ac} - 1/r^0_{Ac})/(1/r_{Ac})$$

where r^0_{Ac} is the ring-free value of the critical ratio r_{Ac}, can be used as a measure of the intensity of cyclization. Contrary to ref. 11, Δr was more correctly related to $1/r_{Ac}$ rather than to $1/r^0_{Ac}$. The value of r^0_{Ac} is obtained by extrapolation of r_{Ac} to zero value of the reciprocal monomer concentration (*Figure 4*). The value of Δr would be equal to the fraction of bonds wasted in cycles if the reacted functional groups engaged in inter- and intramolecular bonds were randomly distributed in the building units (see *Table 2*). The non-random distribution, modelled by the spanning-tree approximation[15], yields the fractions of bonds wasted in cycles, *s*, given in *Table 2*. It can be seen in *Table 2* that *s* is much lower than Δr because the functional groups incorporated in rings are found with a higher probability in units with a higher number of intermolecularly reacted functional groups. Although the differences in the fraction of intramolecular bonds are still not large (an increase in *s* by a factor 6 on passing from the bulk-polymerized sample to the solution-polymerized sample with 80 wt% of solvent), cyclization can substantially affect the molecular-weight distribution and conformational averages of macromolecules, which is reflected in changes of the critical exponents. It is to be pointed out that the values of M_w and R_g are larger in the solution-polymerized samples at the same distance from the gel point (see *Figure 2*).

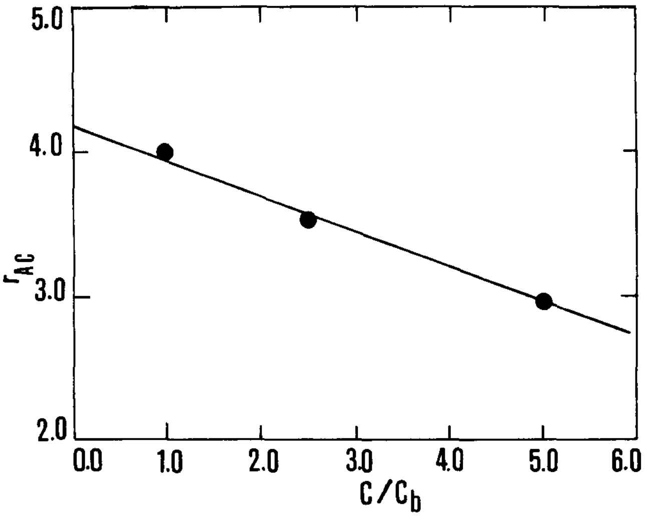

Figure 4 Dependence of the critical value of r_A necessary for gelation, r_{Ac}, on the reciprocal concentration of the monomers, c_b/c; c_b/c is the initial concentration of functional groups in the bulk-polymerized sample relative to that in the dilute ones

Table 2 Fraction of bonds wasted in cycles

Sample	r_{Ac}	$1/r_{Ac}$	Δr^a	s
Bulk-polymerized	4.013	0.249	0.032	0.017
Solvent-polymerized (60%)	3.533	0.283	0.15	0.058
Solvent-polymerized (80%)	2.971	0.337	0.28	0.10
Extrapolated value	4.151	0.241	–	–

[a] $\Delta r = (1/r_{Ac} - 1/r^0_{Ac})/(1/r_{Ac})$

The above results can be supported by experimental data obtained on the DGEBA/Jeffamine D-400 epoxy system ($f_n = 3.75$), published earlier[12]. The experimental critical exponents were found to be close to the predictions of the FS theory for the bulk-polymerized sample. The Δr value of 3×10^{-2} for the latter system is comparable with that for the bulk-polymerized system of the present study. The classic critical exponents were also found for other bulk epoxy systems prepared by step polyaddition[11,16]. However, different results have been published in a paper by Adolf *et al.*[17], where the critical exponents describing the evolution of the static structure were found to be significantly different from the predictions of the classic theory and in reasonable agreement with percolation. Also, Burchard's recent results on rigid epoxy–cyclic anhydride systems suggest that the critical exponents are closer to the percolation ones[18].

These different experimental results obtained in epoxy systems near the sol–gel transition could be due to different curing conditions. Thus, the systems of Adolf *et al.*[17], in contrast to the epoxy systems used in this study and in ref. 12, were prepared with an excess of DGEBA. Under such conditions a different gelation process (e.g. initiated homopolymerization of epoxy groups with an excess of epoxy groups) could have taken place, so that clusters of different structure could have been formed. Indeed, the mean hydrodynamic radius R_h of the clusters in ref. 17 is substantially higher than that in this work and in the paper by Burchard *et al.*[16]; for example, $R_h > 1000$ nm and R_g in the range of 30–40 nm were found for $M_w \simeq 4 \times 10^5$ in ref. 17 and this work, respectively. The clusters studied by us are consequently more compact than those in ref. 17.

Among the other network-forming systems, the critical exponents for bulk-polymerized polyurethane systems have been found to be closer to the classical theory, while samples prepared with 80 wt% of benzene provide[11] $\gamma = 1.7$. Contrary to these results, the exponent $\gamma = 1.71 \pm 0.04$ was found for similar polyurethane systems[19]. Moreover, $\gamma = 1.8 \pm 0.3$ was found for polyester samples[20]. Studies of branched polymers obtained by free-radical copolymerization of styrene with divinylbenzene, with ethylene dimethacrylate or with diisopropenylbenzene gave the value[21] $\gamma = 1.65 \pm 0.08$. The polystyrene solutions crosslinked in a Friedel–Crafts reaction yielded the value[22] 1.65 ± 0.1 for exponent γ. The free-radical vinyl–divinyl copolymerization is known to be dominated by strong cyclization and excluded-volume effects[9].

The ensemble fractal dimension of the branched polymers can only be measured after significant dilution. Since the theories of branched polymers predict dramatic changes in the fractal dimensions of clusters due to swelling upon dilution from the bulk or concentrated solutions into dilute solutions in a good solvent[23], the swelling effect on the cluster fractal dimension of the epoxy clusters was studied. Indirect information on the change in the cluster fractal dimension can be obtained from the dependence of the interaction parameter *B* on the weight-average molecular weight M_w. Parameter *B* can be estimated from the concentration dependence of the normalized scattered intensity extrapolated to zero scattering angle, $Kc/I = (1 + 2Bc)/M_w$. Theoretically it was predicted[24–26] that:

$$B \sim M_w^x \qquad x=\frac{3}{3-\tau}\left(\frac{1}{D}-\frac{1}{D_p}\right) \tag{1}$$

where τ is the polydispersity exponent, D the fractal dimension of the swollen polymer cluster and D_p the fractal dimension of the unswollen polymers. Generally, D should be smaller than D_p.

The analysis of the experimental results obtained for the epoxy samples studied indicated that B was independent of M_w within the limits of experimental error: $B = 34 \pm 10$ for the solution-polymerized system with 80 wt% of solvent. An analogous conclusion can be drawn from the results obtained on epoxy clusters in our previous paper[12]. It means that the effect of swelling on the fractal dimension of the epoxy clusters studied seems to be practically negligible. This is at variance with measurements on polyurethanes[19,27] and silica gels[28,29].

Theoretically, it was predicted that a divergence of the cluster mass with increasing R_g is given by the relation[10]:

$$M_w \sim R_g^{(3-\tau)D} \tag{2}$$

D_z for the three epoxy systems studied and R_g for the solution-polymerized system with 80 wt% of solvent are plotted as functions of M_w in *Figure 3*. The corresponding critical exponents are given in *Table 1*. These values are higher than those found for polyurethane[19] (1.61) and polyester[20] (1.52) samples but they are close to the percolation (2.0) and classical (2.0) predictions for unswollen polymers[6].

The experimental critical exponents ν of the dependence of cluster size R_g on ε determined only for the solution-polymerized system with 80 wt% of solvent are shown in *Table 1*. The experimental values are again higher than FS (0.5) and smaller than percolation (0.88) predictions, which is in agreement with the preceding results.

CONCLUSIONS

At present there are several theoretical approaches simulating or modelling network formation affected by long-range spatial interactions that yield critical exponents different from the classic FS theory. In addition to lattice percolation[6], the off-lattice percolation method[7] and Smoluchowski coagulation equations[2] with a special form of the kernel have been analysed. These three methods give different critical exponents. For the Smoluchowski equations, it has been shown that the critical exponents depend on the values of the parameters determining the degree of interpenetration of clusters. It is, therefore, not surprising that critical exponents may not be universal for all systems and for all conditions that determine the intensity of long-range interactions in space and thus also the structure–growth process.

The polyepoxide system under study, in which the chemical reaction is a stepwise polyaddition, has allowed us to vary the intensity of long-range interaction in space by varying the solvent concentration during polymerization. As a result, polymers with different fractions of bonds wasted in cycles were prepared. Although these differences are not large, they affect the molecular-weight distribution and conformations of the macromolecules, which have been adequately reflected in the critical exponents. The critical exponents of M_w are between the predictions of the FS ($\gamma = 1$) and percolation ($\gamma = 1.74$) theories and they increase with increasing fraction of intramolecular cycles. Moreover, the cyclization can be effectively modified even by the functionality of the crosslinks used. Comparing the results of the present study with the data previously published[12] for DGEBA/tetrafunctional Jeffamine D-400, it is evident that the fraction of bonds wasted in cycles depends on the functionality of the polyamine[13]. Thus, Δr was found to be lower in the DGEBA/Jeffamine D-400 system than in the systems under study. Therefore, it is not surprising that the experimental results obtained with tetrafunctional diamine were found to be in good agreement with the classical theory. These results obtained with the epoxide systems demonstrate that critical exponents are not universal for all gelling systems and can be influenced by preparation conditions determining the degree of cyclization and other long-range correlations.

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