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Light scattering from dilute solutions of critically branched epoxy resins

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Summary

Critically branched polymers were prepared from the bifunctional 4,4'-diglycidyl-2,2-diphenylpropane (diglycidyl ether of Bisphenol A) and tetrafunctional poly(oxypropylene)diamine (Jeffamine D-400) at different distances from the gel point. Solutions of these samples in dimethylformamide were studied by static and dynamic light scattering. The results are discussed in terms of the classical Flory-Stockmayer theory and the percolation theory of gelation. The experimental results were found to be in agreement with the classical theory. The distribution functions of relaxation times were experimentally determined by the analysis of time autocorrelation functions obtained by quasielastic light scattering measurements on critically branched polymer solutions.

Introduction

As the gel point is approached, the degree-of-polymerization distribution in a branching system becomes very broad, and the second and higher moments of the distribution tend to diverge. In the vicinity of the gel point a property, X_c, of the critically branched systems can be scaled as a function of the distance from the critical point $\varepsilon = |1 - \alpha/\alpha_c|$, where α is the conversion of functional groups and α_c is its critical value (1). The scaling $X_c \sim \varepsilon^g$ gives the value of the critical exponent g.

The critical region may be dominated by fluctuations caused by long-range correlations and, therefore, different theories may yield different values of the critical exponents. The long-range correlations are mainly due to cyclization in the branching system where the cyclization probability depends on the size and symmetry of the branched molecule. The classical Flory-Stockmayer (FS) theory (2-4) does not take cyclization into account at all. The spanning-tree approximation (5-7) can correctly predict the fraction of bonds in cycles, but the effect of cyclization is reduced to the level of monomer unit, so that the network build-up is still a Markovian process and classical critical exponents are obtained. Simulation of network formation in n-dimensional space, namely percolation, can take long-range cyclization into consideration. These theories predict the values of the critical exponents to be different from the classical ones. The deviation of the experimentally observed values from one or the other theory depends on the width of the fluctuation dominated, regions covered experimentally and on the intensity of long range correlations.

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Cyclization is strong in fast chain crosslinking (co)polymerizations (6), where conformational rearrangements and chain overlaps do not seem to play any important role, so that they satisfy more the percolation model, especially if initiation of chain growth is taken into account (8,9). The situation is different for systems obtained by step reactions from larger molecules with low cyclization probability. In this connection studies on critically branched polyurethanes (10) and polyepoxides (11,12) should be mentioned. They were based essentially on light-scattering measurements. Branching processes in bulk systems have been found to follow the Flory-Stockmayer theory, while formation of polyurethanes in the presence of 80% solvent has been described better by the percolation theory. The presence of solvent substantially enhanced cyclization.

In this contribution critically branched epoxides prepared by step polyaddition of diglycidyl ether of Bisphenol A (DGEBA) and poly(oxypropylene)diamine (Jeffamine D-400) are studied. The distance from the gel point was varied by varying the initial molar ratio $r_A = 2[NH_2]_0/[EPOXY]_0$; 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 critical exponents for quantities measured by static and dynamic light scattering and to compare experimental data with existing theories. Distributions of relaxation times (i.e. of hydrodynamic radii) of the polymeric particles have been determined from dynamic light scattering data.

Experimental

Materials: Diglycidyl ether of Bisphenol A (DGEBA) (CIBA-Geigy MY-790) having the 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 D-400 (TEXACO) had M_n = 397 and the amino equivalent $\gamma_A = 106$ g/mol H in NH_2 which gives $f_n = 3.75$. Dimethylformamide (DMF) of analytical grade purity, was dried and redistilled.

Sample preparation: The DGEBA was dissolved in Jeffamine at 50°C, stirred for 5 minutes and degassed at room temperature. All samples were reacted at 100°C for 72 h in nitrogen atmosphere. These conditions ensured a practically complete conversion of epoxy groups. For preparation of critically branched samples, the molar ratio of the amine hydrogens to epoxy groups, r_A, varied in the range 2.35 - 2.45.

Determination of the critical molar ratio: The critical molar ratio, r_{Ac}, was determined from solubility measurements of samples in dimethylformamide. The critical value determined in this way was $r_{Ac} = 2.395 \pm 0.002$.

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 DMF. The measurements were performed with a Sofica instrument (angular range 30° to 150°) at 25°C using a He-Ne laser (wavelength $\lambda_0 = 632.8$ nm) as the light source. The refractive index increment of the polymers in DMF, $dn/dc = 0.082$ cm^3 g^{-1}, was determined with a Brice-Phoenix differential refractometer.

Dynamic light scattering was measured with a homodyne spectrometer equipped with a 96 channels digital correlator (13);

the last 8 channels could be shifted by 400 sampling times to determine correctly the baseline of the time autocorrelation function (TAF). As the samples were strongly polydisperse, multi-time autocorrelation functions (MTAF) covering 3.5 decades of delay time were also recorded with the correlator being set to measure with three different sampling times simultaneously.

Treatment of dynamic light scattering data

Simple TAF were analysed using the method of cumulants, and the z-average diffusion coefficient D_z was determined from the first cumulant, Γ, by extrapolation of Γ/K^2, where K is the scattering vector, to zero concentration and scattering vector. The experimental MTAF were analysed by the multiexponential analytical method CONTIN (14) which yields the distribution of relaxation times $A(\tau)$.

Results of the CONTIN calculation showed a distribution $A(\tau)$ with a shoulder or a weak side peak on the low τ side. Unfortunately, the recent testing of CONTIN showed (15) that it has a certain tendency to replace an asymmetric peak by a more symmetric one with the maximum shifted to the side of slower decrease and a shoulder or a side peak developing on the same side. To resolve this ambiguity, we decided to fit the experimental MTAF by the Schulz-Zimm distribution of τ,

$$A(\tau) = \tau^{p-1}\,\tau_o^{-p}\,\exp(-\tau/\tau_o)/\Gamma(p) \quad , \qquad (1)$$

where p and τ_o are adjustable parameters and $\Gamma(p)$ is the gamma function.

Unfortunately, the Laplace transform of this distribution may be expressed in a closed form only for half integer values of p, and hence the refinement program was confined to these values of p. It turned out that this p-grid was too coarse to reproduce the MTAF curves properly; to fill the gap, an increase of $1/\tau$ by an adjustable constant $1/t_o$ was introduced by multiplying the Laplace transform by $\exp(-t/t_o)$, t being the delay time. Plots of residuals of these adjustments showed that the distributions used fitted the experimental MTAF within experimental error (no systematic deviations with the exception of a small one for sample 5 were observed - see Fig. 3 below), confirming the suspicion that the side peaks and shoulders found by CONTIN might be artifacts of the method. A CONTIN calculation penalizing the difference between the CONTIN solution and the modified Schulz-Zimm function found by least squares performed for sample 4 yielded only small deviations from that function and the shoulder was suppressed. This gave the statistical justification of acceptability of the modified Schulz-Zimm distribution.

Results and Discussion

Results obtained by the analysis of light-scattering data are compiled in Table 1 and presented in log-log scales in Figs 1 and 2. Except for the dependences of the second virial coefficient, all other experimental dependences can be fitted by straight lines. This means that, within experimental error, the power laws predicted by theory are adequate for description of the system below the gel point. The critical exponents

Table 1 Molecular parameters of critically branched epoxies

Sample No	$\varepsilon = \|1-r_A/r_{Ac}\|$	$M_w \times 10^{-3}$	R_g (nm)	$A_2 \times 10^4$ ($cm^3 g^{-2} mol$)	$D_z \times 10^7$ ($cm^2 s^{-1}$)	R_h (nm)	ρ	Δp
1	2.27×10^{-2}	154	-	1.76	1.56	17.0	-	3.1
2	1.67×10^{-2}	213	27.1	1.85	1.25	21.3	1.3	3.2
3	1.04×10^{-2}	430	44.6	1.36	0.972	27.3	1.6	2.6
4	6.22×10^{-3}	588	50.8	0.87	0.698	38.1	1.3	2.4
5	2.05×10^{-3}	1640	83.4	0.28	0.479	55.5	1.5	2.1
6*	2.02×10^{-3}	1660	92	0.34	-	-	-	

*Sol extract of gel

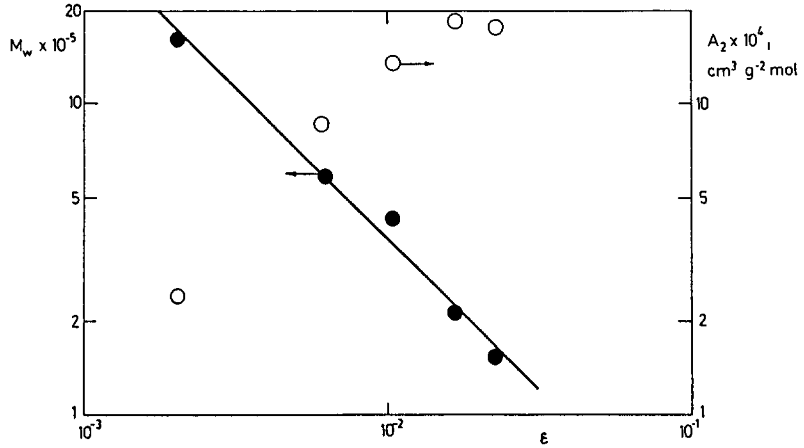

Fig. 1a Dependences of weight-average molecular weight M_w and second virial coefficient A_2 on ε.

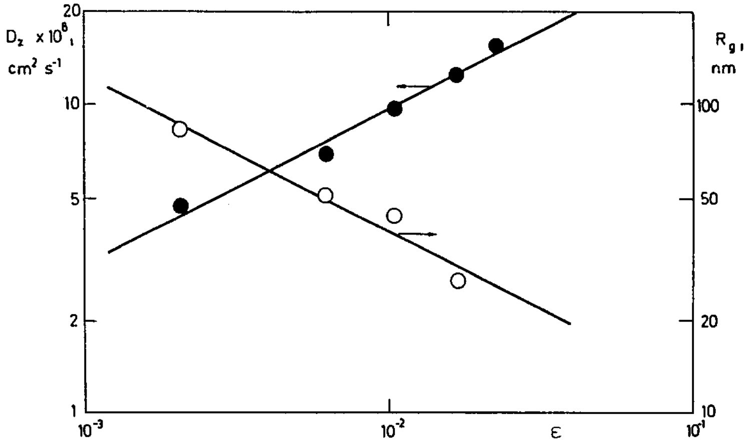

Fig. 1b Dependence of z-average radii of gyration R_g and diffusion coefficient D_z on ε. Full lines represent the best least-square linear fits.

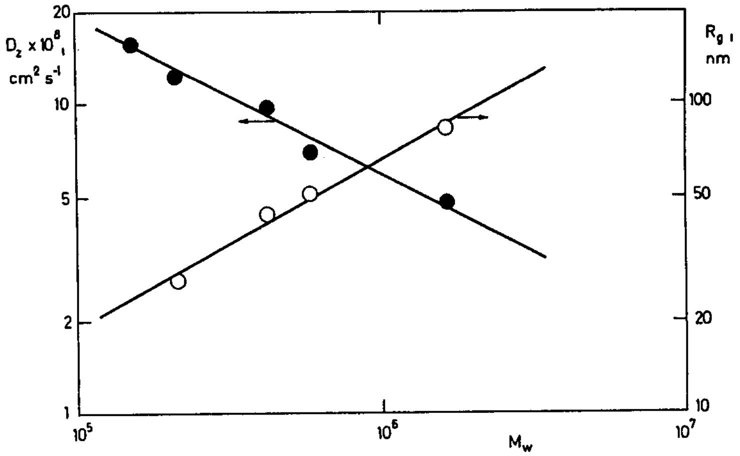

Fig. 2 The dependence of z-average radii of gyration R_g and diffusion coefficient D_z on weight-average molecular weight. Full lines represent the least-square linear fits.

Table 2 Critical exponents

Proportionality	Percolation	FS theory	Experiment
$M_w \sim \varepsilon^{\gamma}$	$\gamma = 1.74(1)$	1(1,3)	0.97 ± 0.04
$R_g \sim \varepsilon^{\nu}$	$\nu = 0.88(1)$	1/2(1)	0.50 ± 0.05
$D_z \sim R_h^{-1} \sim M_w^{\kappa}$	$\kappa = 0.35(10)$	1/2(4)	0.50 ± 0.03
$D_z \sim \varepsilon\gamma\kappa$	$\varepsilon\gamma\kappa = 0.609$	1/2	0.49 ± 0.03
$R_g \sim M_w^{\nu/\gamma}$	$\nu/\gamma = 0.506$	1/2	0.54 ± 0.05

obtained from the slopes of the straight lines in Figs 1 and 2 are compared with the corresponding critical exponents of the FS and percolation theory in Table 2.

From Table 2 one can see that the experimental critical exponents correspond very well to predictions of the FS theory. This finding means that cyclization does not play any significant role.

The fraction of bonds wasted in cycles can independently be determined from the dependence of r_{Ac} on dilution with a solvent. The quantity $\Delta r = (r_{Ac} - r^{o}_{Ac})/r^{o}_{Ac}$ can be used as a measure of the cyclization intensity, where r^{o}_{Ac} is the ring-free value of the critical ratio r_{Ac} necessary for gelation. The value of r^{o}_{Ac} can be obtained by extrapolation of r_{Ac} necessary for gelation. The value of r^{o}_{Ac} can be obtained by extrapolation of r_{Ac} to zero value of reciprocal concentration of monomers. Using data of r_{Ac} in ref.(16), we obtain $\Delta r = 3 \times 10^{-2}$. Such a degree of cyclization, as was shown by Kajiwara et al. (10), is insufficient to influence noticeably the weight and size distributions. Values of the critical exponent found in this work correspond to the published values measured with the bulk systems obtained by step polyaddition (10-12). It seems that cyclization becomes important only if a solvent is present in the reacting system.

The parameter ρ defined as the ratio of the radius of gyration and the hydrodynamic radius, $\rho = R_g/R_h$, may be used as a measure of segmental density and particle polydispersity (4). It increases with increasing polydispersity of molecular weights and decreasing compactness of the particles. Values of the quantity ρ obtained from our measurements (Table 1) are smaller than for linear polydisperse coils ($\rho = 1.73$) and larger than for homogeneous spheres ($\rho = 0.78$), see, e.g., ref. (4). These results agree, within experimental error, with those published by Burchard et al. (12) for branched epoxides. Lower values of ρ for epoxy resins compared to those of linear polymer coils are likely to be due to the higher average segmental density in branched molecules.

The analysis of the MTAF using Eq.(1) and its modification described above yielded estimates of the distribution functions $A(\tau)$ of relaxation times. In Fig. 3., only distributions for dilute samples 1,3 and 5 are shown. The distribution $A(\tau)$ extrapolated to the limit $\Theta \rightarrow 0$ and $c \rightarrow 0$ represents at the same time the distribution function of hydrodynamic radii $A(R_h)$, as $\tau \sim R_h$. Measurement of the angular dependence of $A(\tau)$ shows that within the limits of precision of $A(\tau)$ determination, the distribution obtained at $\Theta = 30°$ is equivalent to the extrapolated one, at least for samples 1-4.

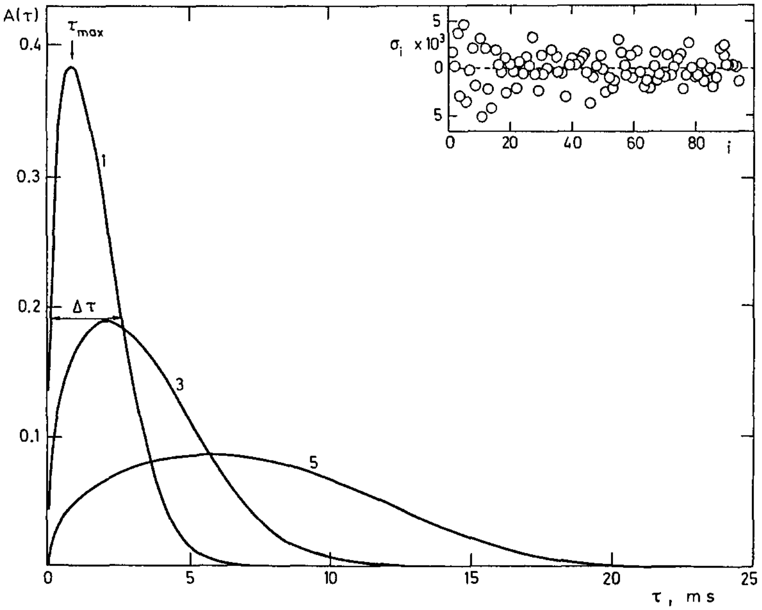

Fig. 3 Distribution functions of relaxation times $A(\tau)$ for samples 1,3 and 5. Insert: distribution of residuals σ_i as a function of correlator channel number i for sample 3

The relative half-width of the distribution function A(τ), Δp, has been calculated as the ratio of the half-width at half-height $\Delta\tau$ of the distribution to the position τ_{max} of the maximum of the distribution; its values for samples 1 to 5 are given in Table 1. As the gel point is approached, Δp decreases slightly, which seems to be at variance with the increase of polydispersity in molecular weights. This apparent paradox may be qualitatively explained by the fact that an increase in molecular weight of a particle changes its density rather than its hydrodynamic radius which thus may not depend much on ε.

Conclusions

The present light-scattering experiments provide a detailed measurements of critical exponents and of the distribution functions of relaxation times of critically branched polyepoxides obtained by step polyaddition. Values of the critical exponents found in this work correspond very well to predictions of the FS theory, which means that cyclization does not play any significant role in the studied system. The distributions of hydrodynamic radii A(R_h) can be well approximated by slightly modified Schulz-Zimm distributions. The relative half-width of A(R_h) slightly decreases as the gel point is approached.

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