Branching in epoxy resins: molecular weight as a function of the extent of reaction and critical behaviour

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Series of linear and branched epoxy resins have been investigated. Molecular weights in the range $M_w = 1500$ to 30000 have been determined by means of static and dynamic light scattering. The dependence of M_w and M_n on the extent of reaction are presented. The polydispersity M_w/M_n shows a clear difference between the two series. Extrapolation to infinite M_w yields the gel point with the critical extent of reaction. A kinetic model of the reaction is tested with the experimental values of the extent of reaction. Branching can be described with a branching parameter that links the extents of reaction of the functional groups. The experimental results are compared with results from the cascade branching theory where good agreement is found. The exponent in the critical plot is found to support the classical treatment rather than the percolation theory.

(Keywords: branching; epoxy resin; molecular weight; extent of reaction; cascade theory; percolation theory; critical behaviour)

INTRODUCTION

In the last three decades research in polymer science has been concerned mostly with linear chains. Great progress has been achieved in this field in laboratories all over the world. This impressive success has been for obvious reasons. The polymerization can in most cases be effected in a controlled manner and this implies kinetic conditions that are not too complicated. As a result, calculations of the molecular weight distribution and the two molecular weight averages M_w and M_n became possible from kinetic data by use of fairly simple statistical techniques[1-8]. Furthermore, it became feasible to develop procedures for the calculation of the chain conformation with results that are very close to the experimentally observed properties[9-11].

The progress has not been so advantageous with branched chains, for many reasons, and this again is easily understood. Most branching and crosslinking reactions of technical interest are random reactions, i.e. branching can occur at any functional group with a certain probability[1]. Thus a large number of different isomeric structures of the same molecular weight are formed, and this number increases immensely with growing molecular weight[12,13]. Furthermore, extremely broad molecular weight distributions are often observed, which makes the preparation of monodisperse fractions virtually impossible[1,14]. Finally, in most cases, a random branching process eventually leads to gelation and network formation.

An important stage in the understanding of branching and gelation was achieved by the, now classical, work of Flory[1,15,16] and of Stockmayer[14]. An essential and, for the chemist, very agreeable feature of the Flory–Stockmayer (FS) theory is the fact that all molecular and conformational properties can be described from the extent of reaction. One result is Flory's well known gelation condition for the random f-functional polycondensation[1,15,17].

$$\alpha_c = 1/(f-1) \qquad (1)$$

where f is the number of the functional groups per monomeric unit and α_c is the critical extent of reaction for gelation. Another typical result is Stockmayer's formula for the weight average molecular weight[14]

$$M_w = M_0(1+\alpha)/[1-(f-1)\alpha] \qquad (2)$$

from which Flory's gel condition (1) results when M_w increases beyond all limits. Stockmayer's equation made clear two facts of general relevance: (i) the point of gelation is defined by the condition that the weight average molecular weight M_w (or the second moment of the molecular weight distribution) goes to infinity, and (ii) gelation is a critical phenomenon similar to that of the critical condensation of a gas, spinodal decomposition of a binary system or spontaneous magnetization below the Curie temperature[18].

The simple model of the random f-functional homopolycondensation is certainly fundamental for a first understanding of a critical branching process, but it does not represent realistic systems. Actually, up to now no known system had strictly fulfilled the condition of the f-functional random polycondensation. In the rare cases where monomers with f identical functional groups have been found, the reactivity of a special group is diminished when one, two or more of the $f-1$ other functional groups have already reacted[19]. This substitution effect also often occurs in co-condensation reactions of two or more different monomers, which represent systems most frequently used in practice. Often the functional groups of

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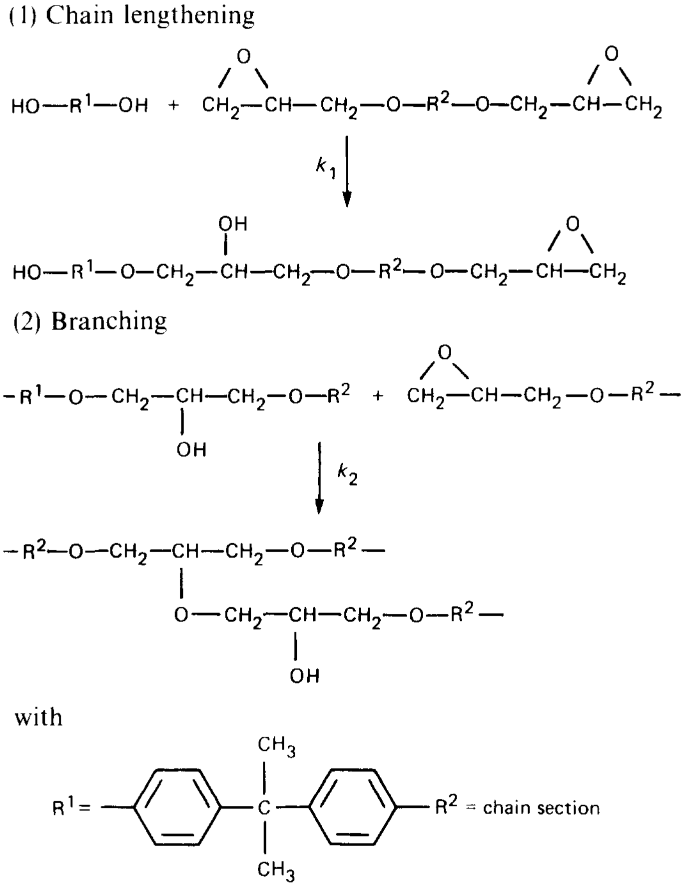
a special type of monomer are dissimilar. A typical example is glycerol with its two primary and one secondary OH-groups. All these examples could not satisfactorily be treated within the framework of the original Stockmayer theory, not for fundamental reasons, but because of difficulties in the algebra.

These difficulties could be overcome in the reformulation of the FS theory, the theory of cascade processes in the modification of Good[20,21] and Gordon[22,23]. In all the cases mentioned a simple analytic solution could be found for which the two molecular weight averages M_w and M_n are given by equations (3) and (4) in this paper[13,24]. A special problem arises if the monomer contains dormant functional groups that become activated in the course of reaction. In this paper we present experimental results on such a system and compare these with calculations from the cascade branching theory[24].

THE SYSTEM

The polymer used in the present work is an epoxy resin obtained from the two comonomers bisphenol A (BPA) and the diglycidyl ether of bisphenol A (BADGE). The reactions are shown in the following scheme.



In each step of the reaction a new functional group (a secondary hydroxyl group) is formed. This group is capable of further reaction with an epoxy group forming a branch. The extent of branching depends on the catalyst used and on the condition of reaction, e.g. temperature. At one extreme there will be no reaction of the secondary OH-group at all, and the effective functionality of the BADGE monomer is two. Here we have no branching, and the polymer is a strictly alternating copolymer. At the other extreme, the newly formed secondary OH-group may react extensively. In this case the effective functionality increases in the course of reaction but can never reach a value of $f=4$.[24] Also this special case is described by the general solution of equations (3) and (4)

$$M_w = \boldsymbol{m}\cdot(\boldsymbol{M} + \langle \boldsymbol{N}(1)\rangle (\boldsymbol{I} - \boldsymbol{P})^{-1}\boldsymbol{M}) \qquad (3)$$

$$M_N = \underset{\sim}{\mathrm{m}}\cdot \boldsymbol{M}/(1 - 0.5(\boldsymbol{n}\langle \boldsymbol{N}(1)\rangle \boldsymbol{I}) \qquad (4)$$

where $\langle \boldsymbol{N}(1)\rangle$ describes the average number of units of different kinds in the first generation, linked either to an A-unit (BPA) or a B-unit (BADGE), and $\boldsymbol{P}$ is the transition probability matrix for getting from unit A to units A or B in the next generation and from unit B to units A or B respectively. The term $\boldsymbol{n}=(n_a,n_b)$ is the composition vector, which contains as its components the mole fractions of the monomers, $\boldsymbol{m}=(m_a,m_b)$ is the vector of the corresponding mass fractions and $\boldsymbol{M}=(M_a,M_b)$ contains the molecular weights of the two monomers.

In a previous paper[24] we have derived from these general equations simple closed expressions for M_w and M_n as functions of the extent of reaction of the different groups. In this case the matrices are given by*

$$\boldsymbol{N}(1) = \begin{bmatrix} 0 & 2\alpha & 0 \\ 2\beta(1-p) & 2\beta p & 2\beta p \end{bmatrix} \qquad (5)$$

$$\boldsymbol{P} = \begin{bmatrix} 0 & \alpha & 0 \\ (1-p)\beta & p(1+\beta) & \beta p \\ (1-p)(1+\beta) & \beta p & p(1+\beta) \end{bmatrix} \qquad (6)$$

Evaluation of equations (3) and (4) together with these matrices leads to

$$\begin{aligned} M_w = (1-p-2p\beta-\alpha\beta)^{-1}\{ & M_a[m_a(1-p-2p\beta-\alpha\beta+2\alpha \\ & -2\alpha p-4\alpha^2\beta p)+2m_b[\beta(1-p)-2\beta^2p^2/(1-p)]] \\ & +M_b[m_b[1-p-2p\beta-\alpha\beta+2\alpha(1-\alpha p-\beta p) \\ & +4p]+2m_a\alpha]\} \end{aligned} \qquad (7)$$

$$M_n = (M_a + RM_b)/(1+R-2\beta R) \qquad (8)$$

where $R=n_b/n_a$ is the ratio of the monomer concentrations. This paper presents an experimental test of these equations and determines to what precision the molecular weights and the position of the gel point can be predicted from measurements of the extent of reaction.

EXPERIMENTAL

Sample preparation

From a number of kinetic runs with different conditions of temperature, catalysts and compositions, the two series B36 and B19 were selected for further investigation. These series represent the cases of low and high branching, mentioned as extremes in the introduction. The series B36 (low branching) was prepared in 50% solution of diglyme (diethylene glycol dimethyl ether) with a ratio of $R=1.0$ of BADGE and BPA at 100°C. The catalyst was TBAH (tetrabutylammonium hydroxide) at a concentration of

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* The matrix $\boldsymbol{P}$ in ref. 24 is slightly different from equation (6) owing to an error. The numerical error, however, was small (under 2.8%).

2×10^{-3} mol/val BPA dissolved in dyglyme. The other series B19 (high branching) was polymerized in the melt of $R=1.26$ of BADGE and BPA at 180°C. BATCl (benzyltriethylammonium chloride) was used as catalyst with a concentration of 8×10^{-3} mol/val BPA dissolved in 2-propanol. The reaction mixture was brought to the desired reaction temperature. Before starting the reaction, samples were taken to check the composition. Then the solutions of the catalysts were injected with continuous stirring of the reaction mixture under an inert atmosphere. At specific times samples were taken out of the reaction vessel, quenched to room temperature and analysed. Details of the kinetic results are given elsewhere[26].

Determination of the extent of reaction

The content of α-epoxy groups in the epoxy resin was determined by direct potentiometric titration[27]. The samples were dissolved in chloroform/acetic acid or chlorobenzene/acetic acid, respectively, and the solutions were titrated with 0.1 N perchloric acid in acetic acid. The content of phenolic OH-groups was determined spectroscopically. The addition of a strong base like TBAH causes the formation of phenolic anions. The absorption peak of the anions is shifted towards longer wavelengths, by 20 to 40 nm, compared with phenol, as shown in *Figure 1*[26,28]. The extinction coefficient was determined from a series of concentrations of BPA and was checked against results obtained from epoxy resins by direct titration of phenol groups. The samples were dissolved in THF, which was freshly distilled over sodium hydroxide and free of phenols. To avoid precipitation of the polymer anion, 3 to 5% methanol was added. The phenolic groups were converted to anions by adding 0.6% solutions of TBAH (40% solution in water) to the sample. The sample was recorded on a Beckman spectrometer and compared with the sample without base. The concentration of phenolate anions was determined from the optical density at 304 nm. The chemicals used were obtained from Fluka, and were of purum or puriss grade.

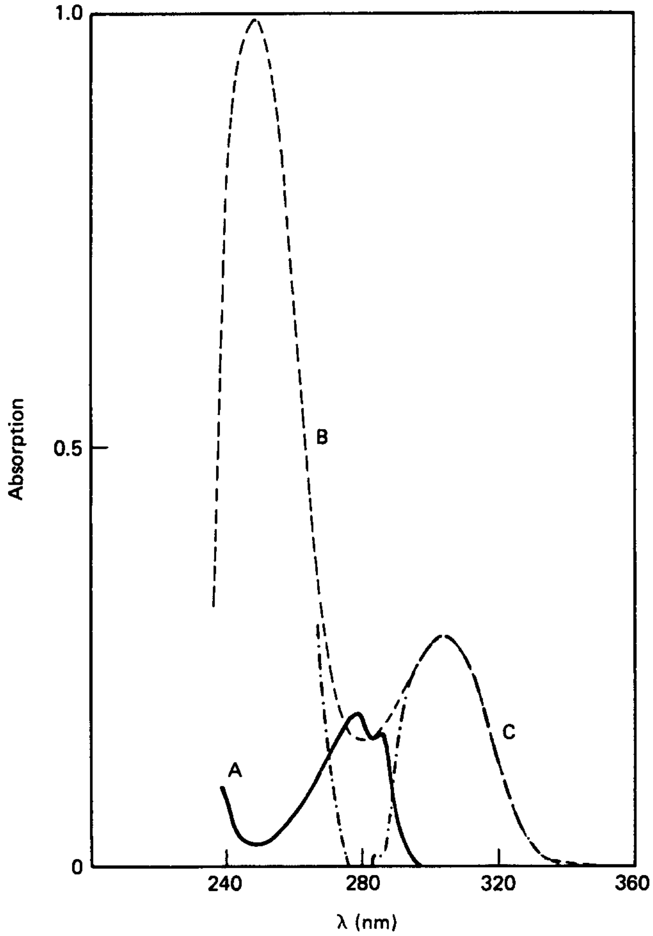

Figure 1 Optical density of BPA in THF: A, solution against solvent (——); B, solution with base against solvent (– – –); C, solution with base against solution without base (– · – · –)

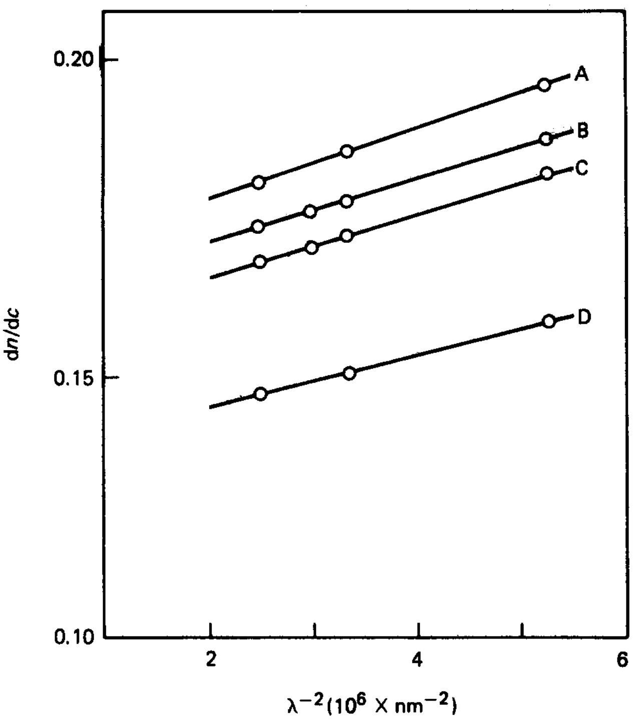

Figure 2 Dispersion plot of the refractive index increment d*n*/d*c* for solutions of monomers: A, BPA; B, BADGE; and the series B19 (C) and B36 (D) in diglyme

Molecular weight averages

The number average molecular weight M_n of the series B19 was measured by vapour pressure osmometry (v.p.o.) in chloroform at 36°C with a Perkin–Elmer apparatus. M_n was also determined from the extent of reaction β by use of equation (8), where good agreement was found. For the series B36, which was polymerized in solution, it was not possible to make v.p.o. measurements after precipitation and freeze drying of the epoxy resin. Because of the agreement between measured and calculated M_n values for the B19 series, the number average molecular weights for series B36 were calculated according to equation (8) from the extent of reaction of the epoxide β.

Weight average molecular weights M_w were determined by means of static light scattering from solutions of the polymers in diglyme. The refractive index increments (d*n*/d*c*) were measured with a Brice–Phoenix instrument for both series of polymers and the monomers. No dependence of d*n*/d*c* on molecular weight was found, but there was a dependence of d*n*/d*c* on composition, as shown in *Figure 2*.

For the light scattering experiments a photon correlation spectrometer was used, which has been further developed at Freiburg for combined static and dynamic light scattering[25,32]. Another advantage of this instrument is the increased sensitivity compared with the available Sofica 4200 instrument, and thus quite low concentrations can be used. The solutions were clarified by ultracentrifugation of the light-scattering cell by using the floating technique[29]. Because of the relatively low molecular weights of the samples no angular dependence of the scattered light was observed. However, the particle scattering factor $P_z(q)$ was determined by small-angle neutron scattering. Part of the results were published in a previous paper[32]. The molecular weight M_w was obtained after extrapolation of $Kc/R(0)$ from five concentrations to $c=0$.

RESULTS

Extent of reaction

As outlined in the Experimental section, the extent of reaction of both monomers can be determined experimentally. For reasons of stoichiometry the extents of reaction of the different groups are related to each other by the equation[24]

$$\alpha = R\beta(1-p) \qquad (9)$$

where $\alpha = (|A|_0 - |A|)/|A|_0$ is the extent of reaction of the phenolic OH, $\beta = (|B|_0 - |B|)/|B|_0$ is the extent of reaction of the epoxide, $p = (R\beta - \alpha)/R\beta$ is the extent of branching, $R = n_b/n_a$ is the initial ratio of epoxide/phenolic OH and k_2/k_1 is the branching parameter, ratio of the rate constants for branching (k_2) and chain lengthening (k_1).

According to the Scheme given earlier, kinetic equations for the two reactions can be set up; after elimination of time, and subsequent integration one obtains[24]

$$\beta R - \alpha = (k_2/k_1)[-\ln(1-\alpha) - \alpha] + C \qquad (10)$$

where C is an integration constant, the meaning of which will be discussed later in this paper. Combination of equation (9) and (10) yields

$$p = \frac{(k_2/k_1)[-\ln(1-\alpha)-\alpha] + C}{\alpha + (k_2/k_1)[-\ln(1-\alpha)-\alpha] + C} \qquad (11)$$

These equations show that the system is defined by the monomer ratio R, the branching parameter k_2/k_1 and the extent of reaction α of bisphenol A; p and β are then related to these three quantities.

To determine the branching parameter, k_2/k_1, use can be made of equation (10). Two extreme cases were taken for a test. In the first, the polymerization was effected under mild conditions, whereas in the second one the comonomers were polymerized at 180°C in the melt. As will be shown, in the first case a linear, alternating copolymer was obtained, while in the second excessive branching was found.

Equation (10) suggests a plot of $R\beta - \alpha$ against $-\ln(1-\alpha) - \alpha$. Since $R\beta$ is essentially the number of reacted epoxy groups and α that of the phenolic OH, the difference $R\beta - \alpha$ should be zero for a linear alternating copolymer. *Figures 3* and *4* exhibit the actual results. In both cases a rather rapid increase of $R\beta - \alpha$ is observed at low conversion α, which means that epoxide is consumed preferentially to phenolic OH. This initial reaction ceases after a while at a value of $R\beta = 0.035$ in *Figure 3* and $R\beta = 0.06$ in *Figure 4*. Evidently a side reaction takes place where an oligomerization of the BADGE monomers occurs. This initial value of $R\beta$ may be absorbed in the integration constant C. The reaction in *Figure 3* is then characterized by the equal consumption of the epoxide and phenolic OH-groups; this corresponds to $k_2/k_1 = 0$ and means no branching.

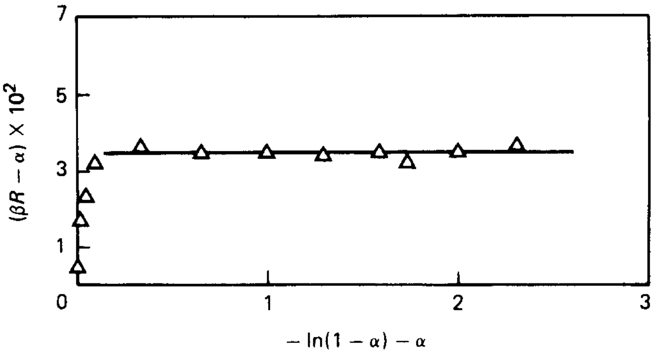

Figure 3 Series B36 (linear). Plot according to equation (10)

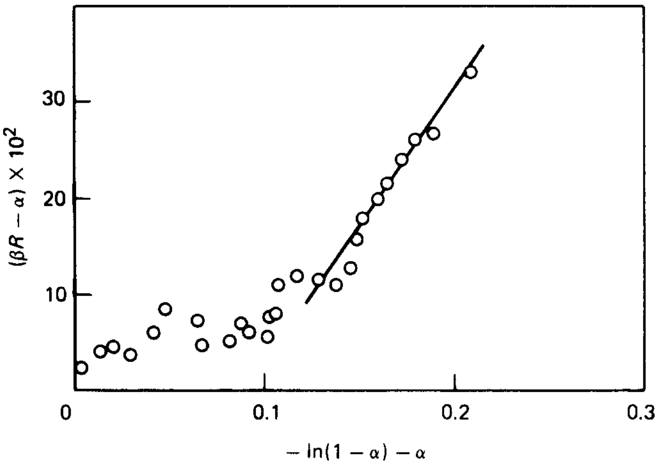

Figure 4 Series B19 (branched). Plot according to equation (10)

Figure 4 shows different behaviour. The initial reaction up to $\alpha = 0.39$ (i.e. $[-\ln(1-\alpha) - \alpha] = 0.104$) is followed by a period with a slight increase of $R\beta - \alpha$ corresponding to a value of $k_2/k_1 \leq 0.1$. Subsequently the slope of the curve changes to a much higher value. A least-squares fit to a straight line yields $k_2/k_1 = 2.4 \pm 0.1$ with an intercept of -0.19 ± 0.02. This increase of $\beta R - \alpha$ means a much greater consumption of epoxide than phenolic groups and extensive branching.

Molecular weights and polydispersity

The molecular weight averages M_w and M_n are plotted in *Figure 5* as a function of the extent of reaction α. The reaction for the series B36 (linear resins) stops at $\alpha = 0.96$ (*Figure 5b*). This is the consequence of the initial oligomerization of BADGE and the resulting consumption of epoxy groups with $\beta_0 = 0.04$; i.e. at $\alpha = 0.96$ all epoxy groups are consumed ($\beta > 0.996$). For a test, the reaction mixture was kept at the reaction temperature (100°C for several hours, where no detectable change in α and M_w was observed. For the branched series B19, M_w increases strongly near $\alpha = 0.5$, while M_n grows only slowly (*Figure 5a*).

The polydispersity M_w/M_n is shown in *Figure 6* as function of α. For the series B36 the polydispersity starts at a value of $M_w/M_n = 3$ and decreases slowly to a value of 2 on further reaction. A value of $M_w/M_n = 2$ corresponds

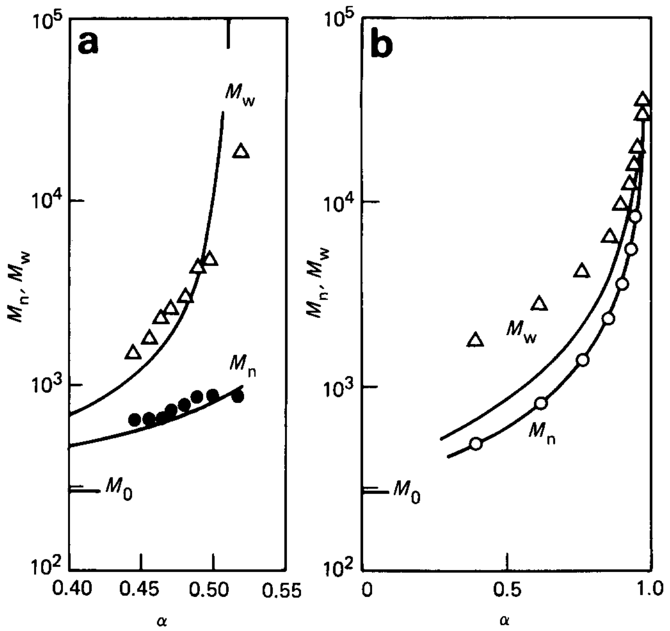

Figure 5 Molecular weight averages M_w (+) and M_n (●) for the branched series B19 (A) and the linear series B36 (B) as function of α. M_w was determined by light scattering; M_n of the branched series was measured by vapour pressure osmometry and was calculated from the extent of reaction β for the linear series. Full lines give the results of calculations for which the conditions are specified in the text

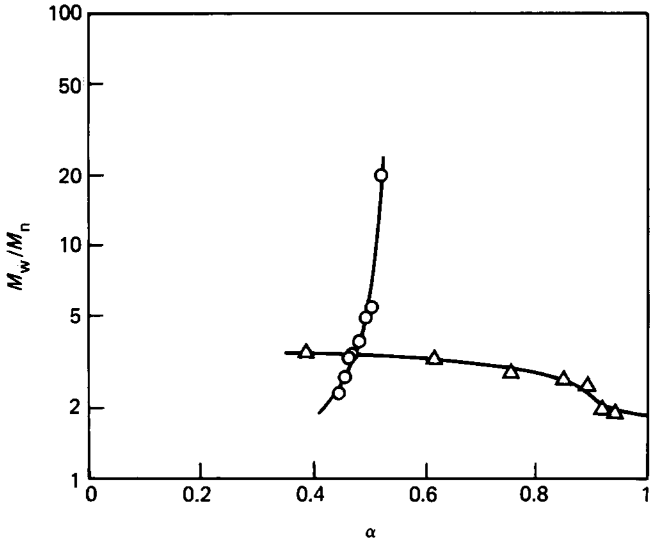

Figure 6 Polydispersity M_w/M_n for the branched series B19 (○) and the linear series B36 (△) as function of α

to a system for stepwise polymerization of linear polymers. In contrast, the polydispersity for the series B19 increases up to a value of 20 near $\alpha=0.5$.

The gel point is defined as that extent of reaction where M_w tends to infinity[14]. *Figure 7a,b* shows the extrapolation of $1/M_w$ to zero. For the series B19 the critical extent of reaction is $\alpha_c=0.520\pm0.003$ and $\beta_c=0.680\pm0.005$. For the series B36 no critical extent of reaction can be found because the reaction stops at $\alpha=0.96$, when all epoxy groups are consumed. The curve can, however, be extrapolated for $1/M_w=0$, resulting in $\alpha_c=1.0$, i.e. an infinite molecular weight is obtained only after complete reaction of the phenolic OH and only if there is no excess of phenolic OH or epoxy groups. The value $\alpha_c=1$ is characteristic for linear chains. For the series B19 a value of $p_c=0.39$ is found for the critical branching probability with equation (9) and a value of $k_2/k_1=1.57$ for the corresponding branching parameter, when the oligomerization of the epoxides is not considered.

Gelation is a critical phenomenon. Two main competing theories, i.e. the FS and the percolation theory[31], exist for the description of the critical behaviour, which do not coincide in their prediction for the behaviour near the critical point, in particular with respect to the critical exponents. The exponent γ can be determined experimentally by plotting the degree of polymerization M_w as function of the parameter $\varepsilon=(\alpha-\alpha_c)/\alpha_c$, which is shown in *Figure 8*.

In the range of our experimental data, i.e. $0.01\leqslant\varepsilon\leqslant0.14$, we find for the branched series an exponential correlation between M_w and ε with an exponent of $\gamma=1.0\pm0.1$, which is the value of the FS theory; the percolation theory demands $\gamma=1.78$. The behaviour of the linear products is more complicated. If

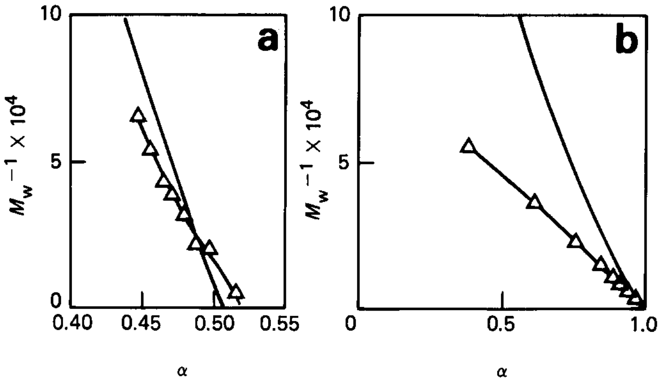

Figure 7 Reciprocal molecular weight, $1/M_w$, as function of α for the branched series B19 (a) and the linear series B36 (b)

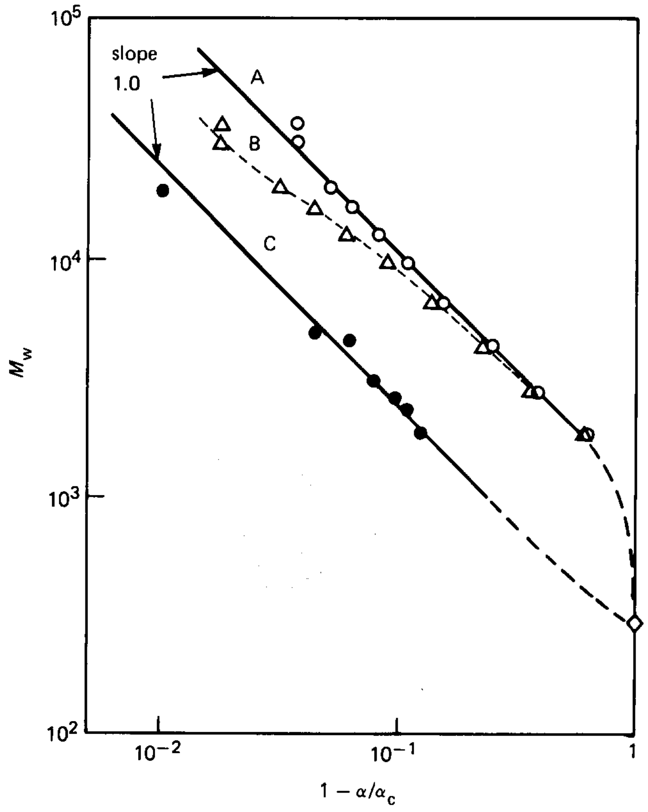

Figure 8 Weight average molecular weights, M_w, for the branched series B19 as function of $\varepsilon=(\alpha-\alpha_c)/\alpha_c$ (curve C (●): $\alpha_c=0.52$) and for the linear resins B36 (curve A (○): $\alpha_c=1$; curve B (△): $\alpha_c=0.98$; ◇: average molecular weight $(M_a+M_b)/2$ of the two monomers

the extrapolated critical value of $\alpha_c = 1.0$ is taken, again a slope of $\gamma = 1.0$ is observed, but if $\alpha_c = 0.98$ is chosen the dotted line in *Figure 8* is obtained. Note that α_c cannot be measured directly for this series because at $\alpha = 0.96$ all epoxide groups have already been consumed.

DISCUSSION AND COMPARISON WITH CALCULATIONS FROM THE CASCADE BRANCHING THEORY

The gel-point

As described in the first section of our results, at the beginning of the addition polymerization an unexpected reaction of epoxides with themselves was observed. The influence of this first stage on the reaction makes the discussion more complicated. We assume that up to a conversion of about 5% a homopolymerization of the epoxide takes place. This prepolymerization reduces the initial ratio R of the epoxide and phenolic groups for the reaction in the Scheme. For the branched series B19 we have to subtract $\beta_0 = 0.05$ from β, and the initial ratio R is reduced to $R' = 1.20$. Applying this procedure we now find from the experiment the following critical extents of reaction at the gel-point

$$\alpha_c = 0.52 \pm 0.01 \qquad \beta_c = 0.63 \pm 0.02$$

$$p_c = 0.31 \text{ (values from experiment)}$$

where p_c has been obtained from equation (9).

To compare these values with those from theory we have to take into account that up to $\alpha = 0.39$ branching does not occur, i.e. $p = 0$ (see *Figure 4*). From then on we have a linear behaviour with a slope of $k_2/k_1 = 2.4 \pm 0.1$. The condition for gelation is given in the cascade theory by the relation

$$[(1-p)(1-p-2p\beta-\alpha\beta)]_{\text{crit.}} = 0 \qquad (12)$$

Substituting p and β in equation (12) with the aid of equation (11) and (9), one obtains a condition for the gel-point that depends only on the branching parameter k_2/k_1 and α; hence α_c can be calculated. Inserting $R' = 1.2 \pm 0.01$ and $k_2/k_1 = 2.4 \pm 0.1$, the result is

$$\alpha_c = 0.506 \pm 0.014 \qquad \beta_c = 0.611 \pm 0.014$$

$$p_c = 0.311 \pm 0.011 \text{ (values from cascade theory)}$$

where p_c and β_c were calculated with α_c from equations (11) and (9) respectively. These data are apparently in good agreement with the experimental values. It is worth mentioning that the initial homocondensation seems otherwise (than via β_0) not to influence the critical extent of reaction.

Molecular weight dependence

The cascade branching theory also allows the calculation of the molecular weight dependence on the extent of reaction. The following calculations were made with the two monomer molecular weights of $M_a = 228$ and $M_b = 340$. For the branched B19 series the result of the calculation is shown in *Figure 5b*. The same parameters as before have been used: $R = 1.20$, $k_2/k_1 = 2.4$ starting at $\alpha = R\beta = 0.39$, ($k_2/k_1 = 0$ before this conversion). For the linear B36 series one has $\beta_0 = 0.035$, and this reduces R to a value of $R' = 0.96$. According to *Figure 3* the branching parameter k_2/k_1 is zero.

As a last point we discuss the critical behaviour. *Figure 8* indicates a critical exponent γ in favour of the predictions of the FS or the cascade branching theory. It should be emphasized, however, that our experiments cover only the region where $\varepsilon > 10^{-2}$, which means that we are still fairly far away from a really critical region. Critical exponents of much higher values than $\gamma = 1.0$ appear to be conceivable for smaller ε. However, this would require an accuracy in determining the extent of reaction of better than 1%. Unfortunately, such high precision appears not achievable at present.

Figure 7 reveals another striking effect. The asymptotic curve for the linear chain is shifted towards higher molecular weights, whereas that of the branched series is shifted towards lower molecular weights. This behaviour remains as yet unexplained by current theories but may result from a substitution effect.

The agreement of the calculated molecular weights M_w with the measured quantities is evidently not good at lower extents of reaction, though a rather good agreement was found for the gel point. These deviations are probably caused for three reasons.

(i) The higher molecular weights observed experimentally are obviously to a large extent produced by the initial homopolymerization of the epoxide groups.

(ii) Ring formation may have taken place to some extent, and in fact the slight shift of the gel point found experimentally to higher extents of reaction is an indication for this intramolecular reaction. This ring formation may also be responsible for the critical extent of $\alpha_c = 1$ of the linear chains that was found by extrapolation, while without an assumption of ring formation $\alpha_c = 0.98$ should occur.

(iii) As a final point it has to be mentioned that the cascade theory resembles a mean field theory where the systems are described by average extents of reaction. Recently, however, Dušek and his coworkers[33] have given examples where the more exact kinetic solutions of the branching process have given significantly different results. These deviations from the cascade theory became expecially large for reaction with substitution effects, i.e. where the reaction of a functional group depends on how many of the other functional groups on a monomer have already reacted.

We thus come to the conclusion that the present cascade calculations give a good first approximation. Refinement within this scheme will be possible by taking into consideration the initial homopolymerization of epoxide groups, some ring formation and a substitution effect. The kinetic approach is certainly more precise in principle, but solutions are possible only if the infinite number of coupled differential equations is truncated liberally; this, however, introduces other errors.

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REFERENCES

1 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953
2 Alfrey, T. Jr, Bohrer, J. J. and Mark, H. 'Copolymerization', Interscience, New York, 1952
3 Stockmayer, W. H. *J. Chem. Phys.* 1945, **13**, 199
4 Peller, L. *J. Chem. Phys.* 1962, **36**, 2976
5 Swarc, M. *Adv. Polym. Sci.* 1983, **50**
6 Price, F. *J. Chem. Phys.* 1962, **36**, 209
7 Bamford, C. H., Barb, W. G., Jenkins, A. D. and Onyon, P. F. 'The Kinetics of Vinyl Polymerization by Radical Mechanism', Butterworths, London, 1958
8 Schulz, G. V. *Z. Physik. Chem.* 1939, **B43**, 25
9 Volkenstein, M. V. 'High Polymers, Vol. 14: Configurational Statistics of Polymeric Chains', Interscience Publishers, New York, 1963
10 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1969
11 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971
12 Zimm, B. H. and Stockmayer, W. H. *J. Chem. Phys.* 1949, **17**, 1301
13 Burchard, W. *Adv. Polym. Sci.* 1983, **48**, 1
14 Stockmayer, W. H. (a) *J. Chem. Phys.* 1943, **11**, 45; (b) *J. Chem. Phys.* 1944, **12**, 125
15 Flory, P. J. *J. Amer. Chem. Soc.* 1951, **63**, 3083, 3091, 3097
16 Flory, P. J. *J. Amer. Chem. Soc.* 1947, **69**, 30
17 Flory, P. J. *Chem. Rev.* 1946, **39**, 137
18 Stanley, H. E. 'Phase Transition and Critical Phenomena', Oxford University Press, New York, 1971
19 Gordon, M. and Scantlebury, G. R. *J. Chem. Soc. B* 1967, 1
20 Good, I. J. *Proc. Camb. Phil. Soc.* 1948, **45**, 360; 1955, **51**, 240; 1960, **56**, 367
21 Good, I. J. *Proc. Roy. Soc. Lond.* 1963, **A272**, 54
22 Gordon, M. *Proc. Roy. Soc. Lond.* 1962, **A268**, 240
23 For further literature see ref. 24
24 Burchard, W., Bantle, S. and Zahir, S. A. *Makromol. Chem.* 1981, **182**, 145
25 Bantle, S. *Ph.D. Thesis*, University of Freiburg, 1982
26 Zahir, S. A. and Bantle, S. 'Epoxy Resin Chemistry II', Amer. Chem. Soc. Symp. Ser. 1983, **221**, 245
27 Dobinson, B., Hofmann, W. and Stark, B. P. 'The Determination of Epoxide Groups', Pergamon Press, Oxford, 1969
28 Shchori, E. and McGrath, J. E. *J. Appl. Polym. Sci.* 1978, **34**, 103
29 Dandliker, W. B. and Kraut *J. Amer. Chem. Soc.* 1956, **78**, 2380
30 Bantle, S., Haesslin, H. W., ter Meer, H.-U., Schmidt, M. and Burchard, W. *Polymer* 1982, **23**, 1839
31 Stauffer, D., Coniglio, A. and Adam, M. *Adv. Polym. Sci.* 1982, **44**, 103
32 Bantle, S., Schmidt, M. and Burchard, W. *Macromolecules* 1982, **15**, 1604
33 Mikeš, J. and Dušek, K. *Macromolecules* 1982, **15**, 93