Epoxy resins based upon 1,4-anhydroerythritol: Kinetics and determination of branching

Elke Wachenfeld and Walther Burchard
Institute of Macromolecular Chemistry, University of Freiburg, Stefan-Meier Strasse 31, 7800 Freiburg, FRG

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Epoxy resins (polyhydroxyethers) based upon 1,4-anhydroerythritol and bisphenol-A diglycidyl ether have been prepared by step-growth reaction in the melt. A kinetic scheme taking into account branching and a substitution effect has been worked out. In addition, the molecular weight averages M_w and M_n have been calculated using the rate constants for step growth and branching obtained from the fit of the conversion curve, where the substitution effect has been taken into account. The conversion of epoxide as a function of time can be described by the present theory adequately up to a conversion of about 90%. Beyond this point diffusion control becomes effective. A reasonable description of M_w as a function of β is possible, where β is the extent of reaction of the epoxy groups. However, predicted polydispersity is consistently lower than that found experimentally.

(Keywords: epoxy resins; kinetics; branching; 1,4-anhydroerythritol)

INTRODUCTION

Epoxy resins are coating materials that are quite extensively applied to protect metallic surfaces against corrosion[1-3]. They are prepared industrially by curing diglycidyl ethers, mostly from bisphenol-A (BA)[4,5], with amines or acid anhydrides[1-3,6-8] (*Figure 1*). However, resins can be prepared also by a step-growth reaction of diglycidyl ethers with diols. This reaction, the mechanism of which is discussed by Bantle *et al.*[9-11], proceeds easily with phenolic and primary hydroxyl groups. Well known commercial products are based on BA as diol, because of the high glass transition temperature T_g of the resulting resins. Aliphatic components yield produces of rather low T_g.

In the present paper we report studies on epoxy resins based upon 1,4-anhydroerythritol (AE) as the diol component. These products appeared to be of interest since the T_g of these materials may be expected to lie in the temperature range between BA and aliphatic resins, resulting from the fairly rigid conformation introduced by the ring structure of AE, which, however, may not be as rigid as BA. Other diol compounds with similar or more complicated ring structures certainly will have similar effects, but AE is of particular interest, because it is obtained from starch by special enzymic reactions more easily and cheaply than by petrochemistry[12-15].

This diol has, however, the disadvantage of less reactive secondary hydroxyl groups. Moreover, these secondary OH groups are virtually indistinguishable from the OH groups created by the reaction of an epoxy group with an alcohol. Therefore, the amount of non-reacted diol OH groups cannot be directly determined. This is regrettable as the extent of branching is closely related to the difference in the extents of reaction of the epoxy groups and the diol OH groups. This difference is just the number of reacted OH groups, created by the reaction of an epoxy ring[9-11]. These OH groups will be abbreviated EP OH groups. In a previous study BA was used as diol component and in this case the phenolic OH groups could be titrated as well as the epoxy groups[9-11].

The desired information on the branching reaction is, on the other hand, contained, though more indirectly, in the time dependence of the epoxy reaction. Therefore, we tried to set up a kinetic scheme that would describe the process of formation as accurately as possible. Once established, the molecular weight averages M_n and M_w can be calculated from the kinetic constants with the aid of cascade branching theory and these results can be compared with measurements. Such comparison gives additional information on the validity of the applied model.

THEORY

Kinetic scheme

Some general remarks. In a previous paper[9] a simplified model for the kinetics of epoxide reaction including branching has been discussed. In that model both OH groups of the diol have been treated as being equally reactive. This assumption is only a first approximation and turned out to be an oversimplification for the more general case. For this reason we considered it necessary to derive a kinetic scheme taking into account a substitution effect on the diol. Substitution effects can occur as soon as one of the two initially indistinguishable OH groups has reacted; then the reactivity of the second OH group may be enhanced (positive substitution effect) or diminished (negative substitution effect), for instance by steric hindrance.

Notation. We shall write C_B = concentration of epoxy groups, C_A = concentration of diol OH groups, and C_H = concentration of EP OH groups. The concentrations at time $t=0$ are indicated by subscript 0.

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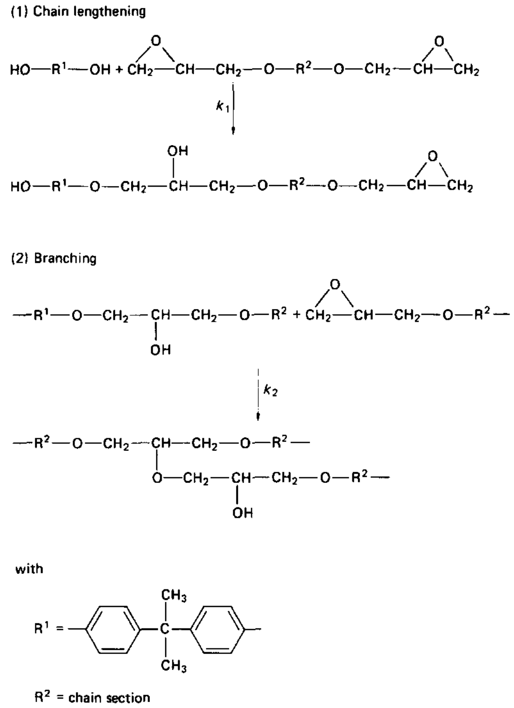

Figure 1 Reaction scheme for polyhydroxyethers

Sometimes it is advisable to use extents of reaction instead of molar concentrations. These are defined as follows:

$$\beta=(C_{B0}-C_B)/C_{B0} \tag{1}$$

$$\bar{\alpha}=(C_{A0}-C_A)/C_{A0} \tag{2}$$

$\bar{\alpha}$ and β are always less than or equal to one and consequently have the meaning of reaction probabilities. As long as no branching reaction occurs, we have in general

$$\bar{\alpha}=R\beta \tag{3}$$

where

$$R=C_{B0}/C_{A0}$$

If branching does occur, more epoxy groups than diol OH groups are consumed, which results from the reaction of epoxy groups with EP OH groups. Under these conditions $\bar{\alpha}$ and β are related as follows[9]:

$$\bar{\alpha}=\beta R(1-p) \tag{4}$$

which defines the branching probability p as

$$p=1-(\bar{\alpha}/\beta R) \tag{5}$$

For the reaction *with* substitution effect the concentration of diol OH groups C_A has to be subdivided into C_{A1} and C_{A2}, where

$$C_{A1}+C_{A2}=C_A$$

and C_{A1} is the concentration of OH groups in the *monomeric* diol, while C_{A2} is the concentration of singly reacted diol.

The kinetic equations. Four different kinetic equations have to be considered, i.e. the consumption of A1, A2, EP OH and B groups.

For the A1 groups:

$$-\mathrm{d}C_{A1}/\mathrm{d}t=k_1C_{A1}C_B+k_1C_{A1}C_B \tag{6}$$

Here k_1 is the rate constant of the reaction between an epoxy group and an OH group of the monomeric diol. The first term represents the actually reacted diol OH groups, whereas the second one represents those which become converted into A2 because of the reaction of the first OH group of the diol.

For the A2 groups:

$$-\mathrm{d}C_{A2}/\mathrm{d}t=-k_1C_{A1}C_B+k_2C_{A2}C_B \tag{7}$$

The first term describes the A2 groups created, the second term those consumed in the reaction with epoxide, running at a rate constant k_2. Equation (7) can be written in a different manner by introducing a factor g for the substitution effect such that

$$-\mathrm{d}C_{A2}/\mathrm{d}t=k_1C_B(gC_{A2}-C_{A1}) \tag{8}$$

where $k_2=gk_1$. Depending on the magnitude of g one has

$g<1$: negative substitution effect
$g>1$: positive substitution effect
$g=1$: no substitution effect

For the EP OH groups one only needs to know how many *diol* OH groups have reacted, since each reaction of an EP OH group with an epoxy group reproduces an EP OH group and thus does not change the concentration. Consequently

$$-\mathrm{d}C_H/\mathrm{d}t=-k_1C_B(C_{A1}+gC_{A2}) \tag{9}$$

The concentration of epoxy groups is diminished by reaction with all three different types of hydroxyl groups.

For the B groups:

$$-\mathrm{d}C_B/\mathrm{d}t=C_B[k_1(C_{A1}+gC_{A2})+k_3C_H] \tag{10}$$

where k_3 is the rate constant of the reaction of EP OH with epoxide (branching).

Solution of the kinetic equations. As only C_B can be measured, one has to find a form to express C_{A1}, C_{A2} and C_H in terms of C_B. First, the time dependence can be eliminated by dividing two of the different kinetic equations by each other. Combination of equations (6) and (8) leads to

$$\mathrm{d}C_{A2}/\mathrm{d}C_{A1}=0.5g(C_{A2}/C_{A1})-0.5 \tag{11}$$

Integration of this inhomogeneous differential equation results in[16]

$$C_{A2}=C_{A10}\{[1/(2-g)](C_{A1}/C_{A10})^{g/2}-(C_{A1}/C_{A10})\} \tag{12}$$

Similarly combining (9) with (6) one finds

$$\mathrm{d}C_H=-0.5\mathrm{d}C_{A1}-0.5g(C_{A2}/C_{A1})\mathrm{d}C_{A1} \tag{13}$$

which cannot be solved analytically. Fortunately this is not necessary, because C_H can be expressed by the extent of reaction $\bar{\alpha}$ of the diol OH groups (see also equation (9)):

$$C_H = C_{A1\,0} - C_{A1} - C_{A2} = C_{A1\,0}\bar{\alpha} \qquad (14)$$

Note that $C_{A1\,0} = C_{A0}$, since at time $t=0$, $C_{A2\,0}=0$. Finally with (6) and (10) one has

$$dC_B = \left(\frac{C_{A1} + gC_{A2}}{2C_{A1}} + \frac{k_3 C_H}{2k_1 C_{A1}}\right) dC_{A1} \qquad (15)$$

and this again cannot be solved analytically, but in this case, too, a solution is not needed for reasons outlined below. Thus, by equations (12), (14) and (15) the concentrations of A2, H and B are expressed in terms of A1.

The last step in solving the set of four differential equations consists of calculating the time dependence of C_B. From (10) one has

$$t = -\int \frac{dC_B}{C_B[k_1(C_{A1} + gC_{A2}) + k_3 C_H]} \qquad (16)$$

The solution of this equation, which has to be carried out by numerical integration, gives with the use of equations (14) and (15) the time-dependent consumption of A1 groups. The time dependence of A2 and B then follow from equations (12) and (15).

Molecular weights and polydispersity

Further information on the extent of branching, or branching density, can be obtained from measurements of the weight and number average molecular weights M_w and M_n and the resulting polydispersity M_w/M_n of the system. An increase of the polydispersity with M_w is a strong indication for random branching[17,18]. Quantitative conclusions on the branching density can be obtained only in connection with a suitable branching theory, which allows calculation of M_w and M_n for a special branching mechanism. Such calculations can be carried out with the aid of the cascade branching theory, which has been shown to be a good approximation to a real system[19,20]. This is in particular true if the first shell substitution effect is taken into account[21–23]. Since the principles of cascade theory have been outlined in several review articles[24–27], only the final formulae will be given in Appendix 1.

The main problem in calculating M_w now consists of the determination of the extents of reaction $\bar{\alpha}$, $\bar{\alpha}_1$, β and p, where β and p have already been defined in equations (1) and (2). The other probabilities $\bar{\alpha}$ and $\bar{\alpha}_1$ are given by (see Appendix 2 for details):

$$\bar{\alpha} = [\alpha - \alpha^2(1-g)]/[1 - \alpha^2(1-g)] \qquad (17)$$

and

$$\bar{\alpha}_1 = \alpha g/[1 - \alpha(1-g)] \qquad (18)$$

where g is the factor describing the substitution effect[21–23], as already mentioned. For $g=1$ (no substitution effect) one has $\bar{\alpha} = \bar{\alpha}_1 = \alpha$.

If a substitution effect is present, then α is the reaction probability of *one* of the two free diol OH groups (A1) of the *monomer* A. If the diol already carries one substituent, then this reaction probability is changed by a factor g; so the extent of reaction (not normalized) is $g\alpha$. Then, $\bar{\alpha}$ is the average extent of reaction of both different diol OH groups, where the denominator represents the normalization factor. With BA as diol $\bar{\alpha}$ can be obtained by titration, but not α. In the present case such titration is not possible, as already outlined in the introduction, and $\bar{\alpha}$ has to be expressed by the extents of reaction β and p as was done earlier. Here $\bar{\alpha}_1$ denotes the transition probability from the nth to the $(n+1)$th shell for the diol, taking into account the substitution effect. Thus $\bar{\alpha}_1$ and $\bar{\alpha}$ are uniquely connected via α.

In addition to the substitution effect, ring closure can occur. In principle the ring formation can be incorporated to first order into the cascade branching process using the 'spanning tree' approximation[21–23]. Ring formation has an influence similar to a negative substitution effect ($g<1$) and causes a shift of the gel point to higher conversion. However, almost nothing is known on the extent of ring formation in these systems. Therefore the 'substitution effect' parameter g, used for the fit, includes implicitly the extent of ring formation.

To calculate M_w and M_n we first determined $\bar{\alpha}$ by the kinetic equations. Then equation (17) was solved for α. The resulting quadratic equation has two roots, only one of which has a physical meaning. With this α value, $\bar{\alpha}_1$ was calculated from equation (18) and inserted in the equations for M_w and M_n (Appendix 1).

COMPARISON OF EXPERIMENT AND THEORY

Experimental

1,4-Anhydroerythritol supplied by Maizena was used for the synthesis of epoxy resins without further treatment. The diglycidyl ether of bisphenol-A (DGEBA), 'Araldit F' from Ciba-Geigy, was crystallized as outlined below.

Crystallization of DGEBA. Equal amounts of Araldit F and methanol were mixed in a round-bottomed flask and put into an ice bath for about one hour; phase separation occurred. The two phases were separated and the more viscous one was kept for 4–7 days at 0°C. DGEBA has then been crystallized. It was filtered, washed with cold methanol and dried for 2 days at room temperature *in vacuo*. Yield: 70–80% of theory (literature[14,15]: 80%). M.p.: 42°C (literature: 42–44°C). Epoxy equivalent: 5.75 eq/kg (theory: 5.88 eq/kg).

Synthesis of epoxy resins. Equimolar amounts of DGEBA and AE were heated in a round-bottomed flask in an oil bath. The molten mixture was stirred vigorously and when it reached the desired reaction temperature the catalyst was added. From this time on, probes were taken for epoxide titration. (The time dependence of the concentrations is given in *Figure 2*.) After about one hour, stirring was terminated. On adding the catalyst, the colour of the mixture turned from colourless to bright yellow.

Epoxide titration. The amount of epoxide was measured potentiometrically by a Titroprozessor 636 from Metrohm; 0.6 to 0.9 meq of epoxide were dissolved in 30 ml chloroform/glacial acetic acid (1:2), 2.5 g cetyltrimethylammonium bromide was added and titrated with 0.1 N perchloric acid in glacial acetic acid. A typical titration curve is shown in *Figure 2*.

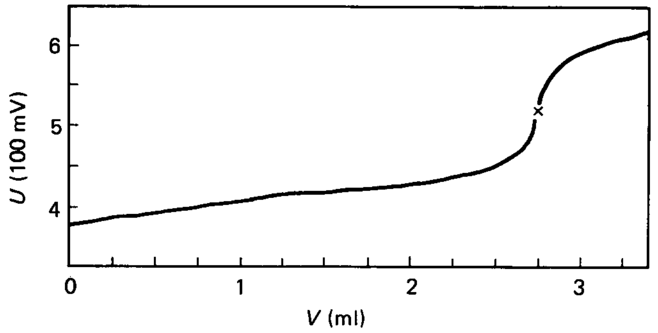

Figure 2 Typical titration curve for the epoxide titration with perchloric acid

Refractive index increment. The value of d*n*/d*c* was measured with a Brice–Phoenix differential refractometer at 20°C in DMF at $\lambda_0 = 488$ nm, giving d*n*/d*c* = 0.139.

Molecular weight determination. The number average molecular weights M_n were measured on a vapour pressure osmometer (Perkin-Elmer 115) using $CHCl_3$ as solvent. The weight average molecular weights M_w were determined by static light scattering in DMF at 20°C with an LS instrument described by Bantle *et al.*[28,29]

Results and discussion

Three sets of experiments have been carried out under the conditions listed in *Table 1*.

For some probes of AE-1 and AE-2 the molecular weights M_n and M_w have been measured. M_n varied only in a small region from 400 to 3000 and could be determined by vapour pressure osmometry. On the other hand, M_w was determined by light scattering and could be measured with sufficient reliability only for M_w greater than 5000. The data are collected in *Table 2*.

Fit of kinetic data. The results of the kinetic measurements at 75°C and 100°C are shown in *Figures 4* and *5*, where *Figure 5* shows the initial part in greater detail.

For reactions without branching and substitution effect, the points of measurement should follow second-order kinetics and lie on a straight line. Branching causes an upturn with increasing time. In fact curve A of *Figure 5* could, in the initial part, be well described simply by branching, with kinetic constants as given in *Table 3*. The curve actually shown was calculated with a positive substitution effect, introduced for reasons to be discussed below. However, at longer reaction times the experimental curve bends down, while the theoretical curve shows a steady increase. A similar deviation from theory is observed for the run at higher temperature. Moreover, the curve can no longer be fitted by simply assuming branching, because already in the early stage the curve shows downward bending. Curve B in *Figure 5* can be approximated better by kinetics *with* substitution effect. The corresponding kinetic constants are listed in *Table 3*. Accordingly the reaction rate of the second OH group is reduced by approximately 70%.

To discuss the different shapes of the curves A and B, we start with the deviation at high extents of reaction; there, diffusion control is evidently effective. In fact, the viscosity increases drastically with time, such that at high extents of reaction a *random* step-growth reaction may no longer take place. Only smaller molecules are capable of significant diffusion and will be taken up predominantly by larger ones.

This interpretation is in agreement with the observation that the deviation occurs at higher kg eq^{-1} values (i.e. extents of reaction) when running the experiment at higher temperature. Reactions which are fully controlled by diffusion can efficiently be calculated by the Smoluchowski equation[30,31]. Unfortunately, there exists at present no theory which covers the transition from chemical kinetics to a developing diffusion control[32–37].

Since diffusion control suppresses reaction among large species[30,31], the gel point is delayed towards higher

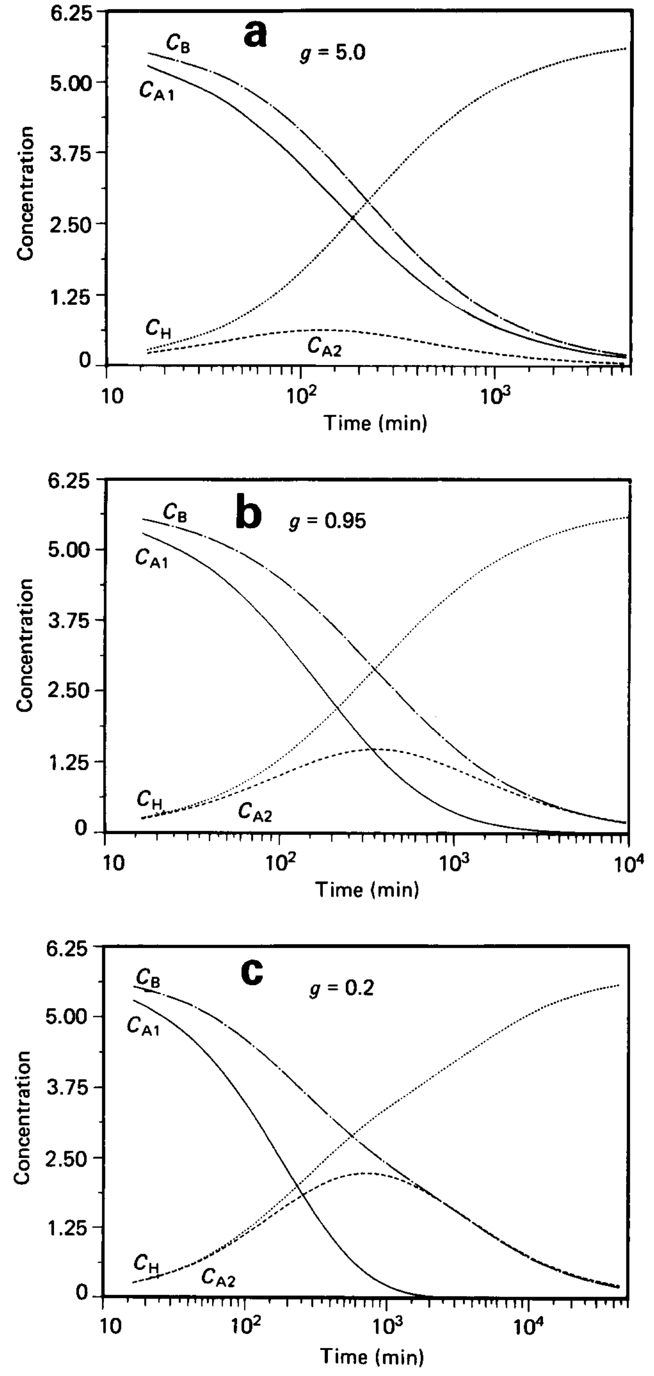

Figure 3 Time dependence of the actual concentrations of the different functional groups. $k_1 = 0.0005$ kg eq^{-1} min^{-1} (step growth), $k_3 = 1.0 \times 10^{-7}$ kg eq^{-1} min^{-1} (branching). The values for the substitution effect *g* are indicated

Table 1 Reaction conditions

Series	DGEBA (g)	AE (g)	Temp. (°C)	Duration (h)	Catalyst[a]
AE-1	153.0	46.8	75	120	4.39 g TMAC, in 2.0 ml methanol
AE-2	153.0	46.8	100	104	4.39 g TMAC, in 2.0 ml methanol
AE-3	15.3	4.68	100	7	0.44 g TMAC, without solvent

Table 2 Measured quantities: reaction time t (h) and M_n and M_w (g mol^{-1})

(a) AE-1

t	β	M_n	M_w
14.9	0.748	1170	–
23.5	0.845	1200	–
27.5	0.882	1370	–
30.0	0.878	1490	–
31.5	0.894	1510	–
34.0	0.900	1555	3100
35.5	0.904	1600	2500
37.0	0.910	1520	2600
51.1	0.934	1690	4900
60.8	0.946	1590	6950
75.8	0.955	1790	8260
87.6	0.962	1770	11800
101.3	0.961	2400	12300
120.0	–	–	14200

(b) AE-2

t	β	M_n	M_w
26.2	0.936	–	–
37.3	0.950	2100	–
45.9	0.958	2440	–
50.0	0.960	2180	9200
55.9	0.963	2500	–
69.5	0.967	2410	17200
79.5	0.968	2495	–
93.9	0.972	2490	–
104.0	0.975	3020	32000

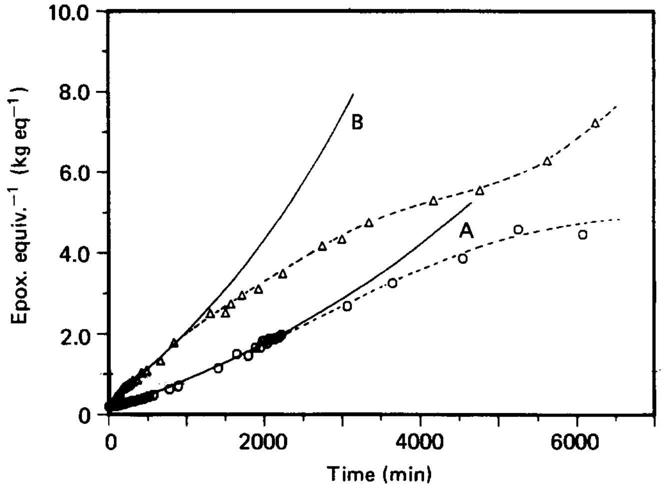

Figure 4 Time dependence of the epoxide conversion. Second-order kinetics ($k_3 = 0$, $g = 1$) yield a straight line in this plot. Upturn is an indication of branching. (○) AE-1, 75°C; (△) AE-2, 100°C. Full curves are calculated (best fit) with A, $k_1 = 5.24 \times 10^{-4}$ kg eq^{-1} min^{-1}, $k_3 = 1.3 \times 10^{-5}$ kg eq^{-1} min^{-1}, $g = 1.5$; B, $k_1 = 4.9 \times 10^{-3}$ kg eq^{-1} min^{-1}, $k_3 = 1.5 \times 10^{-5}$ kg eq^{-1} min^{-1}, $g = 0.31$

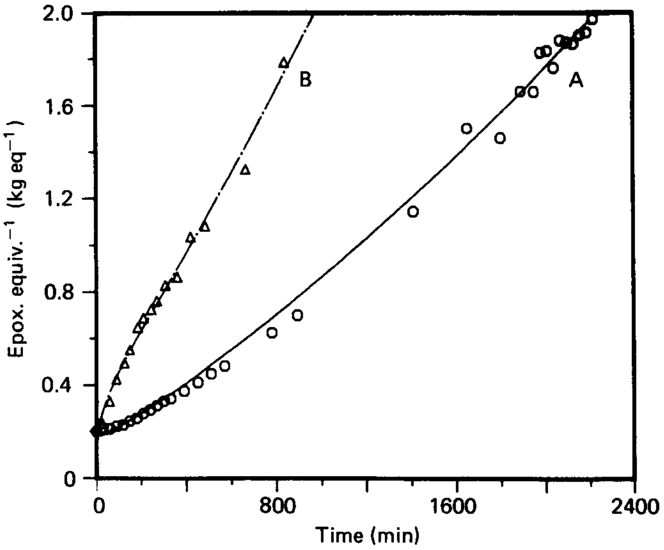

Figure 5 Initial part of *Figure 4*

Table 3 Rate constants fitted (a) without and (b) with substitution effect (SE)

(a) Without SE

Series	k_1 (10^{-3} kg eq^{-1} min^{-1})	k_3 (10^{-3} kg eq^{-1} min^{-1})	k_3/k_1
AE-1	0.583	0.0131	0.01
AE-2	1.33–3.2	0.0147	0.002

(b) With SE

Series	k_1 (10^{-3} kg eq^{-1} min^{-1})	k_3/k_1	g
AE-1	0.524	0.025	1.5
AE-2	4.90	0.003	0.31

extents of reaction and eventually, in a fully diffusion-controlled reaction, no gelation at all occurs[30,31]. Simultaneously the size distribution may be expected to become narrower. The experimentally determined heterogeneity is, however, much larger than predicted by the present theory. At the moment no mechanism can be offered to explain this fact.

Concerning the behaviour at short reaction times, we can only conjecture about possible reasons for the striking differences. It appears conceivable that at low temperatures intramolecular hydrogen bonds are present in the monomer. These may be fluctuating such that the two OH groups appear equivalent. Once one OH group has reacted the second one may become strongly activated to overcompensate the steric hindrance which evidently is effective at higher temperatures. At 100°C the hydrogen bonds are apparently already broken and only steric hindrance plays a role. We are aware of the very speculative character of the interpretation, for it is not known so far whether an intramolecular hydrogen bond causes, under the applied conditions, stimulation or hindrance of the reaction. In the case of 1,6-dianhydrosorbitol both effects have been observed depending on the reactant and the reaction conditions[38,39].

The assumption of a positive substitution effect in the reaction at 75°C was not really required for kinetic reasons, but was useful for a better description of the molecular weights.

According to the data of *Table 3*, the temperature has a considerable effect on the chain lengthening rate constant k_1 and only little influence on the rate of branching k_3. At this point it has to be emphasized that the fit is rather sensitive to changes in k_3; a slight increase in k_3 would cause a considerably stronger upturn of the calculated kinetic curve in *Figure 4*. As expected, k_3 increases with temperature. The change is much smaller than for k_1, but the result is that the branching is not influenced by the discussed substitution effect.

Molecular weight dependence and polydispersity. The results of molecular weight determination by light scattering and vapour pressure osmometry are shown in *Figure 6*. Because of the low molecular weight of the products at even rather high conversion ($\beta > 0.94$), M_w could be determined only for a few samples.

As may be noted, M_n increases only moderately up to 3000, whereas M_w increases strongly up to 30 000. Thus the polydispersity M_w/M_n is much higher than 2, as would be expected for a *linear* step-growth reaction. The pronounced increase of polydispersity is a strong indication for branching.

The full curves drawn in *Figure 6* represent theoretical curves which were calculated by cascade theory using the parameters given in *Table 3*. A reasonably good agreement is obtained for the run at high temperature. The agreement is much poorer for the low-temperature series. The curve shown in *Figure 6* represents a fit where a positive substitution effect was taken into account. This caused a shift of the gel point to higher molecular weight, but not sufficient for a satisfactory description of the experimental data. Of course a much stronger positive substitution effect combined with a decrease of the branching probability could be assumed. This gives a better fit of the M_w vs. β curve, but causes a deterioration in the kinetic fit.

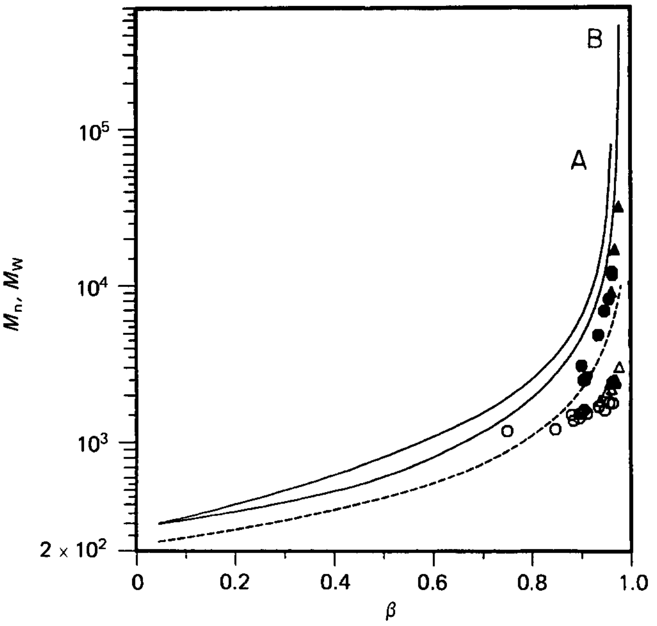

Figure 6 M_w and M_n as a function of epoxide conversion: (———) M_w calculated for A, $k_1 = 5.24 \times 10^{-4}$ kg eq^{-1} min^{-1}, $k_3 = 1.3 \times 10^{-5}$ kg eq^{-1} min^{-1}, $g = 1.5$; B, $k_1 = 4.9 \times 10^{-3}$ kg eq^{-1} min^{-1}, $k_3 = 1.5 \times 10^{-5}$ kg eq^{-1} min^{-1}, $g = 0.31$; (–––) M_n, no noticeable difference between A and B; (●) M_w of AE-1; (○) M_n of AE-1; (▲) M_w of AE-2; (△) M_n of AE-2

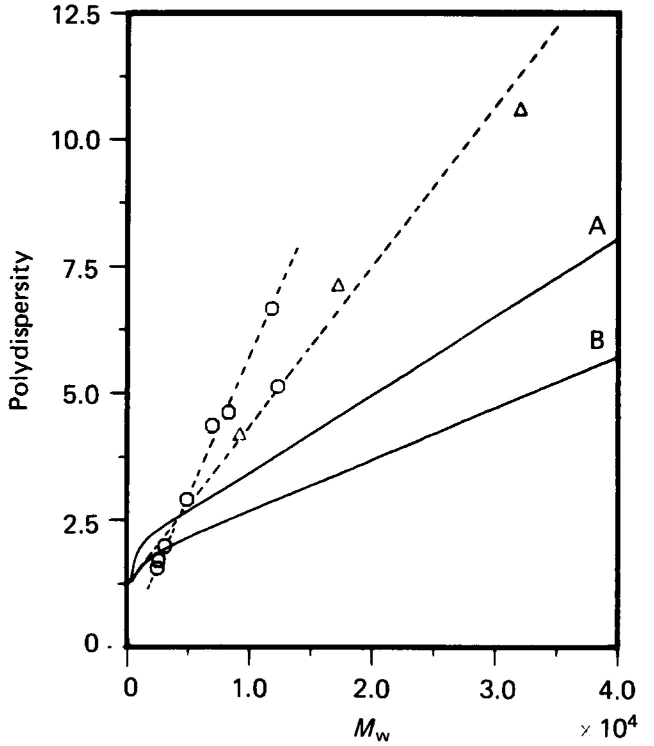

Figure 7 Polydispersity as a function of M_w: (○) AE-1, 75°C; (△) AE-2, 100°C; curve A calculated for AE-1 with $k_1 = 5.24 \times 10^{-4}$ kg eq^{-1} min^{-1}, $k_3 = 1.3 \times 10^{-5}$ kg eq^{-1} min^{-1}, $g = 1.5$; curve B calculated for AE-2 with $k_1 = 4.9 \times 10^{-3}$ kg eq^{-1} min^{-1}, $k_3 = 1.5 \times 10^{-5}$ kg eq^{-1} min^{-1}, $g = 0.31$

Also in the case of AE-2 (100°C) the agreement is not as satisfactory as it appears from *Figure 6*. This becomes evident when examining the polydispersity shown in *Figure 7*. Experimentally a much broader distribution is observed than predicted by theory. In other words, the actually found M_n is considerably smaller than predicted by the present theory.

At present we do not know the origin of this deviation, but two reasons appear to be conceivable. One results from the fact that all molecular weight measurements have been carried out in a region where apparently a diffusion control is noticeable. Secondly, cyclization may occur at rather low conversion, resulting in less reactive low molecular weight species. This second question could possibly be clarified by g.p.c.

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APPENDIX 1

Using a vector/matrix notation[9,20,27] the two molecular weight averages M_w and M_n are given by

$$M_w = \mathbf{m}\cdot\mathbf{M}^t_{02} + \langle\mathbf{N}(1)\rangle\cdot(\mathbf{1}-\mathbf{P})^{-1}\cdot\mathbf{M}^t_{03} \qquad (A.1)$$

$$M_n = (\mathbf{n}\cdot\mathbf{M}_0)/\{1-[0.5\cdot\mathbf{n}\cdot\langle\mathbf{N}(1)\rangle\cdot\mathbf{1}]\} \qquad (A.2)$$

Here **m** is a vector which contains as elements the mass fractions of the two components A and B and **n** is the corresponding vector of the mole fractions. $\mathbf{M}_0$ is a row vector and $\mathbf{M}^t_{02}$ and $\mathbf{M}^t_{03}$ are column vectors containing the molecular weights of the monomers:

$$\mathbf{M}^t_{02} = \begin{pmatrix} M_{0A} \\ M_{0B} \end{pmatrix} \qquad (A.3)$$

and

$$\mathbf{M}^t_{03} = \begin{pmatrix} M_{0A} \\ M_{0B} \\ M_{0B} \end{pmatrix} \qquad (A.4)$$

$$\mathbf{M}_0 = (M_{0A}, M_{0B}) \qquad (A.5)$$

Furthermore $\langle\mathbf{N}(1)\rangle$ and **P** are matrices which contain the extents of reaction:

$$\mathbf{N}(1) = \begin{array}{c c} & \begin{array}{ccc} \mathrm{A} & \mathrm{B} & \mathrm{Epoxy} \end{array} \\ \begin{array}{c} \mathrm{A} \\ \mathrm{B} \end{array} & \begin{pmatrix} 0 & 2\bar{\alpha} & 0 \\ 2\beta(1-p) & 2\beta p & 2\beta p \end{pmatrix} \end{array} \qquad (A.6)$$

$$\mathbf{P} = \begin{array}{c c} & \begin{array}{ccc} \mathrm{A} & \mathrm{B} & \mathrm{Epoxy} \end{array} \\ \begin{array}{c} \mathrm{A} \\ \mathrm{B} \\ \mathrm{Epoxy} \end{array} & \begin{pmatrix} 0 & \bar{\alpha}_1 & 0 \\ \beta(1-p) & p(1+\beta) & \beta \\ (1-p)(1+\beta) & p\beta & p(1+\beta) \end{pmatrix} \end{array} \qquad (A.7)$$

Both matrices have a topological meaning[27] which can be recognized in a rooted tree representation of branched molecules. Such a representation is obtained if one monomer unit of the molecule is chosen at random as the root of the tree. Since we have two different types of monomers, only two different kinds of roots have to be considered. They are schematically shown in *Figure 8a* where only the first generation is given in detail. The first row of the matrix $\langle\mathbf{N}(1)\rangle$ represents the link probabilities for the tree A and the second for tree B. Now, the element $N_{\mathrm{A-Epoxy}}$, for example, denotes the number of epoxy groups linked to a monomer A. $N_{\mathrm{B-Epoxy}}$ is the number of epoxy groups linked to a monomer B via an EP OH group. However, this reaction can only occur if in the root a B group has reacted too, because only then has an EP OH group been created. In *Figure 8* this fact is emphasized by the encircled B2.

The elements of matrix **P** have the meaning of transition probabilities (see *Figure 8b* for illustration). For instance, element $P_{\mathrm{OH-Epoxy}}$ denotes the probability of reaction of a unit in the nth generation, which is linked to the preceding generation via an OH group, with an epoxy group in the $(n+1)$th generation. The other elements have similar meanings.

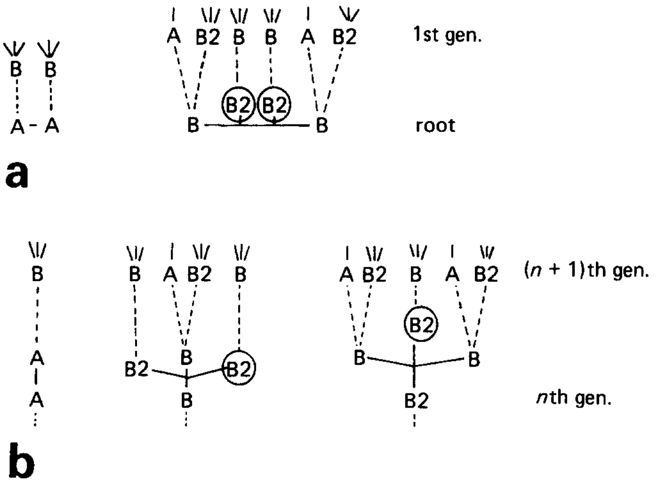

Figure 8 Rooted tree representation of the macromolecules: (a) details of the root for illustration $\langle\mathbf{N}(1)\rangle$ (i.e. population in the first generation); (b) tree structure in the nth generation for illustration of **P** (i.e. matrix of transition probabilities)

APPENDIX 2

For derivation of the equations (17) and (18) use is made of probability-generating functions (p.g.f.)[19]. The p.g.f. is generally defined as follows:

$$F(s) = \sum_{x=0}^{\infty} p_x s^x \qquad 0 \leqslant s \leqslant 1 \qquad (A.8)$$

In this equation s is a dummy variable, x indicates how many monomers have reacted to an x-mer and p_x is the corresponding probability in the whole distribution. The p.g.f. has two essential properties:

normalization condition

$$F(s=1) = \sum_{x=0}^{\infty} p_x = 1 \qquad (A.9)$$

mean value of x

$$\left.\frac{\mathrm{d}F(s)}{\mathrm{d}s}\right|_{s=1} = \left.\sum_{x=0}^{\infty} x p_x s^{x-1}\right|_{s=1} \qquad (A.10)$$

Equations (A.8) and (A.10) give a clear description how to calculate $\bar{\alpha}$ and $\bar{\alpha}_1$.

The non-normalized members of the p.g.f. for the zeroth generation $F_{0A}(s)$ are as follows:

(i)	no reaction	$(1-\alpha)^2$
(ii)	one functionality reacted	$2(1-\alpha)s$
(iii)	both functionalities reacted	$\alpha^2 g s^2$

Thus the non-normalized p.g.f. is:

$$\tilde{F}_{0A}(s) = (1-\alpha)^2 + 2(1-\alpha)\alpha s + \alpha^2 g s^2 \qquad (A.11)$$

The normalization factor follows from (A.9) and (A.11):

$$N_0 = (1-\alpha)^2 + 2(1-\alpha)\alpha + \alpha^2 g \qquad (A.12)$$

and hence the normalized p.g.f. is

$$F_{0A}(s) = [(1-\alpha+\alpha s)^2 - \alpha^2 s^2 (1-g)]/[1-\alpha^2(1-g)] \qquad (A.13)$$

Differentiation yields

$$F'_{0A}(1) = [2\alpha - 2\alpha^2(1-g)]/[1-\alpha^2(1-g)] \qquad (A.14)$$

On the other hand, the average number of units linked to root A is $2\bar{\alpha}$; thus we obtain equation (17):

$$\bar{\alpha} = [\alpha - \alpha^2(1-g)]/[1-\alpha^2(1-g)]$$

Similarly for the first generation we have:

$$F_{1A}(s) = (1-\alpha+\alpha g s)/N_1 \qquad (A.15)$$

where

$$N_1 = F_{1A}(1) = 1-\alpha(1-g) \qquad (A.16)$$

Hence we get equation (18):

$$F'_{1A}(1) = \alpha g/[1-\alpha(1-g)] = \bar{\alpha}_1$$

REFERENCES

1 Lee, H. and Neville, K. *Encly. Polym. Sci. Technol.* 1967, **6**, 209 and further references therein
2 Batzer, H., Lohse, F. and Schmid, R. *Angew. Makromol. Chem.* 1973, **29/30**, 349
3 Lee, H. and Neville, K. 'Handbook of Epoxy Resins', McGraw-Hill, London, 1967
4 Reinking, N., Barnabo, A. E. and Hale, W. F. *J. Appl. Polym. Sci.* 1963, **7**, 2135, 2145, 2153
5 Stenstrom, J. A. and Hale, W. F. *J. Polym. Sci.* 1965, **3**, 3843
6 Dušek, K., Ilavský, M. and Lunák, S. *J. Polym. Sci., Polym. Symp.* 1975, **53**, 29
7 Lunák, S. and Dušek, K. *J. Polym. Sci., Polym. Symp.* 1975, **53**, 45
8 Dušek, K., Pleštil, J., Ledniký, F. and Lunák, S. *Polymer* 1978, **19**, 393
9 Burchard, W., Bantle, S. and Zahir, S. A. *Makromol. Chem.* 1981, **182**, 145
10 Bantle, S. Ph.D. Thesis, Freiburg, 1982
11 Bantle, S. and Zahir, S. A. *ACS Symp. Ser.* 1983, **221**, 245
12 Woelk, H.-U. *Starch/Stärke* 1981, **33**, 397
13 Montgomery, R. and Wiggins, L. F. *J. Chem. Soc.* 1947, 433
14 Otey, F. H. and Mehltretter, C. L. *J. Org. Chem.* 1961, **26**, 1673
15 Klosterman, H. and Smith, F. *J. Am. Chem. Soc.* 1952, **74**, 5336
16 Kamke, E. 'Differentialgleichungen, Lösungsmethoden und Lösungen I', B. G. Teubner, Stuttgart, 1977
17 Burchard, W. *Macromolecules* 1972, **5**, 604
18 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953
19 Gordon, M. *Proc. R. Soc.* 1962, **A268**, 240
20 Gordon, M., Malcolm, G. M. and Butler, D. S. *Proc. R. Soc.* 1966, **A295**, 29
21 Gordon, M. and Scantlebury, G. R. *J. Chem. Soc. B* 1967, 1
22 Gordon, M. and Scantlebury, G. R. *Trans. Faraday Soc.* 1964, **60**, 604
23 Gordon, M. and Scantlebury, G. R. *J. Polym. Sci. C* 1968, **16**, 3933
24 Dobson, G. R. and Gordon, M. *J. Chem. Phys.* 1964, **41**, 2389
25 Dobson, G. R. and Gordon, M. *J. Chem. Phys.* 1965, **43**, 705
26 Dušek, K. and Prins, W. *Adv. Polym. Sci.* 1969, **6**, 1
27 Burchard, W. *Adv. Polym. Sci.* 1983, **48**, 1
28 Bantle, S., Schmidt, M. and Burchard, W. *Macromolecules* 1982, **15**, 1604
29 Dandliker, W. B. and Kraut, J. *J. Am. Chem. Soc.* 1956, **78**, 2380
30 Smoluchowski, v. M. *Wien Ber.* 1915, **124**, 263
31 Smoluchowski, v. M. *Phys. Z.* 1916, **17**, 557, 585
32 Hendriks, E. M., Ernst, M. H. and Ziff, R. M. *J. Stat. Phys.* 1983, **31**, 519
33 Cohen, R. J. and Benedek, G. B. *J. Phys. Chem.* 1982, **86**, 3696
34 Spouge, J. L. *J. Phys. A: Math. Gen.* 1983, **16**, 767, 3127
35 Spouge, J. L. *Macromolecules* 1983, **16**, 121, 831
36 Spouge, J. L. *Proc. R. Soc.* 1983, **A387**, 351
37 Ziff, R. M., Ernst, M. H. and Hendriks, E. M. *J. Phys. A: Math. Gen.* 1983, **16**, 2293
38 Goodwin, J. C., Hodge, J. E. and Weisleder, D. *Carbohydr. Res.* 1980, **79**, 133
39 Buck, K. W., Foster, A. B., Duxbury, J. N., Perry, A. R. and Webber, J. N. *Carbohydr. Res.* 1966, **2**, 122