Epoxy resins based upon 1,4-anhydroerythritol: 2. Conformational properties

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Translational diffusion coefficients and intrinsic viscosity have been measured for selected samples of epoxy resins (polyhydroxyethers) obtained from reaction of the two comonomers, 1,4-anhydroerythritol and diglycidyl ether, of bisphenol A (DGEBA). Branching was found to exert no significant influence on D_z, but to have a strong influence on $[\eta]$. These findings are shown to be in agreement with theoretical predictions.

(Keywords: epoxy resins; conformation; branching)

INTRODUCTION

In paper 1[1] we reported the kinetics of epoxy resin formation and the determination of branching density for two series of samples prepared by reaction of 1,4-anhydroerythritol with the diglycidyl ether of bisphenol A (DGEBA). Determination of the branching density was possible with the aid of the cascade branching theory together with kinetic data, taking into account a substitution effect.

The present paper deals with the conformational properties of these resins and the effect which the branching density has on: (i) the mean square radius of gyration $\langle S^2 \rangle_z$; (ii) the angular dependence of the scattered light R_θ; (iii) the translational diffusion coefficient D_z; and (iv) the intrinsic viscosity $[\eta]$.

EXPERIMENTAL

Intrinsic viscosity

The viscosity of the samples was measured in dimethylformamide (DMF) at 20°C using an Oswald viscometer. The capillaries were chosen such that no kinetic energy corrections were needed.

Light scattering

Static and dynamic light scattering were measured simultaneously on an LS instrument as described by Bantle *et al.*[2]

The blue line ($\lambda_0 = 488$ nm) of an argon ion laser (Ar 165, Spectra Physics) was used. The temperature was maintained at 20°C.

The samples were dissolved in DMF and clarified by ultracentrifugation in a swinging bucket rotor applying the flotation technique[3]. Because of the low molecular weight of the resins, no angular dependence was detectable. Therefore the measurements at 60°, 90° and 120° were averaged.

The samples showed a faint fluorescence emission at longer wavelengths. To avoid errors caused by this weak additional intensity an interference filter with its maximum transmission at 491 nm was mounted in front of the photomultiplier.

The translational diffusion coefficient was determined from the first cumulant[4-6] of the time correlation function of the scattered light. Details of the technique have been described, for instance, by Burchard[7].

A single-bit Malvern 7300 correlator with 124 channels was used. The sample times chosen ranged from 0.5 to 0.8 μs.

To determine the first cumulant a three-cumulant fit of the time correlation function was applied. The observed relatively high values of the second and third cumulant indicated a large polydispersity of the samples.

The data from these measurements are collected in *Tables 1* and *2*.

RESULTS AND DISCUSSION

The results of the measurements of the translational diffusion coefficient (D_z) and the intrinsic viscosity ($[\eta]$) are plotted in *Figures 1* and *2* as a function of M_w. For

Table 1 DGEBA/AE cured at 75°C

M_w (g mol^{-1})	$D_z \times 10^{-6}$ (cm^2 s^{-1})	$[\eta]$ (cm^3 g^{-1})
3100	1.6	8.7
2500	1.3	9.9
2600	1.2	8.7
4900	0.96	10.0
6950	0.80	–
8260	0.75	11.1
11800	0.67	11.9
12300	0.58	12.2
14200	0.55	–

Table 2 DGEBA/AE cured at 100°C

M_w (g mol^{-1})	$D_z \times 10^{-6}$ (cm^2 s^{-1})	$[\eta]$ (cm^3 g^{-1})
9200	0.60	–
17200	0.52	11.6
32000	0.33	13.2

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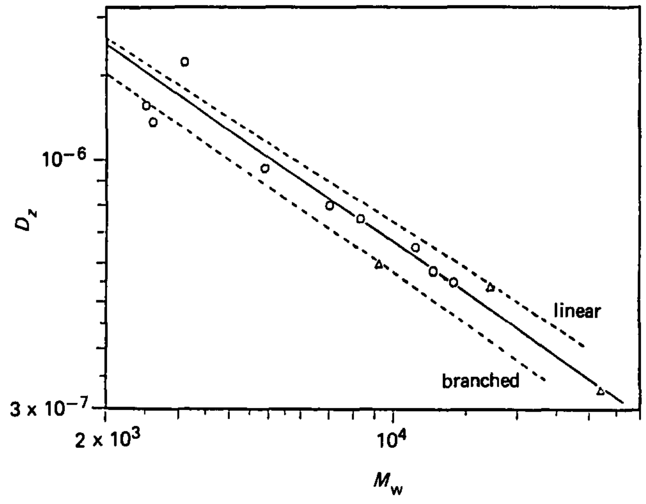

Figure 1 Molecular weight dependence of the diffusion coefficient D_z for the DGEBA-AE resins (○) cured at 75°C and (△) cured at 100°C measured in DMF at 20°C. The broken lines labelled linear and branched correspond to measurements from DGEBA-bisphenol A resins[8]. D_z in units of $cm^2 s^{-1}$ and M_w in units of $g mol^{-1}$

comparison, results obtained by Bantle[8] for DGEBA-bisphenol A resins are shown as broken lines. Bantle prepared one series of highly branched samples and another of essentially linear products. Our results fall well within these margins after correcting D_z for the solvent viscosity η_0. Such correction is necessary since Bantle carried out his measurements in diethyleneglycol-dimethylether (Diglyme); according to Stokes–Einstein, D_z is given by:

$$D_z = kT/6\pi\eta_0 R_h \tag{1}$$

and thus the data of Bantle were corrected by a factor $\eta_{Diglyme}/\eta_{DMF}$. Equation (1) holds exactly for hard spheres and may for the present resins be taken as a definition of a hydrodynamically equivalent sphere radius R_h.

Effect of branching on D_z *and* $[\eta]$

Branching density apparently has little effect on D_z, whereas a pronounced effect is observed for $[\eta]$. The absolute values of $[\eta]$ are decreased by branching and the exponent in the Mark–Houwink equation is no longer constant but decreases from $\nu_\eta = 0.5$ to 0.25 with increasing molecular weight. The reason for this behaviour of the intrinsic viscosity can be explained at least qualitatively. As shown by Flory and coworkers[9] and by Marriman and Hermans[10] the intrinsic viscosity of polydisperse systems is given by:

$$[\eta] = \phi[\langle S^2\rangle^{3/2}]_n/M_n \sim v_{hn}/M_n \tag{2}$$

where the indices n denote the number of averages. This decrease of $[\eta]$ results from an increase in the segment density due to branching, i.e. at the same hydrodynamic volume v_{hn} the molecular weight M_n of the particle increases. On the other hand, the low exponent in the Mark–Houwink equation is a result of polydispersity. According to equation (2) $[\eta]$ is a ratio of two number-averages and can be expected to be approximately proportional to the number-average molecular weight. However, in LS experiments the weight-average molecular weight is determined and since M_w/M_n increases markedly with conversion[11] the $[\eta]$–M_w curve must flatten out.

The weak dependence of the D_z–M_w relationship on branching is not easily explained. An attempt at a detailed explanation is given in ref. 10. Recalling the definitions of D_z and M_w:

$$D_z = \sum_i D_i w_i M_i / \sum_i w_i M_i \tag{3a}$$

and

$$M_w = \sum_i w_i M_i \tag{3b}$$

one notices that both quantities are defined in terms of the weight fraction distribution w_i. Intuitively, an essentially universal relationship between M_w and D_z may be expected since the extent of branching is, to a large extent, included in the weight fraction[12,13].

Comparison with theory

To check this conjecture we carried out model calculations on the basis of the cascade branching theory[14] for: (i) a linear chain; (ii) a highly branched product; and (iii) the parameter sets, which had been determined from kinetic measurements for the epoxy resins discussed in part 1[1]. The equations for D_z and details of the calculations are given in the Appendix. *Figure 3* confirms the low dependence on branching density.

The only adjustable parameter in this theory is the effective 'bond length'. A first estimation could be made by inspection of the chemical structure. Because of the rather inflexible elements in DGEBA and 1,4-anhydroerythritol we defined the following three rigid segments l_1, l_2 and l_3 (see *Figure 4*) as virtual bonds, assuming a *trans* conformation. These segments are supposed to be freely jointed. Then, the two effective bond lengths occurring in the equations for $\langle S^2\rangle_z$ and R_h are, in this first approximation:

$$b_1^0 = (l_1^2 + l_3^2)^{0.5} \tag{4a}$$

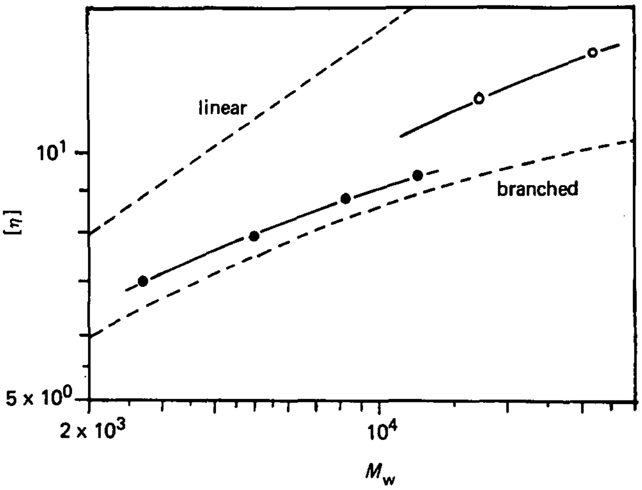

Figure 2 Molecular weight dependence of the intrinsic viscosity for some of the DBEBA-AE resins (●) cured at 75°C (○), cured at 100°C. See *Figure 1* for meaning of broken lines. $[\eta]$ in units of $ml g^{-1}$ and M_w in units of $g mol^{-1}$

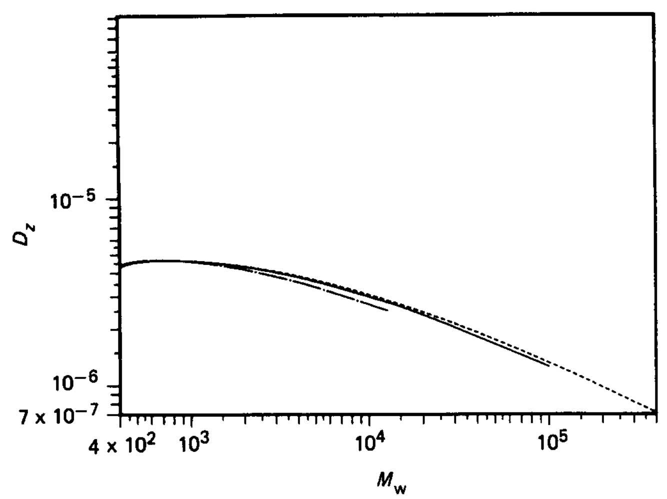

Figure 3 Calculated molecular weight dependence of the translational diffusion coefficient D_z for : -----, a linear resin; ———, a slightly branched resin; and —·—·—, a highly branched resin

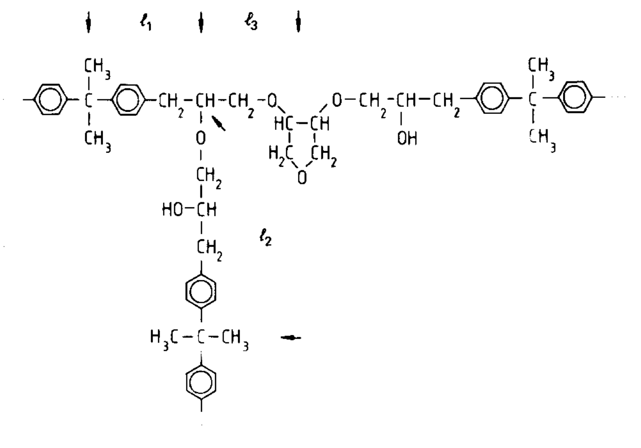

Figure 4 Chemical structure of a branched resin unit of DGEBA–AE. l_1, l_2, and l_3 indicate the three rigid segment lengths used in the calculation

and

$$b_2^0 = (l_1^2 + l_2^2)^{0.5} \quad (4b)$$

The first bond, $b_1^0 = 0.81$ nm, refers to chain lengthening and the second one, $b_2^0 = 1.25$ nm, to the branching step[1,5].

With this rough estimate the calculation of the diffusion coefficient gave much larger values than found experimentally. The effective bond lengths b_1 and b_2 were then increased, both by the same factor, until good agreement with the experimental data was achieved. By this procedure one obtains a factor $C = b^2/b_0^2 \simeq 10$, and thus:

$$b_1^2 = 6.56\,\text{nm}^2 \quad \text{and} \quad b_2^2 = 15.63\,\text{nm}^2 \quad (5)$$

These higher values indicate that the virtual bonds are not freely jointed and that the rotation is hindered to some extent.

A deeper insight into the flexibility will certainly be possible by model calculations on the basis of the rotational isomeric state model of Flory[15] which has not yet been carried out. We should also mention that all these model calculations are strictly valid only for unperturbed chains in the macromolecule. In marginal and good solvents the molecules swell, and the virtual bonds, estimated by these types of model calculations, contain this swelling factor. Furthermore, such swelling will perturb the Gaussian statistics of the subchains, and the applied techniques can give only an approximate description of the local conformational conditions.

Other static properties of the resins

Further quantities of interest are the radius of gyration $\langle S^2 \rangle_z$, the ρ parameter, which compares the geometric radius R_g $(= \langle S^2 \rangle_z^{1/2})$ with the hydrodynamic radius R_h [equation (1)], and the angular dependence of scattered light. Because of the small size of the resin molecules these three quantities could not be measured by means of light scattering. An angular dependence can be determined, however, by small-angle neutron scattering (SANS) and has been performed by Bantle *et al.*[16] with the DGEBA–bisphenol A resins. *Figure 5* shows the particle scattering factor of a sample with $M_w = 3050$ in a Kratky plot. For this reason the quantities mentioned for the present resins have been calculated (for details see Appendix) and the results are shown in *Figures 6* and *7*.

The mean square radius of gyration $\langle S^2 \rangle_z^{1/2}$ increases with the molecular weight M_w and approaches a constant slope of $2\nu_s = 1$ for both linear and highly branched resins. This asymptotic exponent agrees satisfactorily with the asymptotic exponent $\nu_D = 0.5$ for the D_z–M_w relationship. Branching has little influence on the $\langle S^2 \rangle_z$–M_w and D_z–M_w relationships and confirms the conjecture expressed above. However, it is noteworthy that in both cases the power laws are not fulfilled at lower M_w. The deviation in the $\langle S^2 \rangle_z$ dependence at low M_w is a consequence of neglecting the dimensions of the monomers in these calculations.

This mean square radius of gyration $\langle S^2 \rangle_0$ can be calculated from the estimation of the bond lengths assuming a cylindrical shape for the repeating unit. The radius of gyration of a cylinder is given by[17]:

$$\langle S^2 \rangle_0 = 1/12 l^2 + 1/2 r^2 \quad (6)$$

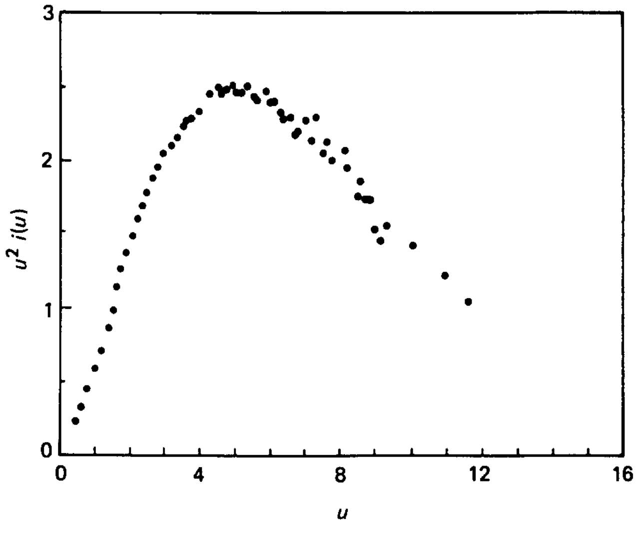

Figure 5 Kratky plot of the particles scattered from a highly branched DGEBA–bisphenol A resin of $M_w = 3050\,\text{g mol}^{-1}$. Measurements were performed by SANS. $i(u)$: scattering intensity (not normalized)

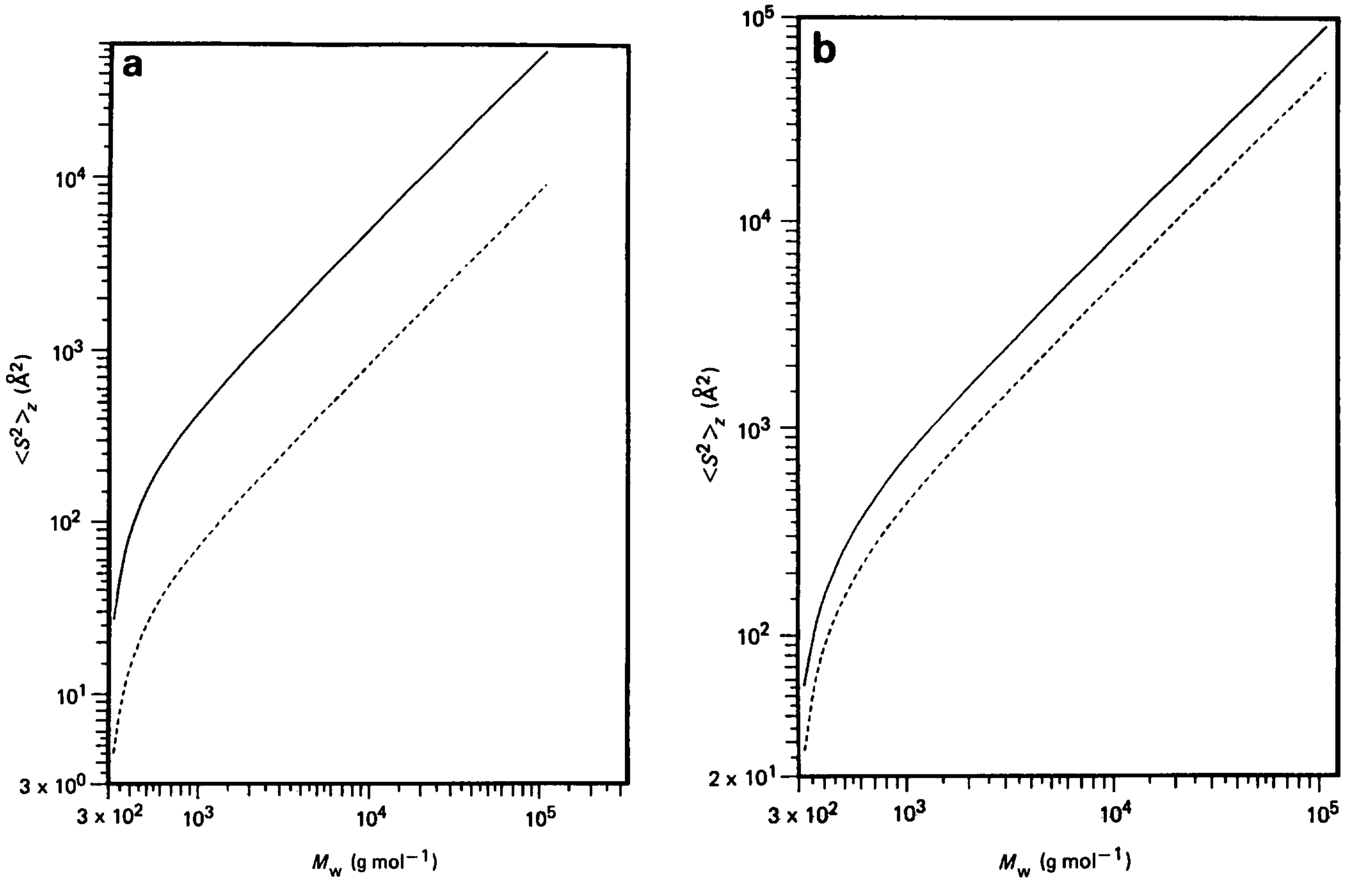

Figure 6 (a) Calculated molecular weight dependence of the mean square radius of gyration for the same system as in *Figure 8*. – – –, Calculated with values of $b_1^0 = 0.81$ nm and $b_2^0 = 1.25$ nm; ———, calculated with values of $b_1 = 2.56$ nm and $b_2 = 3.95$ nm. (b) Same calculation as in (a) but taking into account the finite radius of gyration of the monomer unit

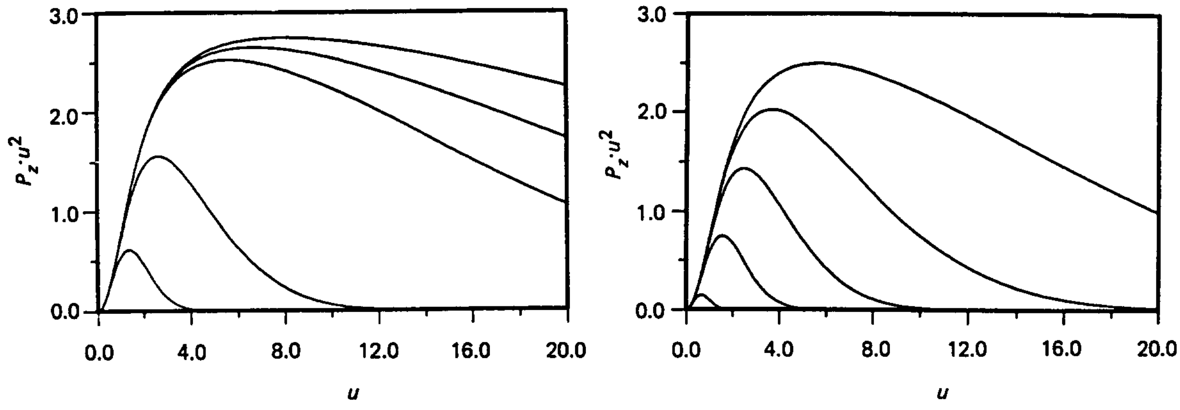

Figure 7 Calculated particle scattering factor for linear (left) and branched (right) DGEBA–AE resins with molecular weights of, from bottom to top, 300, 1200, 5000, 20000 and 100000 g mol^{-1}. $u = \langle S^2 \rangle_z^{1/2} \cdot q$ with $q = 4\pi/\lambda \sin(\theta/2)$

where the length of the cylinder is $l = 2l_1^0 = 1.35$ nm, $l = 2l_2^0 = 0.9$ nm and r is the radius of the cross-section for which a value of $r = 0.15$ nm was chosen. With these data we obtain an average for both units of $\langle S_0^2 \rangle = 12.1$ nm^2. The total mean square radius of gyration of the macromolecule is then given by:

$$\langle S^2 \rangle_{z\text{total}} = \langle S^2 \rangle_z + \langle S^2 \rangle_0$$

After this correction the straight line is extended down to almost three times the monomeric weight.

Similar corrections have to be carried out for D_z. In the Kirkwood–Riseman theory[18,19] the translational diffusion coefficient is expressed as:

$$D_{z\text{total}} = kT/\zeta N_w + kT/6\pi\eta_0 R_h \qquad (7)$$

and this can be rewritten as:

$$D_{z\text{total}} = D_0/N_w + D_z \qquad (8)$$

where $N_w = M_w/M_0$ is the weight-average degree of polymerization and D_z is the translational diffusion coefficient calculated by relationship (A2) of the

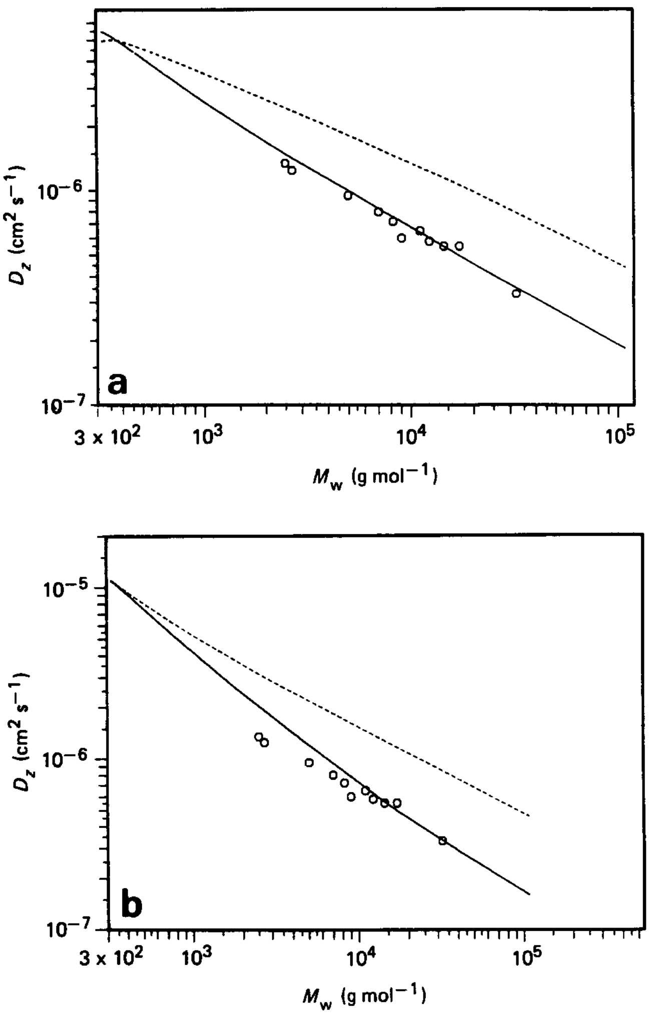

Figure 8 (a) Calculated molecular weight dependence of the translational diffusion coefficient D_z. ---, Calculated with values of $b_1^0=0.81$ nm and $b_2^0=1.25$ nm; ——, calculated with values of $b_1=2.56$ nm and $b_2=3.95$ nm [see equations (4) and (5)]; ○, measurements of DEGEBA–AE resins. (b) Same calculation as in (a) but taking into account the free draining term [see equation (7)]

Appendix. $D_0=kT/\zeta$ is the diffusion coefficient of the monomer which we have not been able to measure and ζ is the frictional coefficient of the monomer. As an approximation we took the value of DGEBA/BA monomers measured previously by Bantle[16]. Since the BA unit is bigger than the AE unit, D_0 for the present resins is, at most, underestimated. With this correction the curves in *Figure 8b* were obtained while without this correction the curves of *Figure 8a* are formed. It still shows a slight curvature and a variable exponent ν_D.

For the calculation of the particle scattering factors it is essential, because of the low molecular weights, to take into account the mean square radius of gyration of the monomeric units and the corresponding particle scattering factor of these units. Without the dimensions of the monomeric units the Kratky plot would show a strong upturn proportional to u^2 $(=\langle S^2\rangle_z q^2$, where $q=(4\pi/\lambda)\sin\theta/2)$. In that u-region $P_z(q)$ has decreased to a constant value; thus by multiplying it by u^2 the above-mentioned u^2-dependence of the Kratky plot results (*Figure 7*). The observed maximum results from interferences caused by the dimensions of the monomeric unit. The influence of the monomeric units gradually disappears with increasing molecular weight. Comparison of the calculated curves with one SANS measurement from a DGEBA–bisphenol A sample demonstrates at least a qualitative agreement.

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APPENDIX

The equations required for the calculation of $\langle S^2\rangle_z$, D_z and the angular dependence of scattered light have a similar structure to that of the weight-average molecular weight, M_w, and the same vectors and matrices occur for the bound units in the first shell and the transition probabilities. The detailed equations were given in paper 1[1] and are not repeated here.

As shown in previous papers, the z-average of the mean square radius of gyration $\langle S^2\rangle_z$ and of the translational diffusion coefficient D_z can for unperturbed branched chains be derived from the particle scattering factor. The relationships are given by equations (A1) and (A2):

$$\langle S^2\rangle_z = -3(\mathrm{d}P_z(q)/\mathrm{d}q^2)|_{q^2=0} \tag{A1}$$

$$D_z = kT/3\pi^2\eta_0 \int_0^\infty P_z(q^2)\mathrm{d}q \tag{A2}$$

Using the matrix/vector notation[11] as in the previous paper, the cascade theory leads to the following equation:

$$M_w P_z(q) = \mathbf{m}^t\mathbf{M}_0 + \mathbf{m}^t(\langle\mathbf{N}(1)\rangle\boldsymbol{\phi}(\mathbf{1}-\mathbf{P}\boldsymbol{\phi})^{-1}\mathbf{M}_0 \tag{A3}$$

where $\langle N(1)\rangle = (N_{AE}(1),\ N_{DGEBA}(1))$ represents the number of units bound to an AE or DGEBA unit respectively, **P** denotes the matrix of transition probabilities, defined in ref. 1 and

$$\boldsymbol{\phi} = \begin{pmatrix} \phi_1 & 0 & 0 \\ 0 & \phi_2 & 0 \\ 0 & 0 & \phi_3 \end{pmatrix} \tag{A4}$$

with $\phi_i = \exp(-b_i^2 q^2/6)$. $(\mathbf{M}_0)^t$ is a row vector which contains as components the molecular weights of the subunits, i.e. in the present case $(\mathbf{M}_0) = (M_{0AE},\ M_{0DGEBA},\ M_{0DGEBA})$ and $\mathbf{m}^t$ is the row vector of the mole fractions of the different components. For $q=0$ all factors ϕ_1, ϕ_2, ϕ_3 equal 1 and the particle scattering factor $P_z(q)_{q=0} = 1$. Thus the equation yields the molecular weight M_w and the formula reduces to equation (A1) of paper 1[1].

For the numerical calculation certain values have to be assigned to the bond length. The values are given in the main part. With these data the particle scattering factor can be calculated for various q-values. The translational diffusion coefficient can now be calculated by numerical integration.

For the mean square radius of gyration, on the other hand, an analytical equation can be derived by applying equation (A1) to equation (A3) and leads to the following equation:

$$\langle S^2\rangle_z = b^2/2\langle \mathbf{N}(1)\rangle(\mathbf{1}-\mathbf{P})^{-2}\mathbf{1}^t \tag{A5}$$

The actual calculation was performed by choosing values for the extent of reaction α from which all other quantities can be calculated. The relationship between β (extent of reaction of epoxide), $\bar{\alpha}$, $\bar{\alpha}_1$ and p (extent of branching) are given in paper 1.