Small-angle neutron scattering from branched epoxide resins*

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Small-angle neutron scattering experiments in the range of q^2 from 0.01 to 25 nm^{-2} have been carried out on branched epoxide resins based on bisphenol-A at the Institute Laue–Langevin (I.L.L) in Grenoble ($q=(4\pi/\lambda)\sin(\theta/2)$). Measurements were made with six samples in the range of M_w from 1500 to 19000 and four concentrations between 1.3 and 10% (w/w) in deuterated diglyme. The results are as follows: (i) The mean square radius of gyration follows a relationship $\langle S^2 \rangle_z=4.69\times10^{-4}M_w^{1.20}$ (nm^2). (ii) In all cases fairly large second virial coefficients A_2 are obtained which, however, decrease strongly with molecular weight. Above M_w=2500, the virial coefficient follows the relationship $A_2=1.6M_w^{-0.85}$ (mol cm^3 g^{-2}). (ii) The reciprocal particle scattering factor as a function of q^2 exhibits only a slight upturn and otherwise shows the behaviour of a randomly branched polycondensate. The slight upturn is discussed as being caused by the finite volume of the monomeric unit. Possible reasons for the high exponent in the $\langle S^2 \rangle_z$ *versus* M_w dependence are briefly discussed.

Keywords Branching; epoxide resins; bisphenol-A; small-angle neutron scattering; second virial coefficient

INTRODUCTION

Structural properties of large macromolecules in solution are mostly determined by means of static light scattering (LS). This method allows the determination of the weight average molecular weight M_w and the z-average of the mean square radius of gyration $\langle S^2 \rangle_z$, and in rare cases also the shape of the molecules from the angular dependence of the scattered intensity. Full use of the great power of the LS technique can be made if the molecules have dimensions larger than at least 1/20 of the wavelength λ of the light in the medium. In practice this means molecules larger than some hundred thousand in M_w.

Epoxide resins[2] based on bisphenol-A and the diglycidyl ether of bisphenol-A are valuable precursor molecules, which in a subsequent curing reaction lead to hard and temperature-stable networks. Since the glass transition temperature increases strongly with molecular weight of the resin[2], the applicability of the products is restricted chiefly to a range of molecular weights from about 1000 to some 10000. For a determination of the structure factor of such small molecules, the much shorter wavelengths of X-rays ($\lambda=0.154$ nm) or of a cold neutron source ($\lambda=0.4$ to 1.2 nm) have to be applied. Contrast calculations[3] and preliminary X-ray small-angle scattering experiments showed that the scattering in excess of the solvent is much too low for X-rays in diglyme, the solvent that was used in all our experiments on the epoxide resins. An estimation of the coherent neutron scattering from the polymer in deuterated diglyme, on the other hand, gave a very satisfactory large contrast.

Neutron scattering from epoxide resins appears of interest also from another point of view. Most small-angle neutron scattering (SANS) experiments so far have been performed either with *linear* molecules in dilute solution or with labelled linear molecules in high concentration or in the bulk[4-6], where, due to entanglements, an apparent network[7] exists. Little is known of the conformation of randomly *branched* molecules in solution[8,9], and the epoxide resins of the present study are extensively branched products[1]. The purpose of the present scattering study was the determination of the structure factor of these branched epoxide resins. In a later stage, these should be compared with the structure factor of the corresponding linear chains and with the scattering behaviour, which can be calculated by means of the cascade branching theory[10].

EXPERIMENTAL

Solvent

Deuterated diglyme was used, without further purifications; 98% D; from Merck, Sharp and Dohme, Canada.

Polymers

A series of epoxide resins in a range of M_w from 1500 to 19000 were prepared by thermal addition polymerization of bisphenol-A and the diglycidyl ether of bishpenol-A (molar ratio 1:1.25) in the melt at a temperature of 180°C. Benzyl triethyl ammonium chloride was used as catalyst. The extent of reaction of these products was determined by a spectroscopic method[11,12] (phenolic OH) and by potentiometric titration[13] (epoxide groups). Furthermore, M_w and M_n were measured by means of static LS, and osmometry, respectively. Details will be given elsewhere.

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* Dedicated to Professor Dr Dr hc Otto Kratky on the occasion of his eithtieth birthday

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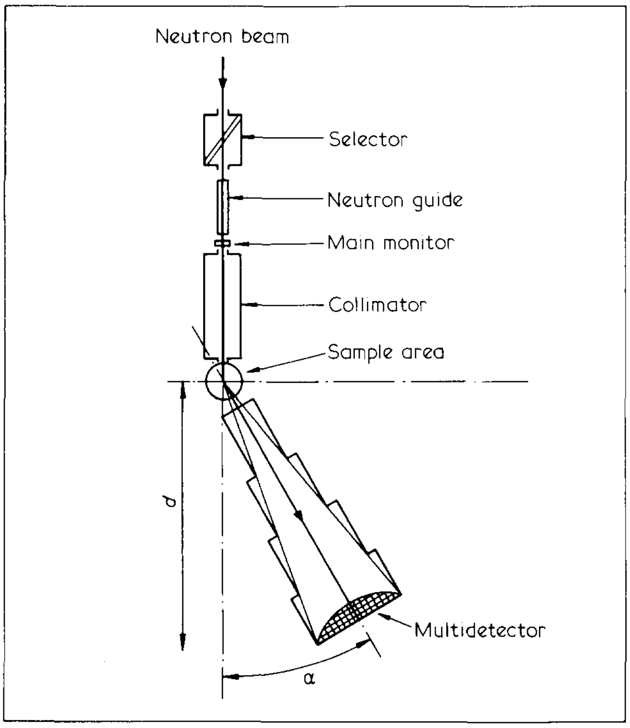


Figure 1 Sketch of the D17 arrangement at the I.L.L., taken from 'Neutron Beam Facilities Available for Users': configuration (a) sample–detector distance d = 2.83 m, angle α = 6°; (b) d = 1.40 m, α = 12°; (c) d = 1.40 m, α = 20°

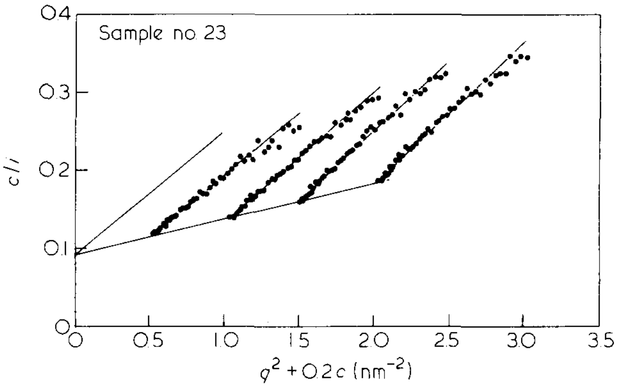


Figure 2 A typical Zimm plot of an epoxide resin (no. 23) showing c/i against $q^2 + kc$

Small-angle neutron scattering

The measurements were performed at the Institut Max von Laue–Paul Langevin (I.L.L.), Grenoble, France, with the D17 (samples no. 21, 23, 25 and 27) and with D11 instruments (samples no. 26, 27 and 28). The scattering intensity was detected by a 64 × 64 cell matrix assembly[14]. Radial averaging and data treatment were performed at the I.L.L., as usual[15].

RESULTS

Mean square radius of gyration

The scattering behaviour at low values of the scattering vector q ($q = (4\pi/\lambda)\sin(\theta/2)$) is governed solely by the mean square radius of gyration[10] ($\langle S^2\rangle_z$). We thus performed our first series of experiments in the q^2 range from 1.0×10^{-2} up to 1.35 nm^{-2}. The arrangement for this experiment is sketched in *Figure 1* using configuration (a). A wavelength of $\lambda = 1.2$ nm was used. Measurements were made with four samples at four concentrations for each sample between 2.5 and 10% (w/w). A typical Zimm plot is shown in *Figure 2*. Straight lines were obtained in the initial part, from which we determined an apparent $\langle S^2\rangle_z^{\mathrm{app}}$, according to the equation

$$\frac{c}{i(q)} = \frac{c}{i(0)}\left(1 + \tfrac{1}{3}\langle S^2\rangle_z^{\mathrm{app}} q^2\right)_{\mathrm{finite}\ c} \qquad (1)$$

for each concentration. These apparent $\langle S^2\rangle_z^{\mathrm{app}}$ depend strongly on the concentration c and have to be extrapolated to zero concentration. A plot of $\langle S^2\rangle_z^{\mathrm{app}}$ against c gave strongly bent curves, and we therefore applied the reciprocal of $\langle S^2\rangle_z^{\mathrm{app}}$ against c. In all cases straight lines are now found (*Figure 3*). The values of $\langle S^2\rangle_z$ agree well with those obtained from the limiting angular dependence in the Zimm plot.

The data of the mean square radii of gyration are collected in *Table 1* together with the molecular weights M_w and M_n and the second virial coefficients A_2. The second virial coefficient was determined from the equation

$$\frac{c}{i(0)} = \frac{1}{K}\left(\frac{1}{M_w} + 2A_2 c\right) \qquad (2)$$

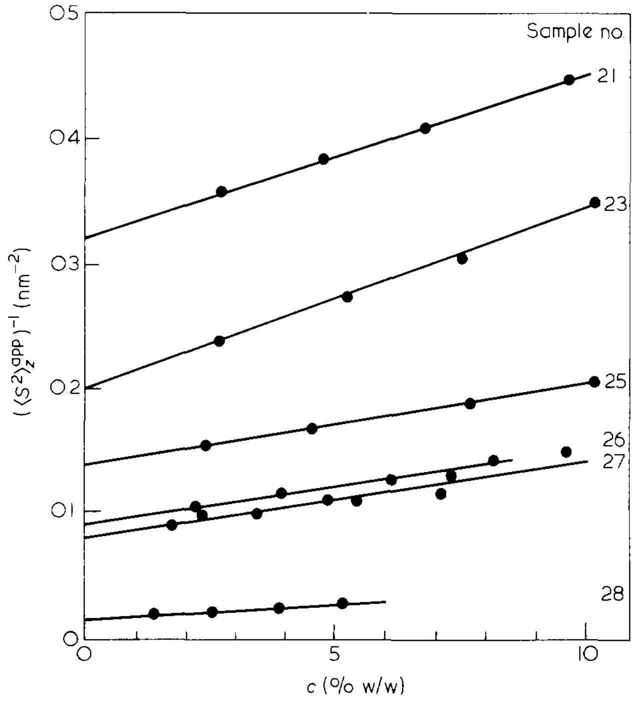


Figure 3 $(\langle S^2\rangle_z^{\mathrm{app}})^{-1}$ as a function of concentration c

Table 1 Number average and weight average molecular weights, mean square radius of gyration $\langle S^2\rangle_z$ and second virial coefficient A_2 for six epoxide resins

Sample	M_n	M_w	M_w/M_n	$\langle S^2\rangle_z$ (nm^2)	$A_2 \times 10^3$ (mol cm^3 g^{-2})
21	647	1540	2.4	3.10	3.5 ± 0.2
23	682	2330	3.4	5.06	2.1
25	790	3050	3.9	7.20	1.9
26	874	4400	5.0	10.99	1.3
27	890	4900	5.5	12.50	1.2
28	911	19000	20.9	65.80	0.3

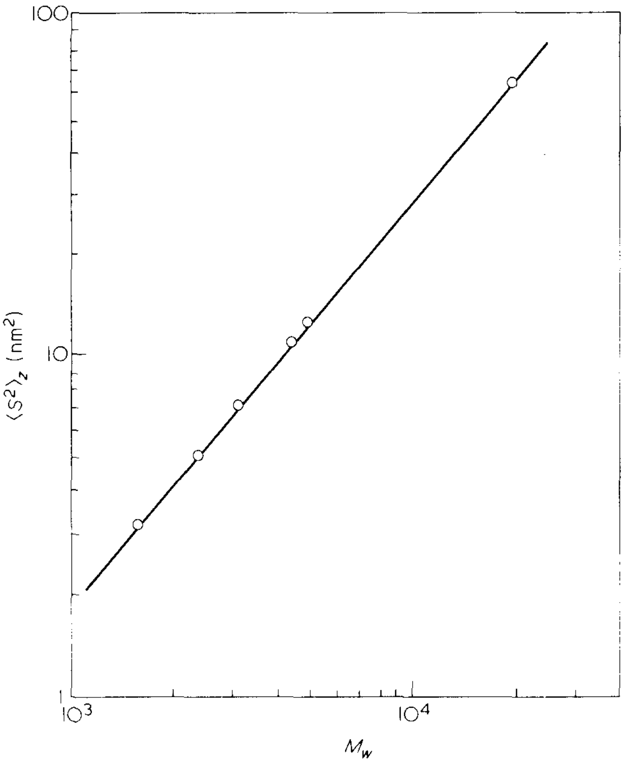


Figure 4 $\langle S^2\rangle_z$ as a function of M_w

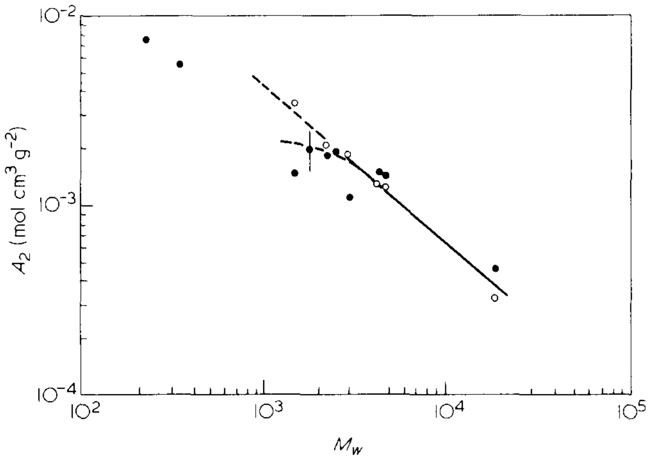


Figure 5 Second virial coefficient A_2 as a function of M_w obtained by SANS (○) and by LS (●). The two lowest molecular weights are the two co-monomers

where K is an apparatus constant that also contains the scattering contrast and

$$\left(\frac{c}{i(0)}\right)_{c=0} = \frac{1}{KM_w} \tag{3}$$

Therefore,

$$A_2 = \text{slope}/(2M_w \times \text{intercept}) \tag{4}$$

where M_w was obtained from light scattering.

Figures 4 and *5* show the molecular weight dependence of $\langle S^2\rangle_z$ and of A_2. The points of $\langle S^2\rangle_z$ fall on a straight line in the log–log plot and can be represented by the equation

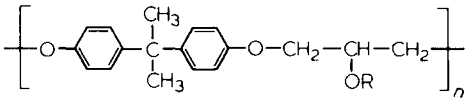
$$\langle S^2\rangle_z = 4.69\times10^{-4} M_w^{1.20}\,(\text{nm}^2) \tag{5}$$

The data for A_2 obtained by neutron scattering also appear to form a straight line in the log–log plot of A_2 against M_w. Good agreement is found with results from LS for $M_w > 2000$, and a discrepancy occurs only with the lowest molecular weight where LS gave a much lower A_2 value. Although the accuracy of A_2 determination is low at these small molecular weights, we have indications that the low A_2 value will be more correct, since it agrees better with the A_2 values of linear epoxides obtained by LS. For $M_w > 2500$ the A_2 curve can be described by the equation

$$A_2 = 1.6 M_w^{-0.85} \tag{6}$$

Particle scattering factor and asymptotic behaviour

The mean square radius of gyration is only a measure of the average molecular dimensions. To obtain information on the shape of the molecules, the scattering behaviour at much larger values of the scattering vector has to be studied[9,10]. Therefore, the detector was positioned now at 1.4 m and was swung out to 12° and 20°, respectively, as demonstrated by the sketches of *Figure 1* using configurations (b) and (c). The wavelength was changed to 0.8 and 0.7 nm, respectively. In this arrangement q^2 values from 0.15 to 12 nm^{-2} and from 2.3 to 25 nm^{-2} were covered. At such large q^2 values the coherent scattering intensity had dropped to very low values, such that incoherent scattering became the predominant[4,5] effect. To take account of this incoherent background scattering, we made the assumption that the scattering intensity approaches a plateau at very high q values (see *Figure 6*), which is fully determined by the coherent and incoherent scattering of repeating units given by



R = H or branch

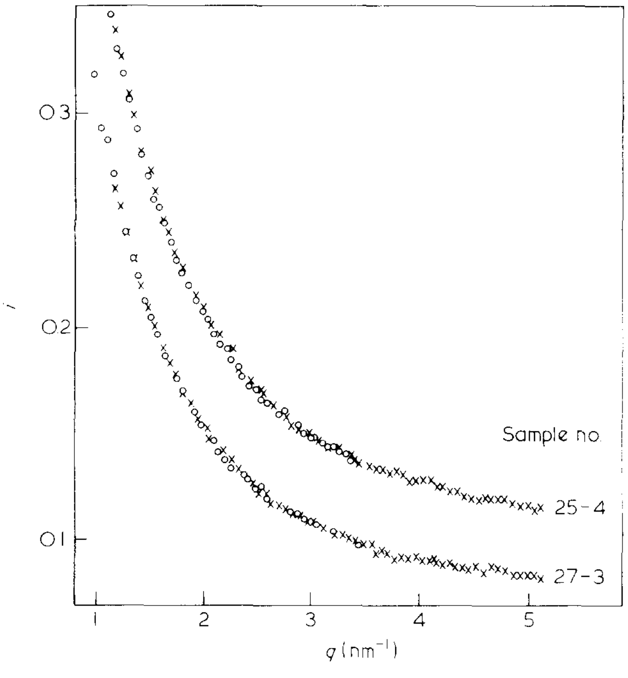


Figure 6 Scattering intensity against q

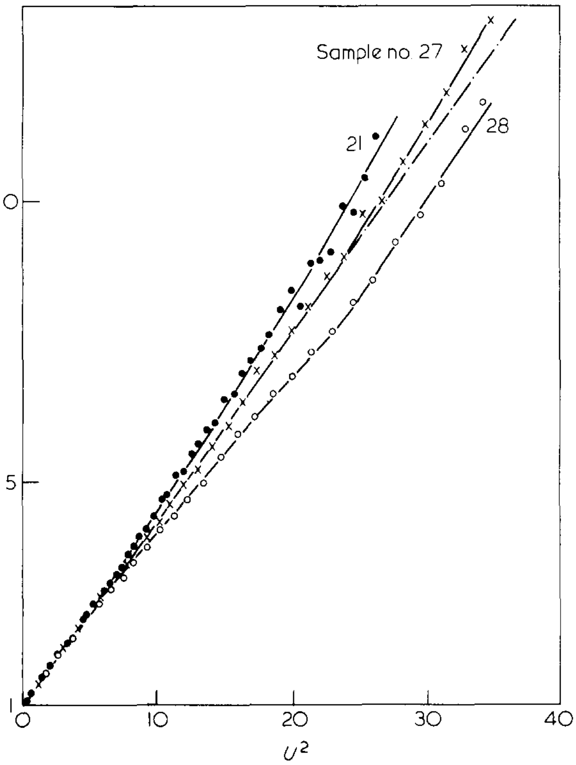


Figure 7 Reciprocal particle scattering factor against $U^2 \equiv \langle S^2 \rangle_z q^2$

The incoherent fraction of the scattering intensity can now be calculated from the coherent and the total scattering cross sections of various atoms. The values of the cross sections were taken from a list, given by Springer.[16] These calculations gave 91.5% of the scattering of the repeating unit being incoherent and 8.5% coherent scattering. The incoherent scattering is usually assumed to be independent of q and gives the flat background, which has to be subtracted. This incoherent background depends, of course, on the concentration of the polymer material, and this was in fact found for the two samples which we measured at these high q values. For the correction of the background scattering of the samples measured with the D11 set-up, the scattering intensity of the monomer was recorded separately, and the corresponding incoherent part was taken for the correction.

The apparent particle scattering factors from the higher concentrations are plotted in *Figure 7*. (The apparent particle scattering factor is obtained after normalization of the scattering intensity for a special concentration to unity at $q^2 = 0$.) The logarithmic particle scattering factor is plotted against q^2 (Gunier plot) in *Figure 8*. These curves appear to approach asymptotically a straight line.

DISCUSSION

Mean square radius of gyration

The mean square radius of gyration (*Figure 4*) of the branched epoxide resins show in the log–log plot against M_w a straight line with an exponent of $2\nu = 1.20$. This exponent is found experimentally for linear chains in good solvents[17–19], and is predicted theoretically as a limit of excluded volume effect for very long chains[7,17,18]. This limiting exponent in the present study is surprising, since (i) the products have rather low molecular weights ($DP_w = 5$ to 65) and (ii) the samples are highly branched. The existence of branching may be recognized from *Table 1*, which shows polydispersities of M_w/M_n up to 21. Such high polydispersities are rare for linear chains but common for randomly branched products[20]. Evaluation of the measurements of the extents of reaction gave[1,21] a critical branching density of $p_c = 0.38$, which means that close to the gel point every third unit is a branching point.

The effect of excluded volume depends on the probability of intramolecular contacts between segments and this is enhanced by branching[18], because of the increase in the segment density. Therefore, an influence of excluded volume may be noticeable for branched molecules already at fairly low M_w. For higher molecular weights a shielding effect due to steric constraints will occur, thus reducing the excluded volume effect. Such shielding has been in fact observed with random polycondensates[22,23], where even in a good solvent the exponent of $2\nu = 1$ for a θ solvent is observed. Possibly, the $\langle S^2 \rangle_z$ curve for the epoxides will bend down at large M_w. Unfortunately, no samples could be prepared in this region.

On the other hand, the high exponent may have its origin in a relatively high rigidity of the chains[8,9], since the bisphenol-A represents almost rigid subunits. Hence, for fairly low molecular weights a pronounced deviation from Gaussian behaviour can be expected and should result in exponents larger than $2\nu = 1$. The limiting value of $2\nu = 2$ for a rigid rod will not be observed because of the appreciable cross-dimensions of the chain.

Particle scattering factor

The shape of the particle scattering factor shows no striking behaviour, which could be interpreted qualitatively without the knowledge of any model calculations. In the plot of the recoprocal scattering factor against $U^2 \equiv \langle S^2 \rangle_z q^2$ only slight deviations from a straight line are observed. Branched monodisperse molecules exhibit a strong upturn, but this becomes weakened by molecular

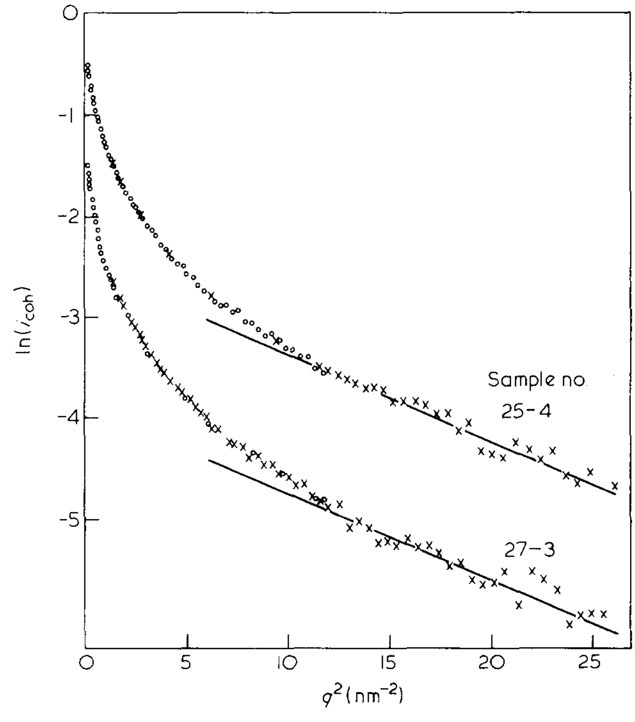


Figure 8 log(I_{coh}) against q^2

polydispersity[8,9]. In randomly branched polycondensates the upturn is just balanced[10] by the very pronounced polydispersity. Similar behaviour may be expected for the epoxide resins. A weak upturn appears to be shifted towards higher U^2 values with increasing molecular weight. Simultaneously a noticeable downturn develops in the intermediate U^2 range and becomes pronounced for the high molecular weight sample. The upturn would be an indication for the effect of the cross-dimension particle scattering factor. The appearance of the downturn is evidence for chain stiffness, which in view of the rigid subunits could be expected. Therefore in context with this shape of the particle scattering factor, the surprisingly high exponent $2\nu = 1.20$ in the M_w dependence of $\langle S^2 \rangle_z$ appears to be the result of chain stiffness. Specific model calculations are in preparation and may clarify further the polymer conformation.

The virial coefficient

High exponents of -0.85, as observed asymptotically for the epoxide resin, are not observed with linear chains[18], where values of about -0.2 are common. Similar behaviour has been observed with branched poly(vinyl acetates), where an exponent of -0.76 was obtained[24,25]. Theories of A_2 of branched polymers show that A_2 decreases drastically with branching[18,26–29]. Therefore, the high negative exponent is strong evidence for an increase in branching density with increasing molecular weight. A quantitative interpretation will be possible by comparison of A_2 from linear epoxides. The measurements on the linear products are not yet completed and a more detailed discussion of the branching effect on A_2 will be postponed to a later stage.

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