Eur. Polym. J. Vol. 21, No. 12, pp. 1021–1025, 1985
Printed in Great Britain. All rights reserved

0014-3057/85 \$3.00 + 0.00

A VISCOMETRIC STUDY OF DILUTE SOLUTIONS OF LOW-MOLECULAR-WEIGHT UNSATURATED POLYESTERS

A. KAŠTÁNEK[1] and M. BOHDANECKÝ[2]
[1]Research Institute for Synthetic Resins and Lacquers, 532 07 Pardubice and [2]Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

(*Received* 30 *May* 1985)

Abstract—The intrinsic viscosities (in methyl ethyl ketone at 25°) of 19 fractions of an unsaturated polyester (prepared from ethane diol, maleic and phthalic anhydrides in the mole ratio 1:0.4:0.6) have been determined and correlated with the number- and weight-average molecular weights ($390 \leq \bar{M}_n \leq 5 \times 10^3$). The theory of intrinsic viscosity developed for the worm-like chain model has been used to evaluate parameters characterizing the conformation of the chain (e.g. the characteristic ratio of unperturbed chain dimensions, the Kuhn statistical segment length, the effective hydrodynamic diameter, etc.). A comparison with unsaturated hexane diol polyesters indicates a higher degree of rotational freedom of chains containing ethane diol units.

INTRODUCTION

Linear unsaturated polyesters, i.e. products of the polycondensation of diols with unsaturated dicarboxylic acids (mainly maleic anhydride), are polymers of great technical importance. Their solution properties have however been the subject of only a few papers [1–3] and their conformational characteristics have not yet been determined.

We now try to estimate parameters characterizing the conformation of polyester chains by analyzing intrinsic viscosity data for fractions of an unsaturated polyester sample (UP) prepared from ethane diol, maleic and phthalic anhydrides (mole ratio of anhydrides 0.4:0.6) [3]. For low-molecular-weight fractions ($390 \leq \bar{M}_n \leq 5 \times 10^3$), the evaluation cannot be made according to the scheme usual with flexible-chain polymers of sufficient chain length and must be based on the Yamakawa–Fujii theory of the intrinsic viscosity of stiff and/or short chains [4] which takes into account non-Gaussian chain statistics and draining effects for short chains.

The model underlying the theory is a continuous worm-like cylinder characterized by its contour length, L, diameter, d, and persistence length, $a = (1/2)\,\lambda^{-1}$, where λ^{-1} is the Kuhn statistical segment length [4]. According to the theory, the intrinsic viscosity, $[\eta]$ (in cm^3/g), of a chain unperturbed by the excluded-volume effect can be written as

$$[\eta] = [\Phi_{0,\infty}\,(\overline{R_0^2}/M)_\infty^{3/2}\,M^{1/2}]F_1 \qquad (1)$$

$$F_1 = \Phi_0(L_r, \mathrm{d}_r)/\Phi_{0,\infty} \qquad (2)$$

where $(\overline{R_0^2}/M)_\infty$ is the limiting (random-coil) value of the ratio of the unperturbed mean-square end-to-end distance, $\overline{R_0^2}$, and of the molecular weight, M. The reduced quantities, L_r and d_r, are defined as

$$L_r = L/\lambda^{-1} \qquad (3)$$

$$d_r = d/\lambda^{-1} \qquad (4)$$

Φ_0 is a function of L_r and d_r. Its limiting value, $\Phi_{0,\infty}$, for $L_r \to \infty$ is independent of d_r. The segment length, λ^{-1}, is connected with $(\overline{R_0^2}/M)_\infty$ thus

$$2a = \lambda^{-1} = (\overline{R_0^2}/M)_\infty\,M_L, \qquad (5)$$

where M_L is the shift factor.

EXPERIMENTAL

Preparation of the polymer (UP) by melt polycondensation, fractionation by successive precipitation, determination of the number-average molecular weight, $\bar{M}_n$, by vapour-pressure osmometry and estimation of the weight-average molecular weight, $\bar{M}_w$, by the GPC method have been described [3].

The intrinsic viscosity was determined in methyl ethyl ketone at 25 ± 0.02°. Measurements were performed in Ubbelohde capillary viscometers adapted for dilution. From the relative viscosity increment values, η_i, measured at three or four concentrations, c, the intrinsic viscosity $[\eta]$ was determined by linearly extrapolating the values of η_i/c to $c = 0$. Corrections for end-effects and the kinetic energy loss were negligible.

The $[\eta]$, $\bar{M}_w$ and $\bar{M}_n$ values are collected in Table 1. The notation of fractions is the same as previously [3].

RESULTS AND DISCUSSION

Estimation of the unperturbed dimensions

The logarithmic correlations with $\bar{M}_n$ and $\bar{M}_w$ of the intrinsic viscosity in methyl ethyl ketone at 25° (Fig. 1) are non-linear. The quotient $\nu = \mathrm{d}\ln[\eta]/\mathrm{d}\ln M$ is surprisingly low ($\nu < 0.5$) and increases with increase in M. This is at variance with the typical behaviour of non-draining random coils but can be explained in terms of the Yamakawa–Fujii theory [4]. According to this theory, $\nu < 0.5$ indicates a rather high value of the reduced chain diameter, $d_r > 0.6$ (see Appendix I for details).

In Fig. 2a the $[\eta]$ values are plotted against $\bar{M}_w^{1/2}$. The plot is linear; its slope evaluated by means of linear regression is $K_{0,w} = 67 \times 10^{-3}$ and its intercept

Table 1. Experimental data for polyester fractions*

Fraction	$\bar{M}_n$	$\bar{M}_w$	$[\eta]$† (cm^3/g)	Fraction	$\bar{M}_n$	$\bar{M}_w$	$[\eta]$† (cm^3/g)
A_1	5020	7260	7.5	F_1	2040	—	4.7
A_2	2510	4690	5.9	F_2	1030	—	3.7
B_1	4390	6190	7.3	G_1	1260	1400	4.2
B_2	2200	3720	4.9	G_2	680	990	3.5
C_1	2930	—	6.9	H_1	1070	—	3.5
D_1	2700	3720	5.0	H_2	590	—	3.3
D_2	1600	2520	4.6	I_1	650	920	3.8
E_1	2200	—	4.8	I_2	450	520	3.2
E_2	1100	—	4.0	K_1	500	—	3.4
				K_2	390	—	2.8

*$\bar{M}_n$ and $\bar{M}_w$ values from Ref. [3]. † Methyl ethyl ketone at 25°.

is positive ($A = 1.4$). The latter fact conforms with the reduced chain diameter, d_r, being larger than 0.4. The value of $(\overline{R_0^2}/M)_\infty$ is estimated from $K_{0,w}$ according to the equation

$$(\overline{R_0^2}/M) = (K_{0,w}/b\ \Phi_{0,\infty})^{2/3}, \qquad (6)$$

where b is a numerical factor and $\Phi_{0,\infty} = 2.6 \times 10^{23}\ g^{-1}$ [5] (if $\overline{R_0^2}$ is expressed in cm^2 and $[\eta]$ in cm^3/g). For reasons explained in Appendix II, we set b equal to its limiting value, $b_\infty = 1.0$, so that the obtained value of $(\overline{R_0^2}/M)_\infty = 0.40 \times 10^{-2}\ nm^2$ may be somewhat overestimated.

The plot of $[\eta]$ vs $\bar{M}_n^{1/2}$ (Fig. 2b) has a lower (positive) intercept and a higher slope ($K_{0,n} = 0.89 \times 10^{-1}$). The value of $(\overline{R_0^2}/M)_\infty$ would be $0.49 \times 10^{-2}\ nm^2$. The plot in Fig. 2b comprises a larger number of data points. Nevertheless, any treatment of the $[\eta]$ data based on the $\bar{M}_n$ values is always more sensitive to polydispersity than a treatment using $\bar{M}_w$. Since the polydispersity index of the UP fractions seems to vary systematically with molecular weight (cf. Table 2 in Ref. [3]), the value of $K_{0,n}$ will be more affected by this factor than $K_{0,w}$. We regard, therefore, the $(\overline{R_0^2}/M)_\infty$ value calculated from $K_{0,w}$ as more reliable, although it also may be somewhat incorrect because the $\bar{M}_w$ values have been obtained by a method (GPC) based on calibration [3].

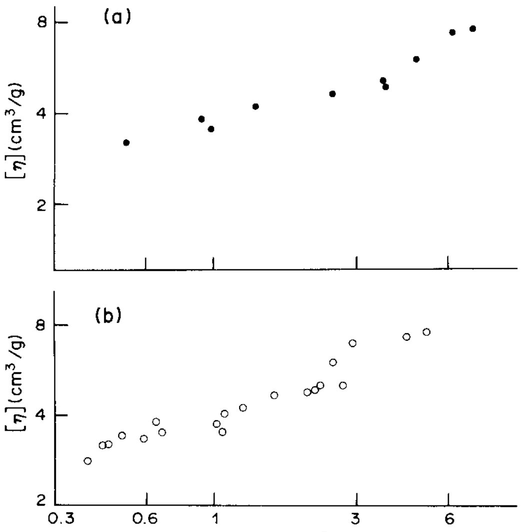

Fig. 1. Logarithmic correlation $[\eta]$ vs M for fractions of unsaturated polyester. Solvent: methyl ethyl ketone at 25°. (a) $[\eta]$ vs $\bar{M}_w$; (b) $[\eta]$ vs $\bar{M}_n$.

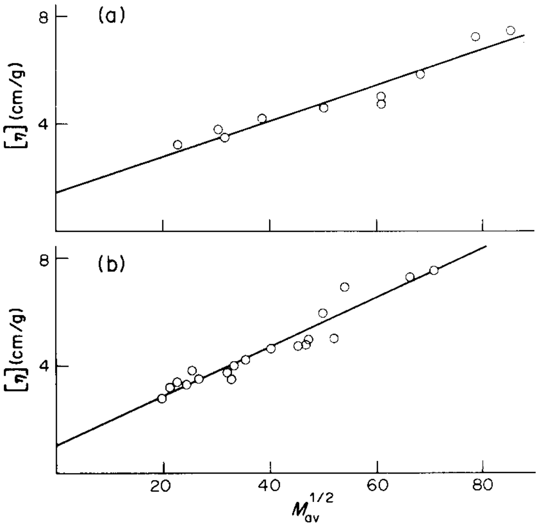

Fig. 2. Plot of $[\eta]$ vs $M_{av}^{1/2}$ for fractions of unsaturated polyester. (a) $M_{av} \equiv M_w$; (b) $M_{av} \equiv M_n$.

The value of $(\overline{R_0^2}/M)_\infty$ is remarkably low in comparison with the values estimated for polyesters of unsaturated acids with hexane diol (Table 2). When interpreting these results, it is reasonable to separate the effects of the structure of acids and diols. To take into account the planarity and rigidity of the acid units, we regard the distance between the CO groups of the acid units as a "virtual" bond, the length of which, l_v, can be obtained by simple geometric considerations (Table 2).

Table 2 shows that the $(\overline{R_0^2}/M)_\infty$ values for polyesters of hexane diol increase in the sequence "maleate, fumarate, acetylene dicarboxylate" and correlate well with l_v^2 (Fig. 3). The double bond of the maleate group being in the *cis* configuration and that of the fumarate unit being in the *trans* configuration, the virtual bond of the former is shorter than that of the latter. The difference in the configuration of the double bond and in the length of the respective virtual bond is responsible for the difference in $(\overline{R_0^2}/M)_\infty$ for the polyesters. The difference is however not large.

The correlation for polyesters of ethane diol comprises two data points only, but shows that the $(\overline{R_0^2}/M)_\infty$ values are typically lower than those with longer diol units. Although the difference between the two sets can be partly due to the differences in molecular weights of the constitutional repeating unit (the molecular weight of the phthalate unit being larger by 50% than that of the maleate or fumarate group), the plot in Fig. 3 indicates that $(\overline{R_0^2}/M)_\infty$ depends not only on the configuration of the double bond of the acid units but also on the number of methylene groups in the diol unit.

The role of the diol unit can also be demonstrated by calculating the characteristic ratio, C_∞, i.e. the factor by which the actual chain dimensions depart from the simple model of the freely jointed chain. It

Table 2. Conformational parameters of unsaturated polyester chains

Polymer	$(\overline{R_0^2}/M)_\infty \times 10^2$ (nm^2)	$(\bar{M}_b/\bar{l}^2) \times 10^{-2}$ (nm $^{-2}$)	C_∞	l_v† (nm)	References
UP	0.40	8.2	3.4	0.33	This paper
PET	0.90	4.46	4.1	0.57	[10]
PHMF‡	0.85	5.7	5.0	0.39	
PHMM‡	0.78	6.9	5.4	0.30	
PHMADC‡	0.96	5.3	5.1	0.42	

*Abbreviations: UP, poly(ethylene fumarate-co-phthalate); PET, poly(ethylene terephthalate), PHMF, PHMM, PHMADC, polyesters of hexanediol with fumaric, maleic and acetylene dicarboxylic acids, respectively.

†Virtual bond length of acid units (see text).

‡$(\overline{R_0^2}/M)_\infty$ evaluated according to equation (6) from K_0 estimated by means of the Stockmayer–Fixman–Buchard method [8, 9] from the [η] data in Refs [6, 7].

is evaluated according to the equation

$$C_\infty = (\overline{R_0^2}/M)_\infty\ (\bar{M}_b/\bar{l}^2), \tag{7}$$

where $\bar{l}^2$ and $\bar{M}_b$ are, respectively, the mean-square length and the mean molecular weight per main chain bond. The values of $\bar{l}^2$ were calculated taking into account the structure of the constitutional repeating units, with the virtual bond lengths given in Table 2 and with the following lengths of the chemical bonds: $l_{CH_2\,CH_2} = 0.15$ nm, $l_{CH_2\,O} = 0.144$ nm, $l_{CH_2\,CO} = 0.151$ nm, and $l_{CO\,O} = 0.133$ nm [5].

The C_∞ values depend somewhat on the selection of virtual bonds. By calculating the characteristic ratio as described, we have eliminated the effect of differences in the length of the virtual bonds. The C_∞ values of unsaturated polyesters of hexane diol are nearly constant (4.9–5.4) and higher than those for polyesters of ethane diol (3.4–4.1; Table 2). This result is consistent with the fact (predicted by statistical mechanical calculation [5] and confirmed by experiment [10]) that strong steric interferences in the polymethylene chain exist between the CH_2 groups which are separated by three or four bonds and that long rigid virtual bonds, such as ester or peptide groups and/or aromatic rings, reduce these interferences by confining the interdependence of the rotation about the CH_2–CH_2 bonds within the chain section between the virtual bonds. The lower the number of CH_2–CH_2 bonds in such a section, the greater the independence of the rotational states of the neighbouring bonds.

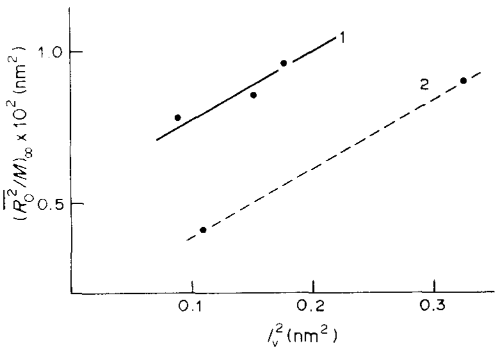

Fig. 3. Correlation of the $(\overline{R_0^2}/M)_\infty$ values of unsaturated polyesters with the length of the virtual bond of acid units, l_v. Polyesters of hexane diol (1) and ethane diol (2). For data, see Table 2.

Estimation of the persistence length and other chain parameters

The main aim of this work is an estimation of the unperturbed dimensions. However, we also estimate other parameters of the worm-like cylinder model in order to check its adequacy for the UP chain.

The shift factor, M_L, is often identified with the molecular weight per unit contour length of the chain at full extension, and this assumption is adequate in many cases. With the UP chain, the situation is more involved. The contour of the chain at full extension is not straight because of the presence of maleate units (with double bonds in the *cis* configuration) and of *o*-phthalate units. Owing to the *cis–trans* isomerization of maleate units during the polyester synthesis, the content of *cis* double bonds is almost suppressed in favour of the fumarate units (with the double bonds in the *trans* configuration) which conform to a straight contour length at full extension; on the other hand the *o*-phthalate units which, from this point of view, are equivalent to *cis* double bonds, give the extended chain a non-linear shape (Fig. 4). The exact shape depends on the ratio of fumarate to *o*-phthalate units and on their distribution along the chain. Since this distribution is not known, we can only assume that it corresponds, on average, to the mole fraction of fumarate and *o*-phthalate units (which is nearly constant for all fractions investigated here [3]).

The shape of a fully extended polyester chain (differing somewhat in composition from our polyester samples) is schematically represented in Fig. 4. The chain axis is not a straight line but a zig-zag curve, composed of linear sections (2.08 nm long), comprising one fumarate unit and bound to two phthalate units (effective *cis* double bonds). The tortuous contour does not fit in with the hydrodynamic model, so we replace the chain with a straight cylinder with axis located in the direction of colinear double bonds (line 1, Fig. 3). The mean length of a straight section between two *o*-phthalate units in the UP chain projected onto this direction is 0.87 nm.

The constitutional repeating unit of our polyester (mole ratio of fumarate:phthalate units being 0.4:0.6) has $M_r = 1720$; its length measured along the

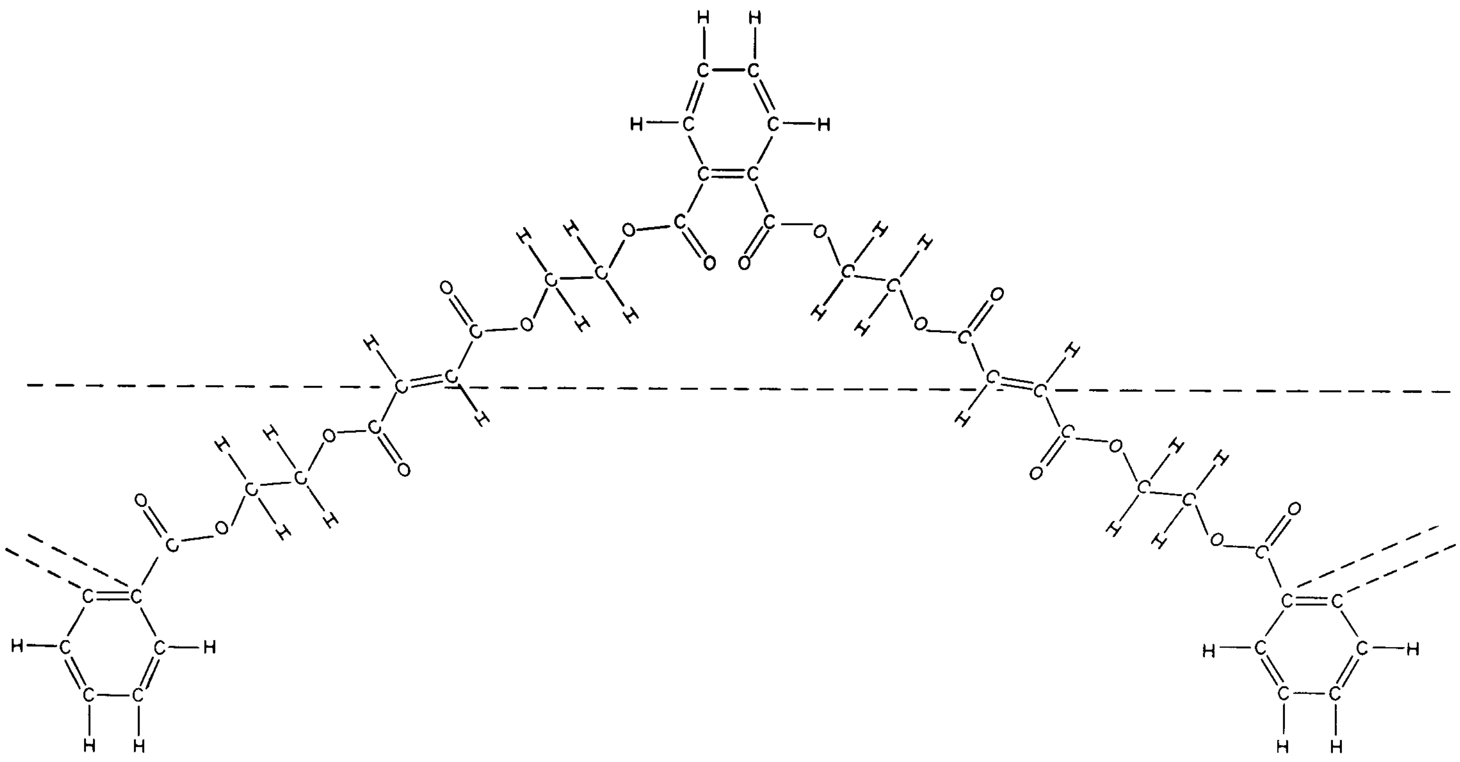

Fig. 4. Schematic representation of the polyester chain. Components: ethane diol, fumaric and *o*-phthalic acid units (mole ratio of acid units 0.5:0.5).

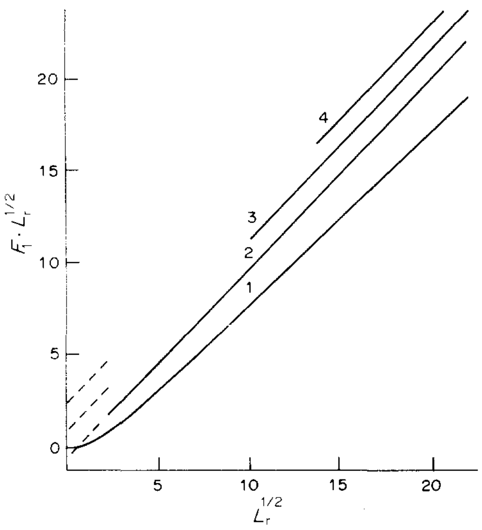

Fig. 5. Theoretical values of $L_r^{1/2} \cdot F_l$ plotted against $L_r^{1/2}$. Curves 1–4 calculated from data in Ref. [4] for $d_r = 0.1$, 0.4, 0.6 and 0.8, respectively. Broken lines: extrapolation to $L_r^{1/2} \to 0$ of lines 2, 3 and 4.

axis of the equivalent cylinder is 8.7 nm, so that the shift factor, $\bar{M}_L$, is 197 nm^{-1}.

To check this calculation, we assume that, from the point of view of hydrodynamics, the molecule with the lowest molecular weight ($[\eta] = 390$) can be represented by a spherocylinder of length L and diameter d with two end-caps of the same diameter. The intrinsic viscosity of such particle is [11]

$$[\eta] = (2\pi N_A/45)(L^3/M) F\eta\,(p; 1) \tag{8}$$

and its volume, v_p, is

$$v_p = (\pi/12)\, d^3 (3p - 1), \tag{9}$$

where $p = L/d$. Assuming that

$$v_p \simeq (M/N_A)\, v_{sp}, \tag{10}$$

where v_{sp} is the specific volume, we obtain from equations (8), (9) and (10)

$$[\eta]/v_{sp} = (8/45)\, \mathrm{K}_\eta\,(p; 1) \tag{11}$$

$$\mathrm{K}_\eta(p; 1) = p^2 F_\eta(p; 1)/(1 - 1/3p), \tag{12}$$

where $F\eta\,(p; 1)$ has been given [11] and $\mathrm{K}_\eta(p, 1)$ is an increasing function of p (cf. Fig. 5 in Ref. [12]).

With $[\eta] = 2.8$ cm^3/g, $v_{sp} = 0.75$ cm^3 [13] and $\bar{M}_n = 390$, we obtain $p = 2.66$, $d = 0.64$ nm, $L = 1.7$ nm and $\bar{M}_L = 230$ nm^{-1}, in fair agreement with $\bar{M}_L = 197$ nm^{-1} obtained above from geometrical considerations.

The persistence length, a, of the polyester chain calculated according to equation (5) with the higher $\bar{M}_L$ value is 0.46 nm, the Kuhn statistical segment length, λ^{-1}, *is* 0.92 nm, and the corresponding molecular weight per segment is $M_\lambda = 211$. With $d = 0.64$ nm, we estimate $d_r = 0.7$.

Uncertain as these estimates are, they still show that the reduced contour length, L_r, of the UP chains is low, ranging from 2 to 30. This information justifies neglect of the excluded-volume effect in the treatment of the intrinsic viscosity data because, according to Norisuye and Fujita [14], this effect can be perceived at $L_r = 50 \pm 20$.

The diameter d of the model cylinder is a poorly defined quantity in the present case, so we regard it merely as an adjustable parameter, although in view of the van der Waals radii of groups forming the UP chain, the value of $d = 0.64$ nm seems reasonable.

APPENDIX I

It follows from equation (1) that for chains unperturbed by the excluded-volume effect

$$v_0 \equiv \mathrm{d}\ln[\eta]/\mathrm{d}\ln M = (1/2) + (\mathrm{d}\ln \Phi_0/\mathrm{d}\ln L_r)_{d_r} \tag{A.1}$$

Figure 1 in Ref. [4] shows that quotient $(\mathrm{d}\ln \Phi_0/\mathrm{d}\ln L_r)_{d_r}$ is positive at $d_r \leq 0.4$ and negative at $d_r \geq 0.6$, the absolute value being a decreasing function of L_r in either case. The quotient v_0 at small chain lengths, therefore, is larger than 0.5 and decreases with an increase in L_r in the former case. It is less than 0.5 and increases with L_r if $d_r \geq 0.6$. The limiting value of $(\mathrm{d}\ln \Phi_0/\mathrm{d}\ln L_r)_{d_r}$ at $L_r \to \infty$ is zero regardless of d_r, so that $v_0 = 0.5$ at high chain lengths.

APPENDIX II

The theoretical equivalent of the dependence of $[\eta]$ on $M^{1/2}$ is the plot of $F_l \cdot L_r^{1/2}$ vs $L_r^{1/2}$ (Fig. 5; cf. also Fig. 3 in Ref. [4]). At high $L_r^{1/2}$ values and at $d_r \geq 0.4$, the plots for different d_r are linear and nearly parallel, their slopes, b_∞, being close to unity. Extrapolation of these (asymptotic) parts to $L_r^{1/2} = 0$ would give positive intercepts, A', at $d_r \geq 0.6$ and negative at $d_r \leq 0.4$. For $d_r = 0.4$, the negative intercept would only slightly differ from zero.

At low L_r values, the plots are concave upward for $d_r \leq 0.4$. Their shape in this region is unknown for higher d_r values because no F_l values have been computed [4] but a downward curvature can be expected. If this part were approximated by a line, its slope, b would be larger than b_∞. Hence, setting $b = b_\infty$ in equation (6) may lead to an over-estimation of $(\bar{R}_0^2/M)_\infty$.

REFERENCES

1. M. J. R. Cantow, R. S. Porter and J. F. Johnson, *J. appl. Polym. Sci.* **8**, 2963 (1964).
2. W. Y. Lee, *J. appl. Polym. Sci.* **22**, 3343 (1978).
3. A. Kaštánek, J. Zelenka and K. Hájek, *J. appl. Polym. Sci.* **26**, 4117 (1981).
4. H. Yamakawa and M. Fujii, *Macromolecules* **7**, 128 (1975).
5. P. J. Flory, *Statistical Mechanics of Chain Molecules*. Interscience, New York (1975).
6. H. Batzer and B. Mohr, *Makromolek. Chem.* **8**, 217 (1952).
7. H. Batzer and G. Weissenberger, *Makromolek. Chem.* **12**, 1 (1954).
8. W. H. Stockmayer and M. Fixman, *J. Polym. Sci.* **C1**, 137 (1963).
9. W. Burchard, *Makromolek. Chem.* **50**, 210 (1961).
10. M. Bohdanecký and L. Šimek, *Eur. Polym. J.* **20**, 943 (1984).
11. T. Yoshizaki and H. Yamakawa, *J. chem. Phys.* **72**, 57 (1980).
12. Š. Štokrová, M. Bohdanecký, B. Sedláček, K. Bláha and J. Šponar, *Biopolymers*. In press.
13. A. Kaštánek, J. Zelenka and K. Hájek, *J. appl. Polym. Sci.* **29**, 447 (1984).
14. T. Norisuye and H. Fujita, *Polym. J.* **14**, 143 (1982).