A Semiempirical Formulation of the Effect of Random Branching on Intrinsic Viscosity

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ABSTRACT: The possibility of estimating an empirical value of the exponent ν in the relation $g_0' = g_0^\nu$ is explored (where g_0' is the ratio of the intrinsic viscosities of branched and linear molecules at the same molecular weight and g_0 is the corresponding ratio of radii of gyration). A simple approximate formula $g_0^\nu = 1/(A_\nu + B_\nu m^{1/2})$ has been found for theoretical $g_0^\nu(m)$ functions describing the effect of the degree of branching (m) on the intrinsic viscosity. The analysis of experimental data available in the literature for five polymers at theta temperatures gives the value $\nu \simeq 0.8$. The values $\nu = 1/2$ and $3/2$ currently used turn out not to be a good approximation. The effect of intrachain rings formed in the copolymerization of bi- and tetrafunctional monomers is analyzed. The possibility of a more reliable estimation of the degree of branching is discussed.

The procedure most frequently used for the estimation of the degree of branching of macromolecular substances is based on the comparison of the intrinsic viscosities, $[\eta]_b$ and $[\eta]_l$, of branched and linear samples at the same molecular weight (M). At conditions justifying the use of the random flight chain statistics, the ratio of $[\eta]_0$ values is defined[1-5] by relations 1 and 2:

$$g_0' = [\eta]_{0,b}/[\eta]_{0,l} \tag{1}$$

$$[\eta]_{0,l} = K_0 M^{1/2} \tag{2}$$

The values of g_0' depend on the type of branching, on the functionality (f), and on the number of branch units (m) in the molecule (degree of branching). The most important type of branched structures is the random one. It is formed by the chain transfer reactions to monomer or polymer in a radical polymerization or by the copolymerization of bifunctional and multifunctional monomers. However, no adequate theory of intrinsic viscosity is available for this case.

As there exists a theoretical approach[3,4] to the effect of the random branching on the radius of gyration, $\overline{S}_0^2$, it has become customary to formulate the dependence of intrinsic viscosity on the degree of branching in an indirect way, namely by means of relations 3 and 4,

$$g_0' = g_0^\nu \tag{3}$$

where

$$g_0 = (\overline{S}_0^2)_b/(\overline{S}_0^2)_l \tag{4}$$

the values $3/2$ and $1/2$ being most frequently substituted for ν. The former is considered adequate for comblike molecules with short lateral chains.[5] The latter has been theoretically found to be satisfactory for certain types of starlike branching.[6] Zimm and Kilb[6] suggested that it might also be used as an approximation for other starlike structures and for randomly branched ones. Experimental investigations carried out with well-defined model polymers have brought to evidence that this approximation holds for starlike branched structures at low degrees of branching only, while higher ν values are to be used at higher degrees (cf. ref 1 and 2 for review). Consequently, the validity of ν values mentioned above for randomly branched chains has been questioned and several attempts at an empirical estimation of the exponent ν have been made.[1,7-10]

The straightforward way, i.e., the correlation of the $[\eta]_{0,b}$ and $(\overline{S}_0^2)_b$ values, meets with a serious obstacle in that the radius of gyration, as measured by means of the light-scattering method, is very sensitive to the polydispersity of the sample. Further inaccuracy may appear in the results if the values $[\eta]_{0,b}$ and $(\overline{S}_0^2)_b$ have been calculated from the data (intrinsic viscosity, radius of gyration, and second virial coefficient) measured in a good solvent, the calculations being based on some relationships whose validity had not been verified for branched polymers.[7-9]

In another paper,[10] the correlation of experimental $[\eta]_{0,b}$ and M data for styrene–tetrachlorodivinylbenzene copolymers was the basis of the estimation of ν, together with the assumption that the content of the tetrafunctional monomer in copolymers (analytically determined) gives the amount of branch units. The effect of ring structures formed during the copolymerization has been neglected.

Another attempt at estimating the ν value is described in this paper. It is based on theoretical $g_0(m)$ functions calculated by Kurata and Fukatsu[3] under the following assumptions: The polymer molecules are homogeneous in the number of branch units as well as in the total number of units per molecule. No ring structures are considered. The number of units between two adjacent branch units or between an adjacent pair of an end and a branch unit is distributed randomly.

Theoretical

We have found (Figure 1) that the dependences g_0^ν vs. m calculated for different values of ν ($1/2 \leq \nu \leq 1$) from theoretical data (ref 3, Table I, column 3) can be described by a simple formula

$$g_0^\nu = 1/(A_\nu + B_\nu m^{1/2}) \tag{5}$$

covering a broad interval of m values. The parameters A_ν and B_ν depend on both ν and f. The range of m or g_0^ν values where approximation 5 holds (Table I) is different for different ν's. It was estimated approximately for individual cases from the plots $1/g_0^\nu$ vs. $m^{1/2}$. The parameters A_ν and B_ν were then determined by means of the least-squares method from the $1/g_0^\nu$ values lying in the respective intervals. As can be seen in Table I, the theoretical dependences were fitted by formula 5 with a standard error lower than 1%, and the dependence on ν of the parameters A_ν and B_ν turned out to be pronounced (Figure 2).

All the dependences $1/g_0^\nu$ vs. $m^{1/2}$ must start at $1/g_0' = 1$ for $m = 0$. Therefore, the initial parts are curved (Figure 1). However, as the theoretical dependences are linear within a rather broad range of m (defined by the lower and upper limiting values, m_1 and m_2) and because the intercepts A_ν are strongly dependent on ν, we expected that an evaluation of experimental data on the basis of eq 5 would provide information about a more adequate (though empirical) value of ν. The procedure is based on the assumption that the degree of branching is proportional to M,

$$m = \lambda M \tag{6}$$

Table I
Values of the Parameters of Equation 5

f		ν			
		$\frac{1}{2}$	$\frac{2}{3}$	$\frac{4}{5}$	1.0
3	A_ν	0.932	0.869	0.811	0.569
	B_ν	0.122	0.183	0.238	0.371
	$\delta \times 10^3$ [a]	6.20	4.0	8.1	3.3
	I[b]	1.05–1.7	1.05–2.2	1.15–3.2	1.3–5
4	A_ν	0.924	0.861	0.810	0.510
	B_ν	0.202	0.302	0.394	0.623
	$\delta \times 10^3$ [a]	7.1	7.7	2.8	2.2
	I[b]	1.1–1.8	1.15–2.4	1.2–2.8	1.4–5

[a] Standard error of the approximation. [b] Range of $1/g_0{}^\nu$ values where eq 5 approximates theoretical functions with an error of less than 1%.

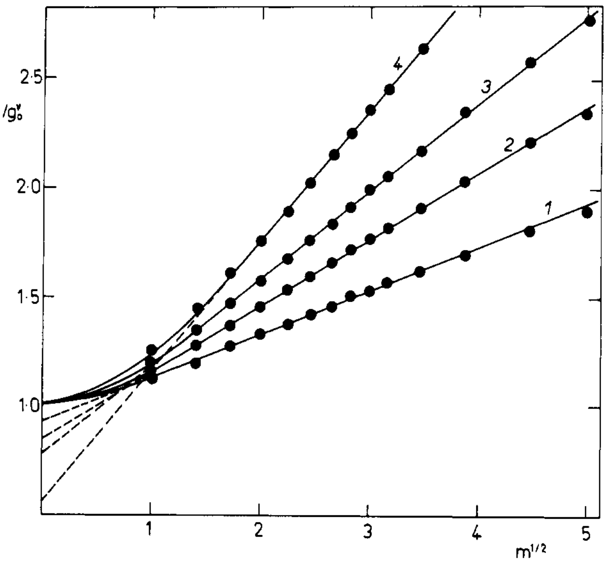

Figure 1. Theoretical data plotted as $1/g_0{}^\nu$ vs. $m^{1/2}$ (for $f = 4$). Curves 1 to 4: $\nu = \frac{1}{2}, \frac{2}{3}, \frac{4}{5}, 1$: (●) theoretical values calculated from values of g_0 (ref 3); (—) approximation by eq 5.

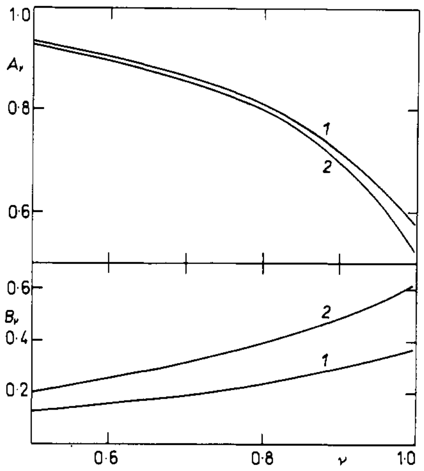

Figure 2. Dependence of the parameters of eq 5 on the ν value. Curves 1 and 2 for f = 3 and 4.

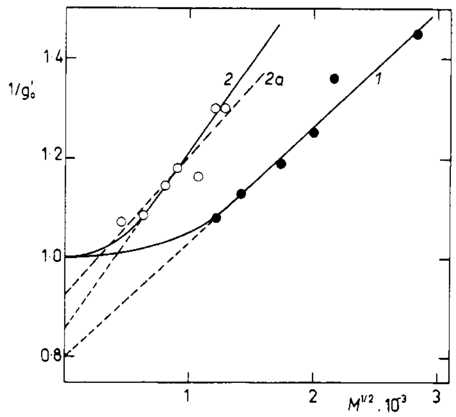

Figure 3. Plot of $1/g_0'$ vs. $M^{1/2}$: (1) poly(dodecyl methacrylate)[14] (●), (2) poly(vinyl acetate)[15] (○). Curves calculated for (ν; $\lambda \times 10^6$): 1 (0.8, 0.97), 2 (0.66, 4.0), 2a (0.5, 4.9).

and that the parameter λ is constant for a series of fractions of a polymer sample. Then, according to eq 3, 5, and 6, it holds

$$1/g_0' = A_\nu + B_\nu \lambda^{1/2} M^{1/2} \qquad (7)$$

so that the plot $1/g_0'$ vs. $M^{1/2}$ constructed on the basis of experimental data should be curved at low molecular weights and assume a linear form at the higher ones ($m_1/\lambda \leq M \leq m_2/\lambda$). By extrapolating the linear part to $M^{1/2} = 0$, one should obtain the intercept A_ν which, on comparison with the theoretical A_ν vs. ν correlation (Figure 2), could lead to the ν value. If the functionality f is known, one can find the corresponding B_ν value from Figure 2 and use it to estimate the parameter λ from the slope ($B_\nu \lambda^{1/2}$) of the plot $1/g_0'$ vs. $M^{1/2}$.

Theoretical functions[3] used here have been calculated assuming that the random-flight chain statistics is valid for both the linear and branched chains. Therefore, the experimental data to be used for the estimation of the exponent ν according to the procedure outlined above should meet this requirement. With a linear polymer this condition is met at the Θ_l temperature, when the second virial coefficient $A_{2,l}$ vanishes. With branched molecules, the situation is more involved, depending on the topology of the chain.[1,2] It has been suggested[11,12] that, generally speaking, the branched chains need not have a random configuration at the Θ_b temperature (when the second virial coefficient is zero for branched chains). However, the problem is far from being solved so that the assumption of validity of the random-flight chain statistics at Θ_b is currently used.

It has also been found (cf. ref 1 and 2) with some comblike and starlike polymers that the Θ_b temperature was lower than Θ_l. As for the randomly branched polymers, no differences have been established between Θ_b and Θ_l in all cases[10,13,14] investigated from this aspect thus far. We assume that this will also be the case with other systems. Even if a small difference exists in some cases, it may be assumed that the g_0' ratio will be less temperature dependent than either intrinsic viscosity so that the potential error following from the difference in theta temperatures will not be serious.

Another assumption on which the theory in ref 3 is based is the homogeneity of molecules in both the molecular weight and number of branch units. In fact, even when well-fractionated samples are considered, there still remains some heterogeneity in the degree of branching m. However, as pointed out by Kurata and Fukatsu,[3] the heterogeneity in m does not affect appreciably the g_0 values.

Discussion

In what follows, experimental data available in the literature for fractions of randomly branched poly(dodecyl methacrylate),[14] poly(vinyl acetate),[15] low-density polyethylene[7,9,16] (LDPE), copolymers of methyl methacrylate with glycol bismethacrylate[8] (MMA–GBMA), and copolymers of

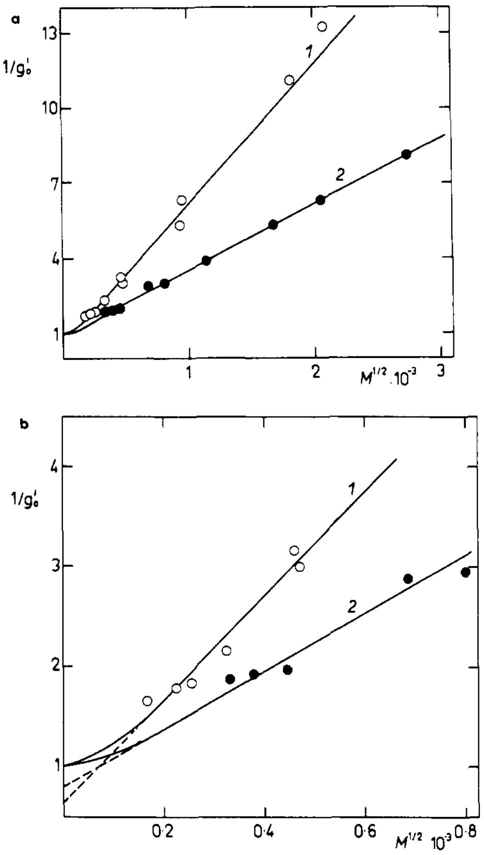

Figure 4. Plot of $1/g_0'$ vs. $M^{1/2}$ for LDPE. Data from ref 7 and 9 (○, ●). Curves calculated for (ν; $\lambda \times 10^4$): 1 (1.0, 2.4), 2 (0.8, 1.4). (a) The whole range of values. (b) Detail for $1/g_0' \leq 3.2$.

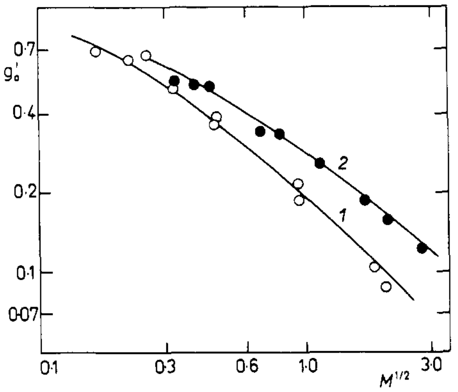

Figure 5. Logarithmic plot of g_0' vs. $M^{1/2}$ for LDPE. Symbols as in Figure 5. Curves 1 and 2: best-fit curves with ν = 1.0 and 0.8, respectively.

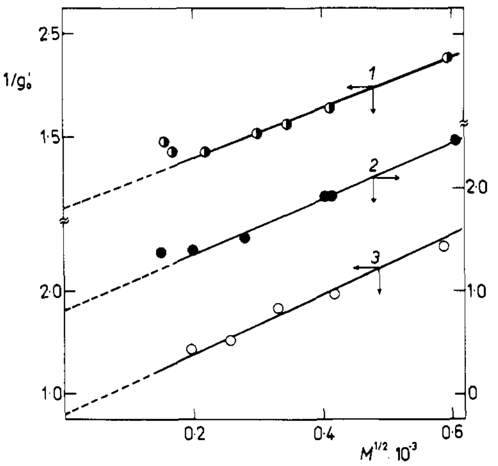

Figure 6. Plot of $1/g_0'$ vs. $M^{1/2}$ for LDPE. Data from ref 16 (samples A (○), B (◑), and C (●)). Curves calculated for (ν; $\lambda \times 10^4$): 1 and 2 (0.8; 1.15), 3 (0.8; 1.4).

styrene with tetrachlorodivinylbenzene[10] (S-TCDVB) are analyzed on the basis of eq 7. As evident from Figures 3 to 8, the plots come up to the expectation.

For poly(dodecyl methacrylate) the intercept A_ν equals 0.8 (Figure 3), which suggests ν to be near $\frac{4}{5}$. The degree of branching (one branch unit per 4.5×10^3 linear ones) is surprisingly close to that calculated[14] from the radii of gyration (1 per 4×10^3). There is a higher degree of ambiguity in treating the data for poly(vinyl acetate)[15] (Figure 3). Therefore, two lines have been drawn through the points in Figure 3, one for $\nu = 0.7$ and other for $\nu = \frac{1}{2}$, i.e., with A_ν values prescribed. The higher ν value appears to be more appropriate. It may be interesting to note that a comparable value ($\nu = \frac{3}{4}$) was found by Graessley et al.[17] for nonfractionated PVAc samples.

Among the polymers with trifunctional branch units, the low-density polyethylene (LDPE) is the most important one. The data for Θ_1 conditions, which can be found in the literature,[7,9,16] have been plotted according to eq 7 in Figures 4 to 6. In calculating the g_0' values, we substituted 30×10^{-4} for the constant K_0 in eq 2, although other K_0 values had been reported for linear polyethylene fractions in some papers quoted (26×10^{-4} in ref 9, 36×10^{-4} in ref 7). The lower value is not easy to understand. The high value seems to be a consequence of the fact that the measurements of linear samples have been made slightly above the Θ_1 temperature. If the $[\eta]/M^{1/2}$ vs. $M^{1/2}$ plot is constructed for linear fractions, a nonzero slope is found and the extrapolation to $M^{1/2} = 0$ gives a more probable value $K_0 = 31 \times 10^{-4}$.

With LDPE from ref 7 and 9, the plots $1/g_0'$ vs. $M^{1/2}$ are linear in a broad range (Figure 4), but for the purpose of the present work only those data points may be used (Figure 4b) which are situated within the interval of $1/g_0'$ given in Table I (i.e., approximately 50% of the data points in Figure 4a). The following ν values were evaluated from the intercepts in Figure 4b: $\nu = 0.8$ and 0.95. Starting from these values and using the slopes of the lines in Figure 4b, the parameter λ was estimated (Table II). Then the whole $1/g_0'$ vs. $M^{1/2}$ dependences were calculated and drawn as full curves in Figure 4a. They fit the experimental data very well.

In order to check the values established from Figure 4 in an independent way, the experimental data were plotted as g_0' vs. $M^{1/2}$ on a logarithmic scale. By a horizontal shift they were brought to coincidence with one of the calculated dependences g_0^ν vs. $m^{1/2}$ plotted in a similar way. The best fit was obtained for $\nu = 0.8$ and 1.0, respectively (Figure 5).

A less clear-cut result is arrived at with the LDPE fractions from ref 16 (Figure 6). The plots are linear, but three points with the lowest molecular weights deviate upwards. If these data are neglected, a good linear dependence is obtained with $\nu = 0.80$ again.

In Figures 7 and 8 the data for polymers with tetrafunctional branch units are plotted according to eq 7. Low ν values have been assigned to these systems in original papers: 0.6 to S-TCDVB[10] and 0.5 to MMA-GMBA copolymers.[8] For the sake of comparison, Figures 7 and 8 are completed with curves calculated for ν and λ values given in the respective papers (Table II). It is evident that the value $\frac{1}{2}$ can be excluded from consideration in both cases, while the best fit of experimental data is obtained with higher ν values (0.8–0.85). However, this treatment of experimental data (as well as that in the original

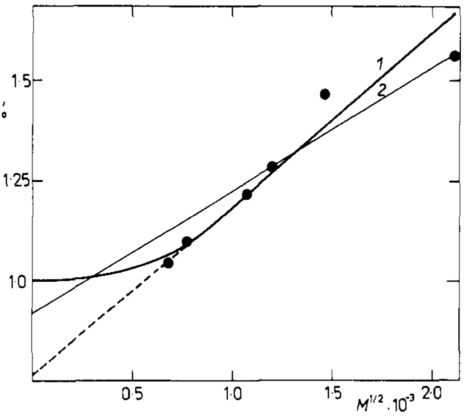

Figure 7. Plot of $1/g_0'$ vs. $M^{1/2}$ for MMA-GBMA copolymers. Data from ref 8 (sample A). Curves calculated for (ν; $\lambda \times 10^6$): 1 (0.85; 0.93), 2 (0.5; 2.1).

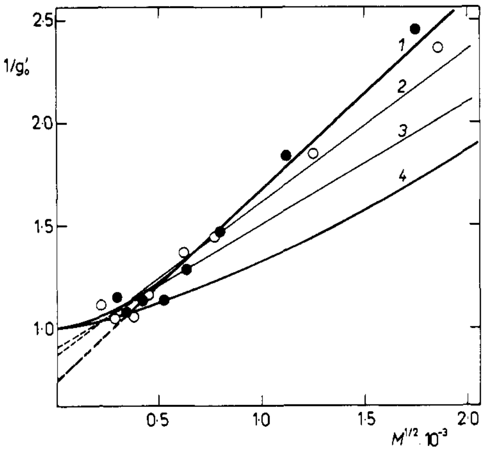

Figure 8. Plot of $1/g_0'$ vs. $M^{1/2}$ for S-TCDVB copolymer. Data from ref 10 (A (○), B (●)). Curves 1 to 3 calculated for branched chains (ν; $\lambda \times 10^6$): 1 (0.85; 4.2), 2 (0.6; 8.0), 3 (0.5; 8.0). Curve 4 calculated for chains with rings ($\lambda' = 4 \times 10^{-6}$).

Table II
Results of the Treatment of Viscometric Data

Polymer	Data from ref	f	ν This work	ν Orig work	$\lambda \times 10^6$ This work	$\lambda \times 10^6$ Orig work
Poly(dodecyl methacrylate)	14	3	0.8		0.97	0.87
Poly(vinyl acetate)	15	3	c. 0.7		c. 4.0	
LDPE[c]	7	3	1.0		240	
LDPE	9		0.8		140	
LDPE, prep A, C	16	3	c. 0.8		140	
prep B			c. 0.8		115	
Copolymer S–TCDVB[a]	10	4	(0.85)	0.6	(4.2)	8.0
Copolymer MMA–GBMA[b]	8	4	(0.85)	0.5	(0.93)	2.1

[a] St-styrene; TCDVB = tetrachlorodivinylbenzene. [b] MMA = methyl methacrylate; GBMA = glycol bismethacrylate. [c] Low-density polyethylene.

papers) would be justified only if no intrachain ring formation occurred in the preparation of copolymers. As this reaction can hardly be avoided in the copolymerization of bifunctional and tetrafunctional monomers, one must ask if the effect of intrachain rings on the hydrodynamic properties may be neglected, and if so, under what conditions. The problem is discussed more in detail in the Appendix. It turns out that the ν and λ values estimated on the basis of eq 7 (or in any other similar way) for chains with tetrafunctional branch units cannot be reliable unless the absence of random intrachain rings has been proved. (That is why they are given in parentheses in Table II.)

It is evident from the discussion of results obtained on the basis of eq 7 that the ν values most frequently used in estimating the branching degree (i.e., $\nu = 1/2$ and $3/2$) are not suitable for randomly branched chains, and that $\nu = 4/5$ is a more adequate value. Thus, the effect of random branching on the intrinsic viscosity at the theta temperature can be formulated by the formulas:

$$(f = 3) \quad \frac{[\eta]_{0,\mathrm{b}}}{[\eta]_{0,\mathrm{l}}} = \frac{1}{0.811 + 0.238m^{1/2}} \qquad 2 \le m \le 100 \tag{8a}$$

$$(f = 4) \quad \frac{[\eta]_{0,\mathrm{b}}}{[\eta]_{0,\mathrm{l}}} = \frac{1}{0.810 + 0.394m^{1/2}} \qquad 1 \le m \le 25 \tag{8b}$$

It is beyond the possibility of the present procedure to establish the g_0' vs. m relationship more precisely because the polymer samples used in the analysis were heterogeneous in both the number of branch units and molecular weight. Therefore, the differences in the values of the exponent ν (Table II) will not be discussed in detail, although it must be admitted that real $g_0'(m)$ functions cannot be approximated by $g_0^{\nu}(m)$ functions with the exponent ν being constant over a very broad range of m.

In this connection, it is necessary to mention the formula

$$g_0' \simeq h_0^3 \tag{9}$$

proposed by Stockmayer and Fixman[18] to describe the effect of branching on intrinsic viscosity ("h^3 rule", cf ref 1). The symbol h_0 stands here for the ratio of friction constants of branched and linear samples (at the same M) measured in the sedimentation. It can be shown that the h_0^3 vs. $m^{1/2}$ function constructed for randomly branched chains on the basis of theoretical data from ref. 3 is very close to the $g_0^{4/5}$ vs. $m^{1/2}$ dependence at lower m values (e.g., $1 \le m \le 9$ for $f = 3$) and to the g_0 vs. $m^{1/2}$ dependence at higher ones ($25 \le m \le 50$ for $f = 3$).

The results of the present analysis also support the idea advanced by Berry[5] that a ν value between $1/2$ and 1, but nearer to one, should be valid for randomly branched molecules.

An estimation of the exponent ν, as precise as it is, does not solve the problem of the intrinsic viscosity of randomly branched molecules fundamentally. However, it may be of some practical importance. It is well known[16] that, using the same experimental data but different values of ν, very different values of m are arrived at, the differences being almost of an order of magnitude with $\nu = 1/2$ and $3/2$. As suggested by Small,[1] large discrepancies in the values of m or λ given for LDPE in the literature may be the consequence of an arbitrary choice of the exponent ν. It is interesting that those established in this paper for fractions of LDPE of different origin are rather near to each other.

It has been shown recently by Mattice and Carpenter[19] that, in consequence of bond interactions in real macromolecules, the g values obtained from the random-flight statistics for starlike chains are in come cases not attained until the number of bonds in the molecule is very high. This effect is likely to also be important for the randomly branched chains. As no treatment of this type has been made for random branching the random-flight statistics is the basis of all the calculations throughout this work.

Appendix

According to Kuhn and Majer,[20] the effect of rings on the radius of gyration and the intrinsic viscosity depends on the ring size. It is very small if only small rings (with five to six carbon atoms) are present, but it may become important if the ring formation is a random process. In this case, the average size of the ring (expressed by the number $\bar{k}$ of statistical segments per ring) is given by eq (A.1)

$$\bar{k} = (2^{3/2}/3)N_m{}^{1/2} \tag{A.1}$$

where N_m is the number of segments per chain. The intrinsic viscosity, $[\eta]_{0,r}$, of chains with n rings is lower than that of linear molecules, the ratio $g_{0,r}'$ being approximately (at low values of n)

$$[\eta]_{0,r}/[\eta]_{0,l} = g_{0,r}' \simeq 1 - \tfrac{3}{2}n(\bar{k}/N_m) \tag{A.2}$$

The number of segments N_m is

$$N_m = N/M_0 s$$

where M_0 is the molecular weight of the monomer unit and s stands for the number of monomer units in the segment. Assuming that n is proportional to the molecular weight ($n = \lambda' M$), we obtain from eq (A.2)

$$g_{0,r}' \simeq 1 - \tfrac{3}{2}(M_0 s)^{1/2}\lambda' M^{1/2} \tag{A.3}$$

On the basis of this equation, the dependence $1/g_{0,r}'$ vs. $M^{1/2}$ has been calculated for S–TCDVB copolymers (with $s = 15$, $M_0 = 104$ and $\lambda' = 4 \times 10^{-6}$) and drawn in Figure 8 (curve 4). Let us compare it with curve 1. In both cases the ratio of the number of tetrafunctional to that of difunctional monomer units in the chain (4 per 10^4) is identical but curve 1 corresponds to a branched structure without intrachain rings, whereas curve 4 corresponds to molecules with rings only. It turns out that the effect of rings (with a random distribution of ring size) on intrinsic viscosity is weaker than that of branched structures but is far from being negligible.

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Intrinsic Viscosity According to Elastic Necklace Model with Hydrodynamic Interaction[†]

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ABSTRACT: The exact calculation of intrinsic viscosity for the necklace model with up to 300 elastic links and hydrodynamic interaction parameter h^* between 0 and 0.4 shows how slowly with increasing M one reaches the limiting case of impenetrable coil where $[\eta]$ is proportional to $M^{1/2}$. Hence according to the model, a finite $a > 0.5$ can be interpreted as a sign of good solvent only if the measurements are extended over so large a molecular weight range that one is certain that one has already reached the limit of impenetrable coil. The limitation of $h^* = (3/\pi)^{1/2}a_h/b_0$ to values below 0.25 caused most likely by the inadequacy of the linear approximation of Oseen's tensor of hydrodynamic interaction interferes with molecular interpretation of the a_h/b_0 ratio derived from $[\eta]$ as soon as h^* is close to 0.25.

The exact solution[1] of the diagonalization problem of the system of linear partial differential equations describing the density distribution function of the elastic necklace model in linear flow field allows more reliable analysis of the influence of the necklace parameters on the excess stress tensor originating from the presence of the macromolecular coil in a theta solvent. The most investigated component of this tensor is the intrinsic shear stress $[\sigma]_{12} = \lim\, (\sigma - \sigma_s)_{12}/c$ and its gradient coefficient, the intrinsic viscosity $[\eta] = \lim\, (\eta - \eta_s)/c\eta_s = [\sigma]_{12}/\dot{\gamma}\eta_s$. Here c is concentration, $\dot{\gamma}$ is velocity gradient, subscript s relates to solvent, and nonsubscripted quantities relate to solution.

The most important parameters are the number Z of statistically independent ideally elastic links with $Z + 1$ beads, the root mean square link length b_0, and the hydrodynamic radius a_h of bead. The hydrodynamic interaction parameter is $h^* = (3/\pi)^{1/2}a_h/b_0$, the mean-square end-to-end distance $Zb_0{}^2$, and gyration radius $Zb_0{}^2/6$. The former relation is valid from $Z = 1$ on, the latter one from $Z = 2$ on. One can make the number of beads proportional to molecular weight, i.e., $Z + 1 = M/M_0$, where M_0 is the molecular weight of a bead. One will adhere to this choice in that which follows. But one puts often Z proportional to M so that each link corresponds to the same molecular weight M_0. The difference between the two choices does not matter very much at high Z but is very marked at small Z. The model containing one single link has in the former case a molecular weight $2M_0$ but only M_0 in the latter case.

The very modest quantitative information about the amount and effects of coil deformation in flow severely restricts the reliable range of gradient dependence investigation to the limit of zero gradient, $\dot{\gamma} \rightarrow 0$. This includes the wide spectrum of dynamic viscosity with the frequency ω ranging from 0 to ∞. On both ends one has a Newtonian range where the viscosity is independent of frequency. In the lower range, $\omega \rightarrow 0$, the first Newtonian viscosity $[\eta]_0$ is higher than in the

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[†] Dedicated to M. L. Huggins on his 80th birthday.