BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 17, pp. 3377–3384, 1995

0032-3861/95/$10.00+0.00

The Mark–Houwink–Kuhn–Sakurada exponent of polymers with long side groups: is $a_0 = 1/2$ a reliable criterion of the theta state?

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(Received 14 January 1994; revised 6 February 1995)

The intrinsic viscosity data for poly(decyl acrylate), poly(cetyl acrylate), poly(vinyl laurate), poly(vinyl stearate) and two polymethacrylates with long mesogenic side groups are reviewed and analysed by means of three sensitive plots. Unusual values of the Mark–Houwink–Kuhn–Sakurada exponent a_0 under theta conditions or in good solvents ($A_2 \neq 0$ but $a_0 = 1/2$) are assigned to a combination of the effects of long-chain branching, chain thickness and, in the last case, excluded volume.

(Keywords: intrinsic viscosity; side groups; second virial coefficient)

INTRODUCTION

The Flory theta temperature of polymer solutions is defined as the temperature where the second virial coefficient A_2 vanishes[1]

$$A_2 = 0 \qquad (1)$$

The theory of polymer solutions[1] predicts that the theta temperature can also be estimated by extrapolating (to infinite chain length) the critical solubility temperature obtained from the phase equilibrium in solution. Since in practice (as we will see later) these values need not be identical, we distinguish them by superscripts (A and PE).

According to the hydrodynamic theory for polymer random coils in the non-draining regime[2], the intrinsic viscosity $[\eta]_\theta$ under theta conditions should be proportional to the square root of the molecular weight M. In other words, the exponent a of the Mark–Houwink–Kuhn–Sakurada (MHKS) equation

$$[\eta] = KM^a \qquad (2)$$

should be

$$a_{A_2=0} \equiv a_0 = 1/2 \qquad (3)$$

The validity of these postulates has been confirmed by experiments with many polymers referred to as 'flexible'. On this basis, the proportionality of $[\eta]$ to $M^{1/2}$ has frequently been used as a criterion of theta conditions which is easier to apply than that given by equation (1).

Nevertheless, some polymers which, by their main chain, can be assumed to be flexible do not comply with these postulates: either $A_2 = 0$ and a_0 differs from 1/2, or, less frequently, A_2 is positive and rather high but the exponent is equal or close to 1/2. Some poly(n-alkyl acrylate)s with long alkyl groups, poly(vinyl laurate), poly(vinyl stearate) and polymethacrylates with long side chains comprising ester, ether and/or amide groups belong to the group of anomalous polymers[3–11] (*Table 1*).

To explain these anomalies Platé and Shibaev[12,13] have advanced the hypothesis that, owing to the difference in structure of the main chain and side groups, polar and non-polar sections of the chain segregate into domains so that intermolecular attractive and repulsive forces between segments mutually compensate at a different temperature (θ^A, where $A_2 = 0$) than for the intramolecular case (θ^η, where $a_0 = 1/2$).

The existence of two or three different theta temperatures with branched polymers has gained theoretical support in the papers by Candau *et al.*[14] and Khokhlov[15]. Anyway, some facts indicate that the above failure of the two-parameter theory of polymer solutions may be merely an apparent one and that other potential explanations should be considered before accepting the hypothesis of Platé and Shibaev[12,13].

According to recent theories of intrinsic viscosity based on the worm-like chain model[16–18], the quotient a_0 should be constant over a broad range of chain lengths and equal to 1/2 only if the reduced chain diameter d_r (i.e. the ratio of the chain diameter d_r and the Kuhn segment length l_K) is close to 0.4. For $d_r \neq 0.4$ the quotient a_0 is not constant. For $d_r > 0.4$, a_0 slowly increases from a value lower than 1/2 to exactly 1/2 at high chain lengths. For $d_r < 0.4$, a_0 decreases to the same limit.

On this basis Magarik and Pavlov[19] were able to explain the unusual behaviour of poly(methyl methacrylate-*g*-styrene) with a high density of grafting (one

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Table 1 Systems analysed in this paper

		Temperature of measurement			
Polymer[a]	Solvent[b]	θ (°C)	Other (°C)	a	Ref.
PDA	EtOAc	10 (PE)[c]		0.46	6
	n-PrOH	70.3 (A_2)[c]		0.41	5
	n-BuOH	24.5 (PE)		0.44	6
		19.5 (A_2)		0.41	5
	n-AmOH	−4.8 (A_2)		0.36	5
	i-AmOH	8.5 (PE)		0.42	6
	n-Decane	−19.6 (A_2)		0.60	5
PCA	n-BuOAc		15.2[d]	0.52	4
	n-HpOH	24.8 (A_2)		0.45	3
	n-Decane	10.2 (A_2)		0.67	3
	n-Heptane		21[e]	0.62	4
PVL	n-Pentane		21[d]	0.60	7
PVSt	n-Octane		17[e]	0.50	8
PMA I	CCl_4		20[d,f]	0.50	10
PMA II	CCl_4		20[d,f]	0.50	10
PMA III	DMF		25[e]	0.50	11
	DMF–methanol	25[g]		0.40	11

[a] PDA, poly(decyl acrylate); PCA, poly(cetyl acrylate); PVL, poly(vinyl laurate); PVSt, poly(vinyl stearate); PMA I to PMA III are polymethacrylates with side groups COOPhOCOPhOR (I and II) and $COOPhCOOPhOCH_3$ (III), where Ph stands for a phenylene group and R for nonyl (I) and cetyl (II) groups

[b] EtOAc, ethyl acetate; AmOH, amyl alcohol; HpOH, heptanol; DMF, *N,N*-dimethylformamide; DMF–methanol was a mixture of DMF with 68 vol% methanol

[c] Method of estimation of θ: phase equilibria (PE); $A_2 = 0$ (A_2)

[d] Thermodynamic conditions not specified

[e] A_2 of the order of $10^{-4}\,\mathrm{cm^3\,mol\,g^{-2}}$

[f] Theta temperature assumed to be 20°C[4,7,10]

graft per two or three main-chain monomeric units) and with branches comprising 16–22 styrene units. This model was also used in studies of polymethacrylates with long mesogenic side chains[11].

The a value can result from a superposition of several effects. For good solvents it should be higher than 1/2, but extensive long-chain branching (provided it increases with increasing molecular weight) can reduce it to 1/2 or even below this value without making the logarithmic plot of $[\eta]$ vs. M conspicuously non-linear[20].

The accuracy of the a value depends on the accuracy of the experimental data and on the breadth of the range of molecular weights.

We believe that it is worth examining these possibilities to explain the inconsistency mentioned above. A discrimination between them can be made by plotting data according to methods which are more sensitive than the simple logarithmic plot of $[\eta]$ vs. M and which are based on theories taking account of different factors affecting the hydrodynamic properties.

This is done in the present paper. In the first part, the methods are described, and their advantages and shortcomings are briefly reviewed. In the second part they are applied to experimental data for polymer–solvent systems where the reported exponent a_0 at the theta condition ($A_2 = 0$) is higher or lower than 1/2 or where a is equal to 1/2 under thermodynamically specified conditions. Data for good solvent systems (where $A_2 > 0$) are employed only where they can help to clear up the problem.

METHODS

Three methods of plotting the intrinsic viscosity data are employed. In view of the large differences in the molecular weights m_0 of the monomeric units of the polymers under study, it is convenient to use the degree of polymerization P instead of the molecular weight M, where $P = M/m_0$. In the following, subscripts standing at P distinguish the weight-average degree of polymerization P_w (mostly estimated by light scattering) and the SD average obtained by combining the sedimentation and diffusion coefficients.

Method A (Burchard–Stockmayer–Fixman (BSF))

The method is based on the equations[2,21,22]

$$[\eta]/P^{1/2} = K_0 m_0^{1/2} + c_\eta B m_0 P^{1/2} \tag{4}$$

and

$$K_0 = \phi_{0,\infty}(\langle R^2\rangle_0/M)_\infty^{3/2} \tag{5}$$

where c_η is a numerical constant, $\phi_{0,\infty}$ is the Flory viscosity constant ($\phi_{0,\infty} = 2.6 \times 10^{21}$ if the intrinsic viscosity is expressed in decilitres per gram) and B is a characteristic of the polymer–solvent interaction. $B = 0$ at the theta condition, is positive in 'good' solvents (where $A_2 > 0$) and negative in 'poor' ones ($A_2 < 0$). The ratio of the 'unperturbed' mean square end to end distance $\langle R^2\rangle_0$ and the molecular weight in the random coil limit, $(\langle R^2\rangle_0/M)_\infty$, is related to the Kuhn statistical segment length l_K by the equation

$$l_K = M_L(\langle R^2\rangle_0/M)_\infty \tag{6}$$

where M_L is the mean molecular weight per unit contour length. For polymers discussed in this paper

$$M_L = (m_0/2.5) \times 10^8\,\mathrm{cm^{-1}} \tag{7}$$

The BSF method has been proposed to eliminate the excluded volume effect by extrapolating data to $P^{1/2} = 0$. Since this effect begins at P values exceeding a critical value P_c (which is the higher the stiffer the chain)[23], the extrapolation to $P^{1/2} = 0$ is not quite correct. Anyway, if applied carefully it usually yields a good approximation to K_0.

Serious errors may arise if the plot is used in the region of low degrees of polymerization where polymer chains cannot be represented by the non-draining random coil model. It has been shown[24] that the cross-sectional diameter plays a role in this region and that, for example, the minimum of the A plot at low values of P indicates $d_r > 0.4$. On the contrary, plateaux and/or maxima at high degrees of polymerization are an indication of long-chain branching (see the Appendix and elsewhere[20]).

Method B (Hearst)

The plot of $P/[\eta]$ vs. $P^{1/2}$ is based on the equation

$$P/[\eta]_\theta = (A'_\eta/m_0) + (1/K_0 m_0^{1/2})P^{1/2} \tag{8}$$

resulting from the theory of the worm-like chain model for[25,26] $d_r > 0.1$. $A'_\eta = 0$ at $d_r = 0.4$, is positive for $d_r < 0.4$ and negative for $d_r > 0.4$.

Equation (8) was derived for linear chains under theta conditions; accordingly, the B plot should be linear only with such systems. It is curved upwards with branched chains under theta conditions and downwards (at $P > P_c$) with linear chains in good solvents. Its shape for branched chains in good solvents depends on the prevalence of the effects of branching or excluded-volume (see the Appendix). Under theta conditions, it may be almost linear and have a non-zero intercept even if $d_r = 0.4$. Thus, its diagnostic power for good solvent data is limited.

Method C

The plot of $[\eta]$ vs. $P^{1/2}$ is based on the equation

$$[\eta]_\theta = A''_\eta + K_0 m_0^{1/2} P^{1/2} \tag{9}$$

which also follows from the theory of worm-like chains[18,27]. It has been shown recently[27] that $A''_\eta = 0$ at $d_r \approx 0.4$, is positive for $d_r > 0.4$ and negative for $d_r < 0.4$. Anyway, using equation (9) is recommended only for[27] $d_r > 0.4$. The expansion of chain dimensions by the excluded volume effect in good solvents makes the plot bend upwards at $P > P_c$. Branching has the opposite effect.

RESULTS AND DISCUSSION

Poly(n-alkyl acrylate)s

Out of the poly(n-alkyl acrylate)s, only the decyl and cetyl derivatives have been studied under theta conditions[3–6]. It is remarkable that the reported a values for these polymers in alcohols and esters are lower than 1/2 while being higher than 1/2 in n-alkanes. Therefore, the discussion is divided into two parts.

Poly(n-alkyl acrylate)s in alcohols and esters. The analysis is simplest with poly(cetyl acrylate) (PCA). The A plot, $[\eta]_\theta/P^{1/2}$ vs. $P^{1/2}$, for solutions in butyl acetate (*Figure 1a*) has a decreasing trend in contradiction to equations (1) and (3). A probable explanation is that the chains have long branches, the degree of branching increasing with increasing P. This is supported by the shape of the A plot for solutions in n-

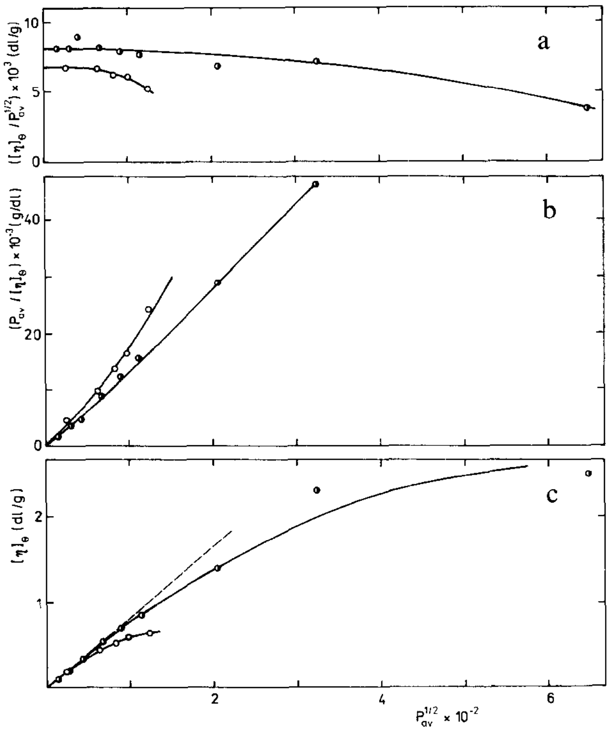

Figure 1 A, B and C plots (a–c, respectively) for poly(cetyl acrylate): (○) n-heptanol at $\theta^A = 24.8°C$[3]; (○) n-butyl acetate[7] at $\theta^{PE} = 15.2°C$[4]. P_{av} stands for P_{SD} (◑) or P_w (○)

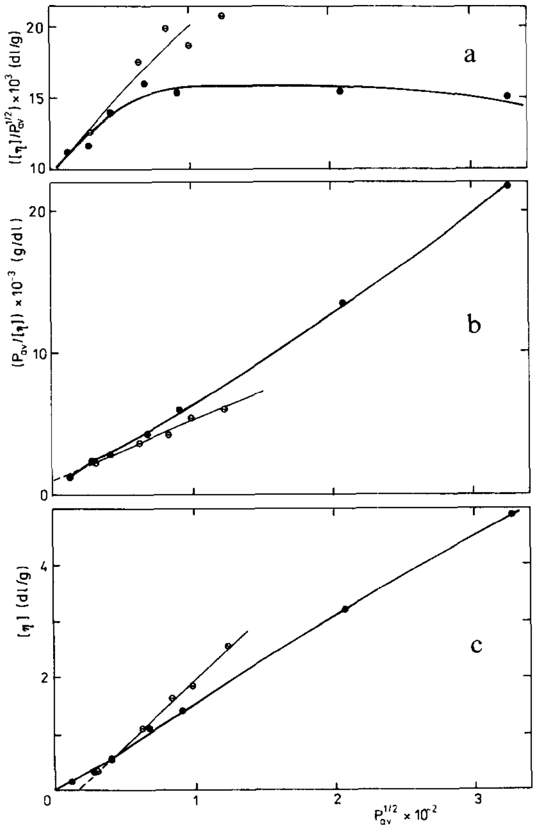

Figure 2 A, B and C plots (a–c, respectively) for poly(cetyl acrylate) in n-alkanes: (⊖) n-decane at $\theta^A = 10.2°C$[3]; (●) n-heptane (good solvent) at 21°C[4]. P_{av} stands for P_{SD} (●) or P_w (⊖)

heptane, a good solvent (*Figure 2a*), which is typical of polymers with long branches[20].

The shape of the A plot for 1-heptanol at θ^A (*Figure 1a*) is similar to that for butyl acetate and can be explained in the same way. The shapes of the B and C plots (*Figures 1b* and *1c*) are those expected for branched chains under theta conditions. Their intercepts are very close to zero, indicating $d_r \approx 0.4$. Thus, low a_0 values for PCA can be attributed to the effect of branching.

Poly(decyl acrylate) (PDA) has been investigated by two groups of authors[5,6] in six theta solvents, four of them being aliphatic alcohols. Theta temperatures were estimated by extrapolating to $1/P = 0$ the threshold temperatures of the cloud point curves[6] or by extrapolating to $A_2 = 0$ the temperature dependence of the second virial coefficient[5].

The A plots (*Figure 3a*) for all the theta solvents have a decreasing trend which contradicts the standard theory of the intrinsic viscosity. The contradiction can be cleared up by a detailed analysis of the data for 1-butanol.

For PDA in 1-butanol, two different theta temperatures ($\theta^A = 19.5°C^5$, $\theta^{PE} = 24.5°C^6$) have been estimated by thermodynamic methods, and a third value ($\theta^\eta = 40°C$) is the temperature where the intrinsic viscosity is proportional to $M^{1/2}$. The difference between the first two values is not large and can be explained. The identity of θ^A and θ^{PE} is postulated by the classical theory of phase equilibria in polymer solutions[1] where only one polymer–solvent interaction parameter χ_1 is considered which becomes equal to 1/2 at the theta temperature. The postulate is not valid if higher order interactions are taken into account by introducing the parameters χ_2, χ_3 and so on. Then, as has been shown recently[28], the θ^{PE} values for systems with an upper critical solution temperature may be higher than θ^A.

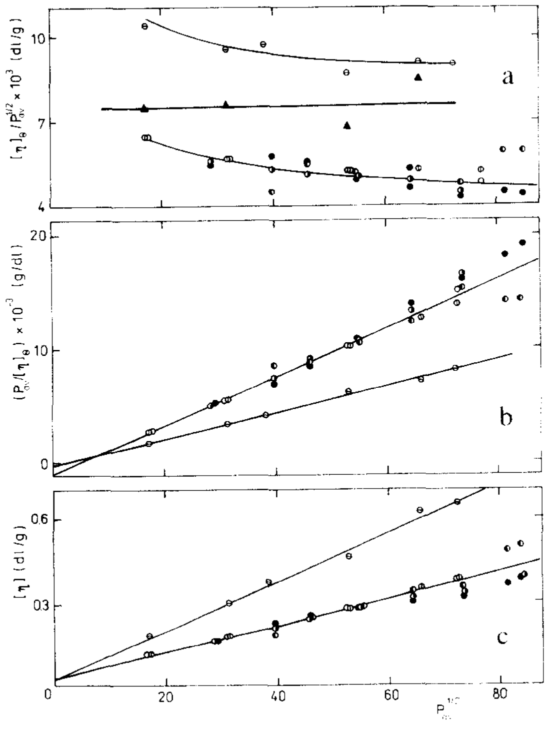

Figure 3 A, B and C plots (a–c, respectively) for poly(decyl acrylate) in aliphatic alcohols and esters: (●) n-amyl alcohol at $\theta^A = -4.8°C^5$; (○) isoamyl alcohol at $\theta^{PE} = 8.6°C$; (⦶) 1-butanol at $\theta^{PE} = 24.5°C^6$; (◑) 1-butanol at $\theta^A = 19.5°C^5$; (▲) 1-butanol at $40°C^6$; (◐) n-propanol at $\theta^A = 70°C^5$; (⊖) ethyl acetate at $\theta^{PE} = 10°C^5$. P_{av} stands for P_w (●, ◑, ◐) or P_{SD} (⦶, ⊖, ○, ▲)

On the other hand, the incorporation of χ_2 has no noticeable effect on the molecular weight dependence of the chain dimensions or intrinsic viscosity (except for very low molecular weights)[29]. Hence, the difference cannot be accounted for in these terms.

We are inclined to accept explanations based on the plots in *Figures 3b* and *3c*. They are linear up to $P \approx 3000$ and their intercepts, though of low precision, are non-zero, their signs indicating d_r to be higher than 0.4. Thus, the a_0 value ($a_0 < 1/2$) for PDA in 1-butanol (and in other alcohols) appears to result mainly from the effect of chain thickness.

The slopes of the B and C plots for PDA in ethyl acetate differ significantly from those for PDA in alcohols and confirm a remarkable solvent effect[6] on K_0 and $(\langle R^2 \rangle_0 / P)_\infty$.

Analysis of the data for PCA and PDA in aliphatic alcohols and esters under theta conditions shows that the contradiction in thermodynamic and hydrodynamic properties ($A_2 = 0$ and $a_0 < 1/2$) is merely an apparent one, and can be explained without abandoning the framework of the two-parameter theory.

Poly(n-alkyl acrylate)s in n-alkanes. The a_0 values for PCA and PDA in n-decane are unusually high (0.67 and 0.60, respectively[3–5]). Data for the latter system cover too narrow a range of P values (825–2100) and are therefore not considered in the analysis to follow.

The theta temperatures for PCA have been determined in n-hexane (5.8°C), n-octane (8°C) and n-decane (10.2°C)[5]. By interpolation between the θ^A values for n-hexane and n-octane, the θ^A value for n-heptane is estimated to be 7°C. Viscosity measurements have been made in n-heptane at 21°C[4] and in n-decane at $\theta^A = 10.2°C^5$.

The shape of the plots for PCA in n-heptane (*Figure 2*) results from a combination of two effects. This is particularly clear with the A plot. The plateau at high values of P can be attributed to long-chain branching, whereas the positive initial slope is indicative of a strong excluded volume effect, consistent with the temperature of measurement being about 14°C above θ^A. The B and C plots extrapolate to zero intercepts, indicating $d_r \approx 0.4$.

The behaviour of solutions of PCA in n-decane is puzzling. The viscosity data refer to θ^A but the A plot (*Figure 2a*) is not horizontal. Its similarity to the initial part of the plot for n-heptane rather suggests that n-decane at this temperature is not a theta solvent but a good one, comparable to n-heptane at 21°C. Then, of course, linear extrapolation of the B and C plots is inappropriate and to non-zero intercepts are questionable.

If, on the contrary, we accepted the θ^A value to be correct, the behaviour of PCA in n-decane would be unlike that in n-heptane. Despite the similarity to the plot for the latter system, extrapolation of the A plot would be inappropriate and the plots in *Figures 2b* and *2c* should be preferred. Their intercepts ($A'_\eta > 0$, $A''_\eta < 0$) would indicate d_r to be lower than 0.4.

We arrive at a dilemma which actually cannot be solved. The value of θ^A should be checked and the intrinsic viscosity measured over the broadest range of P values possible to make the plots more convincing.

Esters of poly(vinyl alcohol)

Values of the exponent a reported for poly(vinyl laurate) (PVL) in n-pentane[7] and poly(vinyl stearate) (PVS) in n-octane[8] are close to 1/2 and seemingly indicate theta conditions. However, the second virial coefficient for the latter system[8] is of the order of 10^{-4} cm^3 mol g^{-2}, so the effect of the excluded volume on the hydrodynamic properties should be taken into consideration. No specifications of the thermodynamic interaction are available for the former system.

The A plots (*Figure 4*) have a maximum and a plateau for $P > 2500$ and are similar to those for polymers with long branches dissolved in a good solvent. However, the B and C plots show that the situation is more involved. They are non-linear, the sense of their curvature confirms long-chain branching, and their intercepts are non-zero and correspond to $d_r < 0.4$.

The effect of branching appears to be stronger than the excluded volume effect, which would make the B and C plots bend in the opposite sense. Thus, three factors combine to make the exponent a close to 1/2: long-chain branching, chain thickness and the excluded volume effect. However, the last of these is 'hidden' and cannot be detected without knowledge of the second virial coefficient.

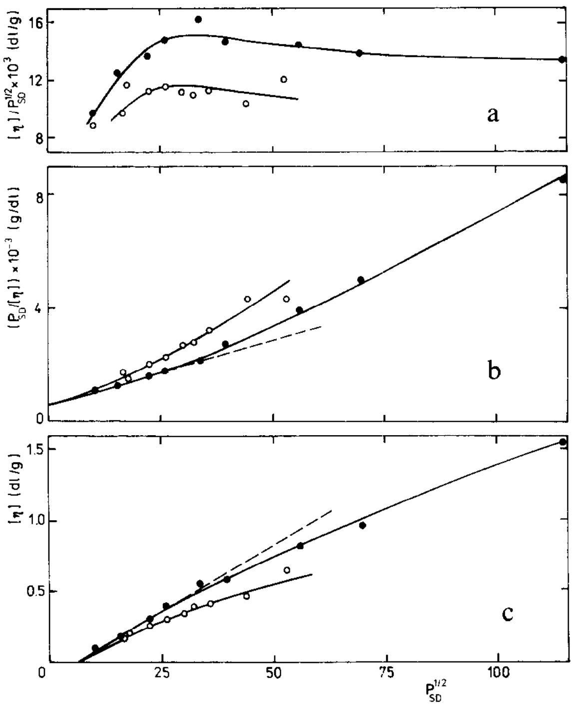

Figure 4 A, B and C plots (a–c, respectively) for esters of poly(vinyl alcohol): (○) stearate in n-octane[8]; (●) laurate in n-pentane[7]

Polymethacrylates

The anomalies observed with poly(n-alkyl acrylate)s and esters of poly(vinyl alcohol) with long side groups raise the question of whether the corresponding polymethacrylates are anomalous, too. As for poly(n-alkyl methacrylate)s, an unambiguous answer cannot be given. In a study of the cetyl ester, Ricker and Schmidt[30] found $a_0 < 1/2$ for theta systems, whereas Zhongde *et al.*[31] detected no anomalies with this or other similar derivatives in poor or good solvents.

On the other hand, two examples can be presented where the exponent a being close to 1/2 probably results from a superposition of the effects of chain thickness and excluded volume.

In a study[11] of polymethacrylates containing a sequence of methylene groups, ester and ether units, and aromatic rings in their side chains, the exponent a was found to be 1/2 in N, N-dimethylformamide, even though the second virial coefficient was of the order of 10^{-4} cm^3 mol g^{-2}, and lower than 1/2 under conditions close to the theta state. This behaviour was assigned to the effect of chain thickness ($d_r > 0.4$).

A similar value of the exponent a was reported for polymethacrylates I and II (*Table 1*), and, on this basis, the solvent (tetrachloromethane) was classified as a theta solvent. No independent thermodynamic data were presented in support of this statement.

Hydrodynamic data for these polymers are now analysed. The A plot (*Figure 5*) has a distinct minimum which is typical[24] of solutions in good solvents of polymers whose reduced chain diameters d_r are higher than 0.4. The minimum can be identified with the region where the excluded volume effect starts to prevail over the effect of the chain thickness. It can be seen that tetrachloromethane is not a theta solvent for these polymers. The shapes of the other plots (*Figures 5b* and *5c*) are consistent with this conclusion.

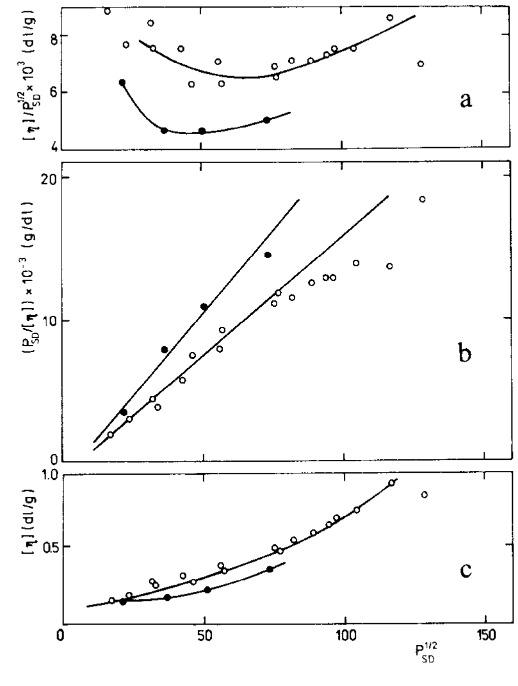

Figure 5 A, B and C plots (a–c, respectively) for polymethacrylates in tetrachloromethane: (●) PMA I; (○) PMA II[9]. For the structures of the polymers, see *Table 1*

Conformational parameters of polymer chains

The plots for esters of poly(vinyl alcohol) are examples of an involved case where the effects of the excluded volume, chain branching and chain thickness combine to preclude the evaluation of the conformational parameters from the initial slopes of the B and C plots or from the intercept of the A plot. The situation is more

Table 2 Conformational characteristics of polymer chains[a]

Polymer[b]	Solvent[b]	Temperature (°C)	$10^3 K_0$ (dl g^{-1}) A plot	B plot	C plot	$10^{16}(\langle R^2\rangle_0/M)_\infty$ (cm^2)	C_∞	$10^8 l_K$ (cm)	d_r	$10^8 d$ (cm)
PDA	EtOAc	10		0.59	0.60	0.38	19	32.5	>0.4	>13
	BuOH	19.5		0.35	0.31	0.25[c]	16[c]	22[c]	>0.4	>8
PCA	HpOH	14.8	0.38	0.42	0.38	0.28	19	34	≈0.4	≈13
	BuOAc	15.2	0.46	0.44	0.46	0.31	21	37	≈0.4	≈15
PMA II	CCl_4	25			0.22	0.20	23	40	>0.4	>16
PMA III	DMF–methanol	25			0.15	0.16	15.1	28	>0.4	>11

[a] Values of $(\langle R^2\rangle_0/M)_\infty$, C_∞ and l_K were computed from the arithmetic means of the K_0 values

[b] Abbreviations as in *Table 1*

[c] Almost identical values were obtained with other alcohols

favourable with three polymers where only two factors operate (chain branching and/or thickness with PCA and PDA; chain thickness and excluded volume effects with polymethacrylates II and III). With polymethacrylate I, where these conditions are also met, the data are too few.

Table 2 summarizes the molecular parameters obtained for PDA, PCA, and polymethacrylates II and III. Some of these parameters differ somewhat from those reported in the original papers where the analysis had neglected some factors which, as is shown in the present paper, are significant.

The parameters were computed from the K_0 values by means of equations (5)–(7) and (10)

$$C_\infty = (\langle R^2\rangle_0/M)_\infty m_0/2l_b^2 \qquad (10)$$

where C_∞ is the characteristic ratio (in the random coil limit), $l_b = 1.5 \times 10^{-8}$ cm is the length of the main-chain C–C bond[32]. The effective hydrodynamic diameter d was calculated for systems where d_r was close to 0.4 ($A'_\eta = A'' \approx 0$), whereas the lower limit is presented for the other cases where only the lower bound to d_r could be estimated.

CONCLUSIONS

The results of the present analysis of the intrinsic viscosity data may be summarized in the following points.

1. With poly(decyl acrylate) and poly(cetyl acrylate), long-chain branching or chain thickness ($d_r > 0.4$) or both are responsible for the exponent a_0 in alcohols under theta conditions being lower than 1/2.
2. The behaviour of poly(cetyl acrylate) in n-decane ($a_0 > 1/2$) can be explained by d_r being less than 0.4. However, in view of the similarity of the data for solutions in n-decane (under theta conditions) and n-heptane (a good solvent), this explanation could merely be a working hypothesis to initiate new experiments.
3. With esters (laurate and stearate) of poly(vinyl alcohol) in n-alkanes, which are good solvents, the value $a \approx 1/2$ results from a combination of three effects: chain thickness, excluded volume and long-chain branching.
4. Only the first two factors operate with polymethacrylates with long mesogenic side groups, and they are mutually compensated to make $a \approx 1/2$.
5. With polymers of this type, the value $a \approx 1/2$ is not an indication of the theta state.
6. The presence of long branches on the chains of polyacrylates and esters of poly(vinyl alcohol) is in line with the well-known fact that chain transfer reactions are extensive during the radical-initiated polymerization of acrylics and esters of vinyl alcohol (e.g. vinyl acetate)[33,34]. Since the degree of branching depends on the polymerization conditions and conversion and usually increases with increasing degree of polymerization, differences in the structure and behaviour of different polymers and different samples of the same polymer can be expected, particularly at high degrees of conversion or polymerization or both.

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APPENDIX

To show the impact of branching on the A and B plots, we calculate the intrinsic viscosities of randomly branched polymers in good solvents by means of the equations

$$[\eta_b]/[\eta_l] = g' \tag{A1}$$

$$[\eta_l] = K_{0,l} M^{1/2} \alpha_{\eta,l}^3 \tag{A2}$$

$$\alpha_{\eta,l}^3 = 1.05 + 0.87z \tag{A3}$$

and

$$z = k_1 M^{1/2} \tag{A4}$$

where the subscripts l and b refer, respectively, to linear and branched chains. Equation (A3) is the Yamakawa–Tanaka semiempirical formula[2] relating the viscosity expansion factor of linear chains to the excluded volume variable z. It is valid for $\alpha_{\eta,l} < 2.5$. The constant k_1 in equation (A4) comprises, among other things, the polymer–solvent interaction parameter B. The symbol g' stands for a function of the number m of branch units per chain. The latter is assumed to be proportional to the molecular weight

$$m = k_2 M \tag{A5}$$

which is a reasonable assumption with randomly branched chains.

Strictly speaking, g' also depends on the B parameter. However, since this effect has not yet been cleared up satisfactorily, we replace g' by the g_0' function derived for unperturbed chains

$$g_0' = [\eta_b]_\theta / [\eta_l]_\theta \tag{A6}$$

This approximation does not introduce serious errors into the results.

It has been shown[35] that the $g_0'(m)$ function can be nicely fitted by the formula proposed by Stockmayer and Fixman[36]

$$g_0 \approx h_0^3 \tag{A7}$$

where h_0 is the ratio of the effective hydrodynamic radii for the translational motion of branched and linear chains. The h_0 values for the trifunctional random type of branching have been computed by Kurata and Fukatsu[37].

The properties of the A plot for branched chains can be visualized by plotting $\alpha_{\eta,l}^3 g_0'$ vs. z. The z values were computed for selected values of m and $k_2^{1/2}$ by means of the formula

$$z = (k_1/k_2^{1/2}) m^{1/2} \tag{A8}$$

resulting from equations (A4) and (A5). The shape of the curve depends on the ratio $k_2^{1/2}/k_1$, i.e. on the proportions of the effects of the branching density and the polymer–solvent interaction. Curve 1 in *Figure A1* depicts the behaviour of the linear chains ($k_2^{1/2}/k_1 = 0$). At low branching densities (low $k_2^{1/2}/k_1$), the dependence has a flat maximum. As the density of branching increases, the maximum becomes sharper and lower, and shifts to lower values of z (to lower molecular weights). Curves of type 2 were found with poly[2-(triphenylmethyloxy)ethyl methacrylate][20]; those with maxima are obtained by plotting data for some low density polyethylene samples.

To construct a generalized form of the B plot, we plot $z/(\alpha_{\eta,l}^3 g_0')$ vs. z (*Figure A2*). The plots are curved and start at $z/(\alpha_{\eta,l}^3 g_0') = 0$, which is given by the assumption that $A_\eta' = 0$. While curve 1 for linear chains in a good solvent ($k_2^{1/2}/k_1 = 0$) is concave with respect to the

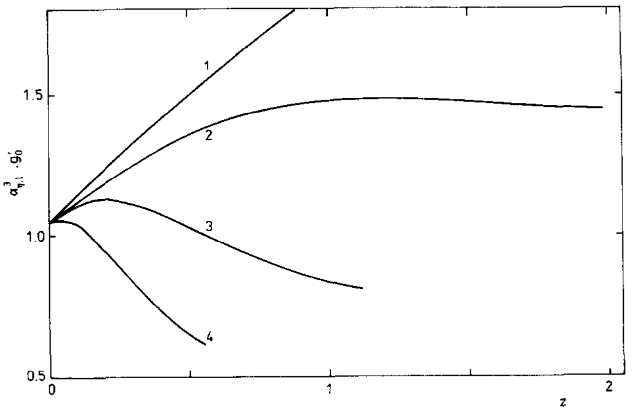

Figure A1 Generalized form of the A plot. The curves were calculated as described in the text: (1) linear chains ($k_2^{1/2}/k_1 = 0$); (2–4) branched chains ($k_2^{1/2}/k_1 = 2$, 3.33 and 10, respectively)

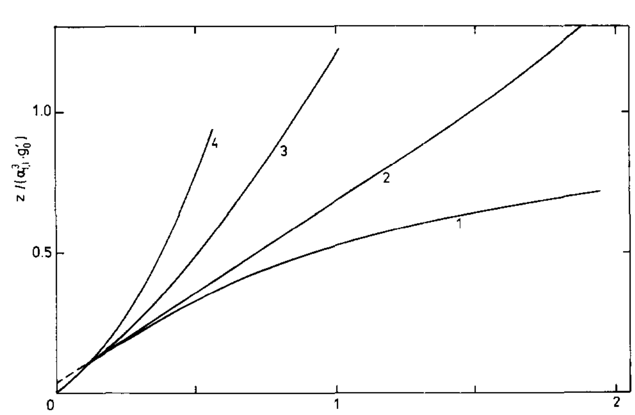

Figure A2 Generalized form of the B plot for good solvent systems (curves as in *Figure A1*) abscissa, curves 3 and 4 (high density of branching) are concave with respect to the ordinate. If, in practice, the data cover a broad range of molecular weights and the density of branching is very high (curves 3 and 4) or zero (curve 1), non-linearity is easily detected and linear extrapolation is avoided.

Curve 2 in *Figure A2* represents a special situation where the effects of the polymer–solvent interaction and branching are in a sort of balance, making curve 2 nearly linear over a broad span of molecular weights ($0.2 \leq z \leq 0.4$). In this case, extrapolation of the apparently linear part (dashed line) would lead to a positive intercept ($A'_\eta > 0$), at variance with the assumption of the calculations ($A'_\eta = 0$), and to erroneous conclusions about the strength of the hydrodynamic interaction.