NON-NEWTONIAN BEHAVIOUR OF DILUTE POLYSTYRENE SOLUTIONS. ANALYSIS IN TERMS OF WOLFF'S EQUATION

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The data published in the literature about the non-Newtonian behaviour of dilute polystyrene solutions were treated in terms of Wolff's equation. The parameters of this equation were correlated with the molecular weight of the polymer, solvent power and viscosity. For $M > 1 . 10^6$, the dependence on molecular weight and solvent power can be summarized into one dependence on the expansion factor. At $M < 1 . 10^6$ the dependence on molecular weight is more involved. The effect of solvent viscosity plays a second-rate role. The results have been compared with the theories of the non-Newtonian flow which take into account the effect of excluded volume and of the viscosity of the solvent.

In 1962 Wolff showed[1] that the dependence of the intrinsic viscosity of polymer solutions, $[\eta]$, on shear stress, τ, can be very well described by the equation

$$[\eta]_r \equiv [\eta]/[\eta]_0 = 1 - \beta_0/(b + a\beta_0) , \qquad (1)$$

$$\beta_0 = M[\eta]_0 \, \tau/RT , \qquad (2)$$

where M is the molecular weight of the polymer, $[\eta]_0$ is the intrinsic viscosity at zero shear stress, β_0 is the reduced shear stress, T is the absolute temperature and R is the universal gas constant. The parameters a and b of Eq. (1) can be determined from the slope and the intercept of the dependence $\beta_0(1 - [\eta]_r)^{-1}$ vs β_0. The parameter a is related with intrinsic viscosity at extreme values of shear stress, $[\eta]_\infty$:

$$[\eta]_\infty/[\eta]_0 = 1 - 1/a . \qquad (3)$$

The success with which the above equation was applied to various polymer systems in later years[2,3] has led us to a summarized treatment of available (our own[4,5] and literary[2,3,6-8]) data on the non-Newtonian behaviour of dilute polystyrene solutions. This polymer (together with cellulose nitrate) was the most frequent object of non-

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-Newtonian studies, so that a comprehensive treatment of the results obtained became desirable a long time ago. The differences between the conditions of measurement (shear stress region, molecular weights of samples, solvent power and viscosity were however such that it was very difficult to compare the results more precisely than only qualitatively. The simplicity of Eq. (1) offers a hope that this difficulty may be overcome and that the treatment of the results obtained so far may contribute to the elucidation of the view of the importance of various factors determining the non--Newtonian dependence of intrinsic viscosity.

While investigating some theoretical dependences $[\eta]_r$–β_0 (model of rigid rotational ellipsoids and of a coil with internal viscosity) Wolff found[9,10] that the dependence $\beta_0/(1 - [\eta]_r)$ on β_0 is not linear in the region of very low β_0. The same appears in the treatment of more recent theoretical functions[11,12] (Figs 1,2) and experimental data (Fig. 3). Almost all theories formulate the dependence $[\eta]_r$–β_0 at low shear stresses in terms of a series expansion according to the even powers of the reduced shear stress β_0

$$[\eta]_r = 1 - A_1\beta_0^2 + \ldots ; \qquad (4)$$

on the other hand, Eq. (1) gives for $\beta_0 \to 0$ the expression

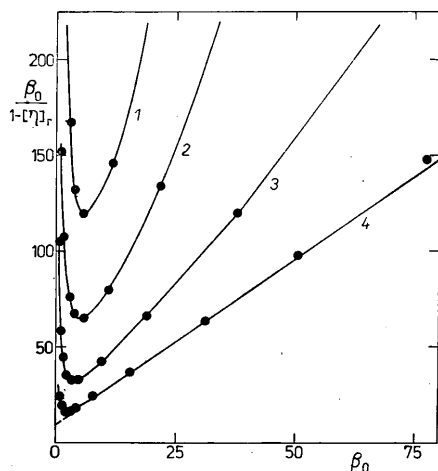$$[\eta]_r = 1 - (1/b)\,\beta_0 + \ldots . \qquad (5)$$

FIG. 1

Dependence $\beta_0/(1 - [\eta]_r)$–β_0 Constructed According to Fixman Theory[11]
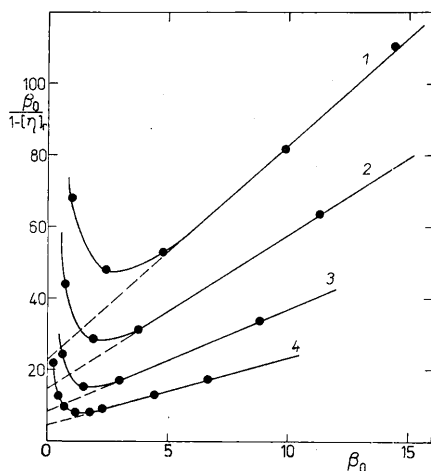
Curves 1—4 for $\alpha_\eta^3 = 1$; 1·31; 2·23; 5·06.

FIG. 2

Dependence $\beta_0/(1 - [\eta]_r)$–β_0 Constructed According to Chikahisa Theory[12]

Curves 1—4 for $\alpha_\eta^3 = 1$; 1·31; 2·07; 4·80.

According to Eq. (4) we have

$$\lim_{\beta_0 \to 0} \left[\beta_0 (1 - [\eta]_r)^{-1} \right] = (1/A_1) \lim_{\beta_0 \to 0} (\beta_0^{-1}), \qquad (6)$$

but according to Eq. (5) it holds

$$\lim_{\beta_0 \to 0} \left[\beta_0 (1 - [\eta]_r)^{-1} \right] = b . \qquad (7)$$

The nonlinear (decreasing) course of the dependence $\beta_0 (1 - [\eta]_r)^{-1}$ on β_0 at low β_0 is easy to understand.

As can be seen from Figs 1 and 2 and from the graphical plot of experimental dependences, the minima are the more pronounced and the β_0 values at which they occur are the higher the closer one approaches the θ-conditions. This is the reason why especially at the θ-temperature the determination of the parameters of Eq. (1) is difficult unless the measurements reach very high shear stresses. Indeed, the parameters a, b cannot be determined by using the results of the majority of measurements carried out with polystyrene solutions at the θ-temperature.

In this connection it seems suitable to stress the importance of the manner in which $[\eta]_0$ is determined. Very often $[\eta]_0$ is determined by the extrapolation of intrinsic
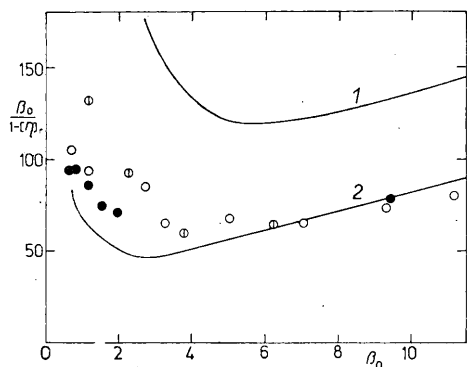

FIG. 3

Dependence $\beta_0/(1 - [\eta]_r)$–β_0 for Polystyrene under the θ-Conditions

Data[4] for $M \cdot 10^6$: ● 0·76; ○ 2·45; ⊕ 3·45 (trans-decalin). Curves 1 and 2 according to Fixman[11] and Chikahisa[12] theory.
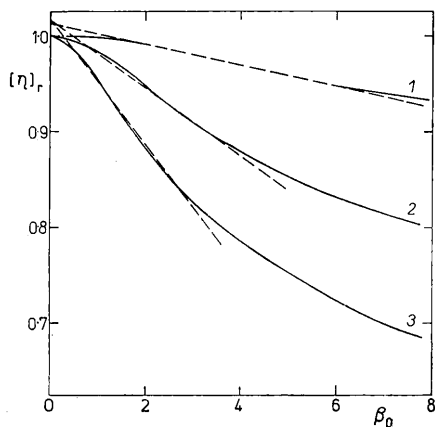
FIG. 4

Dependence $[\eta]_r - \beta_0$ according to Fixman[11]

Full curves 1–3 for $\alpha_\eta^3 = 1·0$; 2·23; 5·06. Broken lines: linear approximation of the central part.

viscosity to zero shear stress or velocity gradient. Since there is no simple, reliable and at the same time physically justifiable extrapolation method known, this operation is always rather arbitrary and brings errors into further work, particularly if the non--Newtonian effects are not much pronounced. This is illustrated by Fig. 4. In this Figure, $[\eta]_r$ calculated theoretically by Fixman[11] are plotted against β_0. Their dependence on β_0 can be easily represented by a straight line in the central (comparatively broad) region. However, the intercept of this straight line is not $[\eta]_r = 1$, but is larger by $1-2\%$. Thus, the linear extrapolation of the dependence $[\eta]-\tau$ usually leads to a higher $[\eta]_0$. The error in itself is not very important, but may play an important role in the further treatment of data according to Eq. (1), particularly at $[\eta]_r$ close to unity; it reduces the values of $[\eta]_r$, makes the minimum on the $\beta_0/(1 - [\eta]_r)$ vs β_0 curves flatter, and can also unfavourably affect extrapolation. Consequently, the necessity of a cautious approach in the determination of the parameters of Eq. (1) in cases of a little pronounced non-Newtonian effect (e.g. in poor solvents, at low molecular weights, low shear stresses etc.) is obvious. For these reasons it was not possible, for instance, to determine the parameter a for fractions having a low molecular weight $0\cdot13 . 10^6$ and $0\cdot39 . 10^6$; the value of b (Table I) is only an estimate (upper limit).

Theoretically speaking, the dependence of intrinsic viscosity on shear stress is determined by a number of factors[13]. Of these, only the effect of excluded volume and the effect of „internal viscosity" can be experimentally studied for polystyrene, the former by varying the solvent power and the molecular weight of the polymer, the latter by varying the solvent viscosity and the molecular weight of the polymer. However, the contributions of these factors are additive[14] only at very low β_0, while at higher β_0 they can affect each other, so that the additivity is not justified. Therefore, a quantitative evaluation of the individual contributions is virtually impossible, unless one can determine the coefficient A_1 in Eq. (4) from experimental data with sufficient accuracy and reliability. Nevertheless, if the parameters of Wolff's equation are correlated with the expansion factor α_η^3 (as a measure of the excluded volume), one can find out whether this correlation is unambiguous for a given polymer or whether its unambiguity is limited by other factors (the solvent viscosity, more complicated dependences on molecular weight), and whether it depends on the polymer structure.

Parameter a

The dependence of the parameter a for polystyrene on the expansion factor α_η^3 in Fig. 5 has been constructed from data obtained in this laboratory[4,5] ($M = 1\cdot7 . 10^6$), from those of Passaglia and coworkers[7] ($M = 1\cdot9-3\cdot2 . 10^6$), Wolff[2,3] ($M = 10 . 10^6$), Čopič[6] ($M = 1\cdot6 . 10^6$) and Lohmander and Strömberg[8] ($M = 7\cdot8 . 10^6$). The α_η^3 values were calculated by using the relationship $\alpha_\eta^3 = [\eta]_0/K_0 M^{1/2}$, where

$K_0 = 7\cdot6 \cdot 10^{-4}$. Although the molecular weights cover the whole logarithmic decade and the viscosities of the solvents more than two logarithmic decades, the parameter a is an unequivocal function of the expansion factor. At $\alpha_\eta^3 \geqq 1\cdot8$ in particular the scatter of data is very small. A significant deviation was found only in the data for toluene[7]. Since however other data presented in ref.[7] fit in with the other data, we believe that the deviation is only a random one.

At $\alpha_\eta^3 < 1\cdot8$ and particularly at $\alpha_\eta^3 \simeq 1$ the scatter of data obtained in various laboratories is larger. For the θ-conditions direct measurements give $3\cdot4^2$ and $8\cdot4^7$, while extrapolation of the dependence $a - \alpha_\eta^3$ (Fig. 5) gives $\sim4\cdot5$.

Fig. 6 shows that the dependence of the parameter a or of the ratio $[\eta]_\infty/[\eta]_0$ on the expansion factor can approximately be expressed by the equation

$$[\eta]_\infty/[\eta]_0 \equiv 1 - 1/a = a_1 + a_2/\alpha_\eta^3 . \tag{8}$$

For polystyrene we obtain two pairs of parameters a_1, a_2: one according to the result of measurements from ref.[7] $(a_1 = 0\cdot54; a_2 = 0\cdot32)$, the other according to data of other authors $(a_1 = 0\cdot38; a_2 = 0\cdot40)$. The causes of this difference are not clear. One of them may consist in the fact that the data of Passaglia and coworkers[7] cover rather a broad interval of shear stresses, so that also the parameter a was determined more precisely, especially in poor solvents.
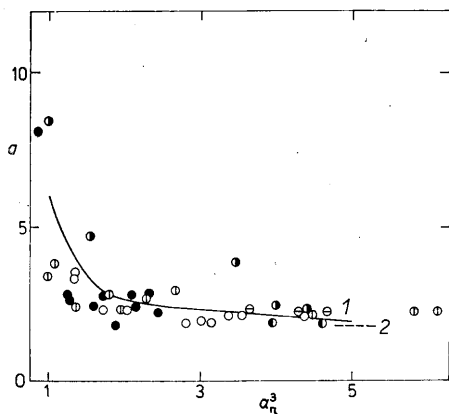

FIG. 5

Correlation of the Parameter a with the Expansion Factor

Points denoted in an order according to ref.[2,4-8]: ①, ○, ●, ⊖, ◑, ◐. Values according to Chikahisa[12] (———), or Fixman (------) theory.
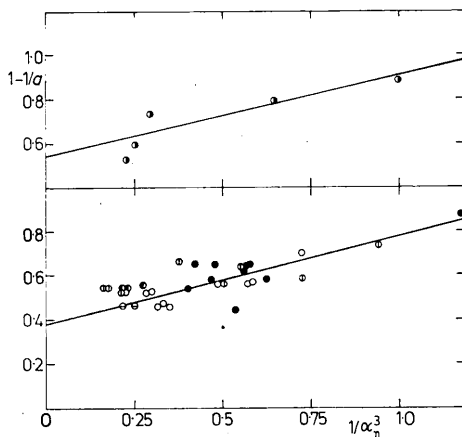
FIG. 6

Dependence of the Ratio $[\eta]_\infty/[\eta]_0$ on $1/\alpha_\eta^3$ Data denoted as in Fig. 5.

It follows from Fig. 5 and Table I that the ratio $[\eta]_\infty/[\eta]_0$ is independent of the solvent viscosity and that its dependence on molecular weight at $M > 1 . 10^6$ is given

TABLE I

Parameters of Eq. (*1*) for Polystyrene

Solvent	t °C	η_s P	$M . 10^{-6}$	$[\eta]_0$ dl/g	a	b	$[\eta]_\infty/[\eta]_0$
trans-Decalin[4]	40	0·0149	1·76	1·43	3·5	22·0	0·71
			2·45	1·71	3·3	15·0	0·70
trans-Decalin[4]	65	0·0102	0·76	1·04	6·0	6·5	0·83
			1·76	1·85	2·3	17·0	0·57
			2·45	2·18	2·3	19·0	0·57
			3·45	3·05	2·3	15·5	0·57
Dioctyl phthalate[5]	25	0·557	1·95	1·04	8·1	19·0	0·88
Butylnaphthalene[5]	25	0·054	2·32	2·60	2·8	16·5	0·65
			2·40	3·06	2·2	16·0	0·55
			4·50	3·97	2·8	18·0	0·65
Ethyl butyrate[5]	25	0·0062	4·00	2·98	1·8	17·0	0·44
Tricresyl phosphate[5]	25	0·618	1·95	1·95	2·8	16·0	0·65
			2·98	2·97	2·4	10·5	0·59
Octyl benzoate[5]	25	0·057	1·95	2·00	2·6	15·5	0·62
Dioctyl phthalate[5]	25	0·161	1·85	1·73	2·4	15·0	0·59
			4·00	2·78	2·8	15·0	0·65
Toluene[4]	25	0·0055	0·131	0·554	—	2	—
			0·390	1·33	—	6	—
			0·76	1·94	1·7	—	0·41
			1·76	3·60	2·1	11·0	0·52
			3·45	6·50	2·1	11·0	0·52
Cyclohexanone[4]	25	0·0199	1·55	2·81	1·8	14·5	0·44
			1·76	3·33	1·8	14·5	0·44
			3·3	4·38	1·9	14·5	0·47
			3·45	5·30	2·1	14·5	0·52
Benzene[6]	25	0·0065	1·65	3·75	2·25	7·0	0·55
			3·70	6·67	2·2	12·0	0·55
			5·00	8·40	2·2	14·0	0·55
Toluene[8]	25	0·0055	7·8	10·3	1·9	44·0	0·47
α-Methylnaphthalene[8]	25	0·0283	7·8	8·8	1·9	44·0	0·47
Cyclohexane– –tetrachloromethane[7]	25		3·22	1·35	8·4	16	0·88
Toluene–n-heptane[7]	25		2·83	2·00	4·7	48	0·79
Toluene[7]	25	0·0055	2·83	5·1	2·45	22	0·59
Tetralin[7]	25	0·02	2·83	5·1	2·45	12	0·59
			1·89	4·6	2·11	12	0·53

only by the relationship between the molecular weight and the expansion factor (and thus through the excluded volume parameter, z). Whether the same rules also hold at $M < 1 \cdot 10^6$ cannot be said because there are only very few experimental works concerning this field, the non-Newtonian effects are little pronounced and the determination of the parameter a is practically impossible.

The independence of the solvent viscosity seems understandable, because at extreme values of τ the polymer molecule is permanently deformed, the effect of intramolecular viscosity is not operative and the decisive role is played by the orientation of the coil.

Parameter b

The differentiation of Eq. (1) with respect to β_0 leads to

$$\mathrm{d}[\eta]_r/\mathrm{d}\beta_0 = -(1/b)(1 + a\beta_0/b)^{-2} . \tag{9}$$

Fig. 7 shows that for polystyrene the ratio a/b is practically constant $(0{\cdot}16 \pm 0{\cdot}04)$ within wide limits of values of the expansion factor $(\alpha_\eta^3 = 1{\cdot}2-5)$. This means that the gradient of the dependence $[\eta]_r-\beta_0$ at a certain β_0 (in a region where the dependence can be described by Wolff's equation) is determined only by the parameter b. Thus, the latter can be regarded as the main criterion of the intensity of the non-Newtonian decrease in the intrinsic viscosity of polystyrene.

An analysis of theories[11,12] which examine the effect of excluded volume on the dependence $[\eta]-\beta_0$ demonstrates that the relationship between the parameter b and molecular weight is determined exclusively through the excluded volume parameter, z, and thus through the expansion factor α_η^3 (according to the Fixman theory[11], this
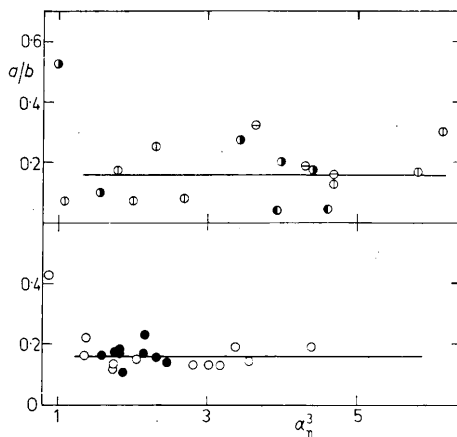

FIG. 7

Dependence of the Ratio a/b on the Expansion Factor α_η^3

Data denoted as in Fig. 5.

holds at least for very high molecular weights). According to both theories, b should decrease with increasing α_η^3 and thus with increasing molecular weight. An analysis[9,10] of the Cerf theory[15], which takes into account the effect of the internal viscosity, predicts (for θ-conditions) an increase in the parameter b with molecular weight.

In Fig. 8 the parameter b is correlated with the expansion factor. The majority of data are related to polystyrene fractions having molecular weight higher than $1 \cdot 10^6$. At $\alpha_\eta^3 < 2$ the data derived from different papers differ considerably (most likely because of difficulties involved in their determination); on the other hand, at $\alpha_\eta^3 > 2$ the agreement is quite good (with the exception of two data[8]). For these fractions the parameter b decreases with increasing α_η^3 (probably to a limit ~ 10) and is unequivocally defined by the latter.

Data for fractions having molecular weight lower than $1 \cdot 10^6$ (Fig. 8a) depart from the above dependence in a downward direction, the more so the lower α_η^3 (or molecular weight). Although not too accurate, they still can be used in this discussion, because they are the upper estimate of the correct value. They show that the dependence $b–M$ in toluene has an upward branch, and thus a maximum (though unpronounced), and that in this region of molecular weights the parameter b is not determined unambiguously by the expansion factor.

The effect of solvent viscosity can be evaluated by comparing the b values determined in solvents having different viscosity at the same (or approximately the same) α_η^3, if $M > 1 \cdot 10^6$. Although the solvent viscosities differ by more than two orders of magnitude, the b values at the same α_η^3 differ either insignificantly (Fig. 8a) or unsystematically (Fig. 8b). It seems moreover that the effect of the solvent viscosity is unimportant also under the θ-conditions. This is derived from the fact that we have found identical b values for three solvents having very different viscosities (decalin,
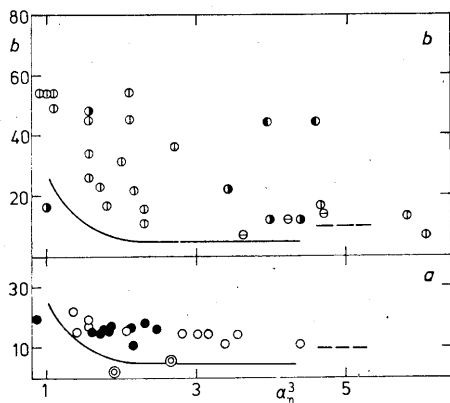

FIG. 8

Correlation of the Parameter b with the Expansion Factor α_η^3

Data denoted as in Fig. 5, double circles $M \cdot 10^{-6} = 0.131$ and 0.390 (Table I). Values according to Chikahisa (———) and Fixman (-------) theory.

octyl benzoate, tricresyl phosphate[5]) at $\alpha_\eta^3 \simeq 1\cdot 3$, and very similar values for a low-viscosity θ-solvent (cyclohexane–tetrachloromethane) and a solvent having a very high viscosity (dioctyl phthalate[5]) at a temperature only a little lower than the θ-temperature (Fig. 9).

Comparison with Theory

According to the Cerf theory[15], at the θ-temperature an increase in molecular weight and solvent viscosity should lead to an increase in the parameter b. If we started with the experimental value $b_0 = 18$, the increase in η_s and M within two orders of magnitude should cause a change in b amounting to almost an order of magnitude. In the actual fact however, as has been shown above, the solvent viscosity has no perceptible effect. Data are missing which would allow us to evaluate the effect of molecular weight under the θ-conditions. In good solvents one observes an increase in the parameter b with molecular weight only at $M < 1 . 10^6$; at higher molecular weights the parameter b very slowly decreases. If more detailed measurements under the θ-conditions do not prove the contrary, we believe that as far as the molecular weight is concerned, the agreement between the above theory and experimental results is only partial.

An analysis of the effect of solvent viscosity and molecular weight, as well as the correlation $b - \alpha_\eta^3$ or $a - \alpha_\eta^3$ (Figs 6 and 8) indicate the decisive effect of the excluded volume on the non-Newtonian behaviour of polystyrene $(M > 1 . 10^6)$ at low and high shear stresses. This is why it seems worthwhile to compare the experimental dependences $a - \alpha_\eta^3$ or $b - \alpha_\eta^3$ with those derived from theoretical investigations taking into account the effect of excluded volume. In the discussion that follows we shall restrict ourselves to the Fixman and Chikahisa theories[12]. Both these theories predict – in accord with reality – the non-Newtonian behaviour also under the θ-conditions (in contrast with the Subirana theory[16]) and a strengthening of the non-Newtonian effect at higher values of the parameter z.

In the Chikahisa theory[12] the polymer molecule is modelled by a rotational ellipsoid whose half axis ratio is determined only by the effect of excluded volume at rest $(\tau = 0)$ and remains unchanged by hydrodynamic forces. The Fixman theory[13] takes into account the deformation of the coil at the same time, an unlimited deformability of the chain (and thus also the upturn on the curves of the dependence $[\eta]_r-\beta_0$) follows from the nature of the model.

The $\beta_0/(1 - [\eta]_r)-\beta_0$ dependences constructed according to both theories are shown in Figs 1 and 2. One of the main assumptions of the Chikahisa theory, namely the negligible deformation of the coil, restricts its results and applicability to the region of low shear stresses $(\beta_0 < 10-15)$. Although the dependences in Fig. 2 can be linearized, one may still have doubts as to the accuracy of the a and b values obtained,

and particularly as to the fact whether the parameter a can be compared with the value found experimentally for a deformed chain.

On dependences according to the Fixman theory (Fig. 1) the abovementioned upturn is reflected in a nonlinear course of the curve beyond the minimum, especially at low expansions $(\alpha_\eta^3 = 1 - 2\cdot23)$. In this case extrapolation would be completely arbitrary. Only for a system designated in the original paper by I-7 $(\alpha_\eta^3 = 5\cdot06)$ the dependence $\beta_0/(1 - [\eta]_r)-\beta_0$ is linear within a broad range of β_0 so that the determination of the parameters of Eq. (1) becomes feasible. Not even in this case however is it worthwhile to consider the meaning of the parameter a, because the "upturn" — although it appears here only at very high β_0 — rules out the existence of a second non-Newtonian region.

The above limitations should be borne in mind while approaching a further analysis of theoretical and experimental dependences (Figs 5 and 8). The value of b which is derived from the Chikahisa theory for the θ-conditions $(b_0 = 24)$ is close to the lower limit of the interval $(b_0 = 18)$ which was found by analyzing compiled data. The b values for higher expansion coefficients amount only to values from 1/3 to 2/5 of the experimental values of b and of the value obtained by using the Fixman theory (system I-7). The cause of the difference between the theoretical results might be due to a different approach to the deformation of the polymer chain in the Chikahisa theory. The sign of the difference coincides with what is expected $(cf.$ the effect of deformation[13]$)$.

As to the parameter a, we can see from Fig. 5 that at $\alpha_\eta^3 > 2$ experimental values almost coincide with the theoretical ones. We believe however that this coincidence is only a random one. It would mean that the deformation of the polystyrene molecule at extreme shear stresses would be negligible (from comparison with the Chikahisa theory), although judging by the b values an important deformation may be present already at lower β_0.

In conclusion one may summarize that the analysis of dependences $[\eta]-\tau$ found for polystyrene shows that the magnitude of the non-Newtonian effect is affected in a decisive way by the solvent power, while the effect of the solvent viscosity is imperceptible. Whether the same rules hold also for other polymers of the vinyl type cannot be said for certain. A similar analysis for polyisobutylene and poly(methyl methacrylate) is prevented by the lack of experimental data (especially as far as the effect of solvent viscosity is concerned) or by complicated secondary effects (negative thixotropy of poly(methyl methacrylate) solutions[17]).

REFERENCES

1. Wolff C.: C. R. Acad. Sci. *254*, 4296 (1962).
2. Wolff C.: J. Chim. Phys. Physicochim. Biol. *59*, 1174 (1962).
3. Wolff C.: J. Phys. Rad. *32*, C5a—263 (1971).

4. Quadrat O., Bohdanecký M.: This Journal *33*, 2130 (1968).
5. Poupětová D.: This Journal *39*, 2410 (1974).
6. Čopič M.: J. Chim. Phys. Physicochim. Biol. *54*, 348 (1957).
7. Passaglia E., Jen Tsi Yang, Wegemer N. J.: J. Polym. Sci. *47*, 333 (1960).
8. Lohmader U., Strömberg R.: Makromol. Chem. *72*, 143 (1964).
9. Wolff C.: *Thesis*. Université de Strasbourg, Strasbourg 1967.
10. Cerf R., Wolff C.: Eur. Polym. J. *4*, 317 (1968).
11. Fixman M.: J. Chem. Phys. *45*, 793 (1966).
12. Chikahisa Y.: J. Phys. Soc. Jap. *21*, 2324 (1966).
13. Peterlin A.: *Advances in Macromolecular Chemistry*, Vol. 1, (W. M. Pasika, Ed.) p. 225. Academic Press, London 1968.
14. Peterlin A.: Symposium on Non-Newtonian Viscometry, ASTM Pub. *299*, p. 115 (1962).
15. Cerf R.: Advan. Polym. Sci. *1*, 382 (1958).
16. Subirana J. A.: J. Chem. Phys. *41*, 3852 (1964).
17. Quadrat O., Bohdanecký M.: J. Polym. Sci. Part A2, *5*, 1309 (1967).

Translated by L. Kopecká.