

INFLUENCE OF THE THERMODYNAMIC QUALITY OF A SOLVENT UPON THE VISCOSITY OF MODERATELY CONCENTRATED POLYSTYRENE SOLUTIONS

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Measurements carried out with polystyrene solutions in eleven solvents of different thermodynamic quality have shown that the dependence of the relative viscosity of moderately concentrated solutions upon the expansion factor at a given concentration has a minimum, while the viscosity of more diluted solutions continuously increases. The shape of the dependence in the case of moderately concentrated solutions is explained by superposition of two effects, namely, an increase in the radius of gyration of the polymer coil due to expansion in a thermodynamically better solvent, along with a simultaneous weakening of the strength of mutual contacts between the polymer chains which does not appear to any considerable extent in more diluted solutions. The experimental curves have been compared with those calculated from Baker's equation and Imai's dependence of Huggins' constant upon the expansion factor.

The dependence of the viscosity of concentrated polymer solutions upon molecular parameters has been derived^{1,2} from the relationship for the viscosity of polymer melt

$$\zeta = (1/6) N(\overline{S}_0^2/M) (Z_c/v_2) (Z/Z_c)^a \zeta \quad (1)$$

by replacing the specific volume of the polymer, v_2 , by the ratio of partial specific volume to the volume fraction of the polymer \bar{v}_2/φ_2 . The expression thus obtained was

$$\eta = (1/6) N X_c (X/X_c)^a \zeta \quad (2)$$

Here $X = (\overline{S}_0^2/M) Z(\varphi_2/\bar{v}_2)$ and $X_c = (\overline{S}_0^2/M) Z_c(\varphi_2/\bar{v}_2)$, Z denotes the number of atoms in the polymer chain, ζ the friction coefficient of the part of the macromolecule corresponding to one of these atoms, $(\overline{S}_0^2)^{1/2}$ the radius of gyration of an unperturbed polymer coil, M molecular weight and N is Avogadro's number. The exponent a depends upon the magnitude of X with respect to a certain critical value X_c dependent upon the magnitude of Z_c ; $a = 3.4$ for $X > X_c$ and $a = 1.0$ for $X < X_c$. The friction coefficient ζ is a function of temperature and concentration. Expression (2) does not comprise explicitly the effect of the thermodynamic quality of the solvent, because it is assumed in the theory that similarly to the melt, the size of the coil also remains unperturbed in solutions at a concentration $\varphi_2 > 0.1$. A question then arises how far this assumption is justified, especially for moderately concentrated solutions. On the contrary, the polymeric coil is quite likely to be expanded in this region in thermodynamically better solvents, so that instead of the characteristic ratio \overline{S}_0^2/M it would be more justified to use in expression (2) the ratio \overline{S}^2/M which includes the radius of gyration of the expanded coil, $(\overline{S}^2)^{1/2} = (\overline{S}_0^2)^{1/2} \alpha$. Al-

though the actual value of the radius of gyration at a given concentration will be lower^{3,4} than in an infinitely dilute solution, it nevertheless will increase with a better quality of the solvent. As a consequence, we can expect, under otherwise identical conditions, also an increase in viscosity with increasing expansion factor α . This effect ought to decrease with increasing polymer concentration in accordance with the radius of gyration approaching the value of $(\overline{S^2})^{1/2}$ taken for the melt of the amorphous polymer.

Although a number of papers have been published on the viscosity of concentrated polymer solutions in various solvents, the effects outlined above have not been investigated in more detail. Their elucidation, and particularly a thorough check up based on the experimental data, both our own and taken from the literature, are the subject of this paper.

EXPERIMENTAL

Material. A polydisperse polystyrene sample ($\overline{M}_n = 2.7 \cdot 10^5$) was obtained by block polymerization initiated with di-tert-butyl hyponitrite. It was reprecipitated from benzene solutions by methanol and dried over phosphorus pentoxide at 60°C. Molecular weight was determined from the intrinsic viscosity of benzene solutions at $25 \pm 0.05^\circ\text{C}$ according to Meyerhoff⁵, $[\eta] = 1.23 \cdot 10^{-4} M^{0.72}$.

Solvents and solutions. Cyclohexanone, butyl acetate, toluene, ethylbenzene, *p*-xylene (anal. purity grade) and decalin (mixture of isomers), tetralin and butyl propionate, pure, were redistilled; dibutyl phthalate, dimethyl phthalate and 1-butyl-naphthalene were purified by column distillation. The solutions were prepared in conic flasks by stirring with steel balls, c. 15 mm dia., revolving the flasks on an inclined plane at 60°C; at higher concentrations the polymer took as long as several weeks to dissolve. The solutions were filtered by squeezing through glass fritted discs S2.

Viscometry. Both the determination of $[\eta]$ in diluted solutions and the measurements of moderately concentrated solutions were carried out in diluting capillary viscometers of Ubbelohde's type. The correction for the loss of kinetic energy and the end effect were negligible owing to long flow times. The extrapolation method has been described⁶.

RESULTS AND DISCUSSION

Before starting the discussion of our own experimental results, let us make a brief survey of information obtainable by an analysis of literary data. Nakayasu and Fox^{2,7} give virtually identical dependences of η vs M for polyvinyl acetate solutions ($\phi_2 = 0.25; 0.5; 0.75; 1$) in a thermodynamically good solvent — diethyl phthalate and a Θ -solvent — cetyl alcohol. However, such a coincidence of the systems is only an apparent one. In view of the fact, that the viscosity of cetyl alcohol is approximately double that of diethyl phthalate, a coincidence of the viscosities of the solutions means that there is a difference in the relative viscosities in which the effect of viscosity of the solvent alone is eliminated and which are given by the hydrodynamic effect of the polymer molecules. Accordingly, the relative viscosities of solutions in diethyl phthalate are larger than in the Θ -solvent (cetyl alcohol), which is in agreement with our above reasoning concerning the possibility of a change $(\overline{S^2})^{1/2}$ due to thermodynamic expansion. Tabulated results of measurements of the dependence of viscosity upon weight concentration (10–80%) of polystyrene and polyisobutylene in a number of solvents are given by Dreval, Tager, Chasina and Fomina^{8,9}. We recalculated the values to the dependence of relative viscosity (η_r) upon concentration in grams

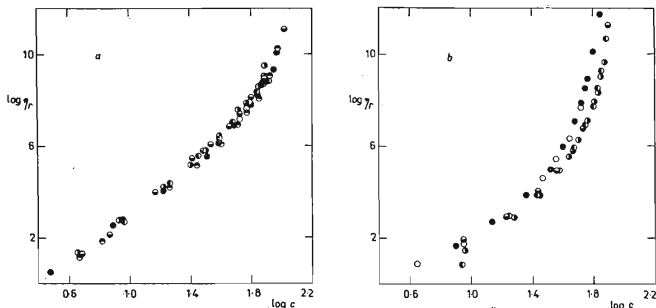


FIG. 1

Dependence of Relative Viscosity and Concentration (g/dl) of Polymer Solutions at 20°C According to the Recalculated Tabulated Results^{8,9}

a Polyisobutylene, $\overline{M}_\eta = 1.2 \cdot 10^6$; solvents: ○ butyl propionate, ● cyclohexane, ⊖ toluene, ⊙ isooctane, ⊕ decalin, ⊗ tetrachloromethane. *b* Polystyrene, $\overline{M}_\eta = 2.82 \cdot 10^5$; solvents: ○ decalin, ⊙ ethyl acetate, ⊕ ethylbenzene, ⊖ benzene, ● tetrachloromethane.

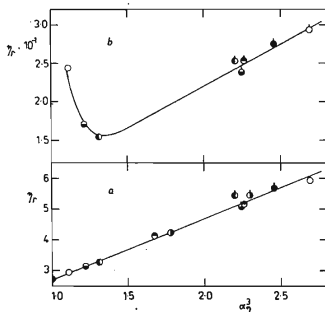


FIG. 2

Dependence of Relative Viscosity Upon the Expansion Coefficient ($\alpha_\eta^3 = [\eta]/[\eta]_0$) for Polystyrene Solutions According to the Recalculated Tabulated Results¹²

$\overline{M}_\eta = 3.7 \cdot 10^5$, temperature 25°C, polymer concentration: *a* 2 g/dl, *b* 12 g/dl. Solvents: ● ethyl laurate, ○ decalin, ⊖ ethyl acetate, ⊕ methyl ethyl ketone, ⊙ *x*-chlorotriethylbenzene, ⊕ *x*-dichlorodiethylbenzene; pipped: ⊕ *o*-dichlorobenzene, ⊖ dioxan, ⊕ ethylbenzene, ⊕ tetralin, ● toluene, ○ benzene. Measurements in ethyl laurate, *x*-chlorotriethylbenzene, *x*-dichlorodiethylbenzene and tetralin at the polymer concentration 12 g/dl were not performed by the authors. Full line: curve drawn through the experimental points.

of the polymer per dl of solution (Fig. 1). In the case of polyisobutylene the scatter of curves for various solvents is small, even if their thermodynamic quality is different (butyl propionate is a poor solvent, cyclohexane and tetrachloromethane are good solvents). For polystyrene, the dependences in a poor solvent (decalin) and a very good one (tetrachloromethane) have identical shapes; however, the η_r values in both solvents are higher than the values for a solvent of medium quality.

Ferry, Grandine and Udy¹⁰ measured viscosities of the polystyrene solutions in decalin and xylene (good solvent) within the concentration range of the polymer from 14 to 60 g/dl. After our recalculation the relative viscosities η_r in decalin at the same concentrations of polymers in the range of higher concentrations are clearly higher, which in view of the solvent quality represents a result opposite to the above results by Nakayasu and Fox^{2,7}. On the other hand, at lower concentrations the viscosities in xylene are higher. Similar crossing of the η_r vs c curves for solutions in a poor and a better solvent were found by Ferry, Foster, Browning and Sawyer¹¹ in the case of poly(vinyl acetate). They explain the higher viscosity values in a poor solvent at higher concentrations by an easier formation of the polymer-polymer contacts, leading to stronger entanglements.

Finally, let us mention here the results from a paper by Streeter and Boyer¹² for polystyrene solutions at concentrations not exceeding 12 g/dl, but in a larger number of solvents. We calculated the dependence of the relative viscosity on the expansion factor $\alpha_n^3 = [\eta]/[\eta]_0$ as a measure of the thermodynamic quality of the solvent at two polymer concentrations: a low one (2 g/dl) and the highest one (12 g/dl) (Fig. 2). The curve representing the higher concentration has two branches: first, starting from the unexpanded polymer coil the viscosity abruptly decreases; on reaching the minimum it again gradually increases with increasing expansion. At a low concentration η_r increases with α_n^3 only monotonously. It is likely that both effects, namely, the decrease and increase in viscosity, appeared independently of each other in the previous works;

TABLE I

Characteristics of Polystyrene Solutions at 25°C

| Solvent | [η] dl/g | α_n^3 | η_r | | |
|----------------------|--------------------|--------------|-----------|------|-------|
| | | | $c = 1.6$ | 9.13 | 20.2 |
| Decalin ^a | 0.393 | 1 | 1.88 | 36.3 | 3 120 |
| Decalin | 0.429 | 1.092 | 1.96 | 33.9 | 2 400 |
| Dimethyl phthalate | 0.459 | 1.167 | 2.00 | 36.3 | 969 |
| Butyl acetate | 0.502 | 1.277 | 2.20 | 30.1 | 692 |
| Butyl propionate | 0.556 | 1.415 | 2.21 | 31.4 | 575 |
| Dibutyl phthalate | 0.575 | 1.463 | 2.25 | 38.0 | 887 |
| 1-Butylnaphthalene | 0.726 | 1.847 | 2.78 | 31.4 | 496 |
| Cyclohexanone | 0.816 | 2.076 | 2.88 | 42.2 | 579 |
| <i>p</i> -Xylene | 0.816 | 2.076 | 2.82 | 52.5 | 865 |
| Ethylbenzene | 0.820 | 2.086 | 2.80 | 47.5 | 908 |
| Tetralin | 0.848 | 2.158 | 2.96 | 49.8 | 840 |
| Toluene | 0.853 | 2.170 | 2.95 | 52.7 | 1 030 |

^a Results are related to 19°C.

in the work referred by Dreval and coworkers⁹ they were not so evident because of the small number of solvents used.

Our experiments were carried out with polystyrene solutions in eleven solvents of different thermodynamic quality and viscosity at concentrations 1.6, 9.13 and 20.2 g/dl. Moreover, we measured the intrinsic viscosity in each solvent and calculated the respective expansion coefficients, α_n^3 (Table I). The relative viscosity of the solution 1.6 g/dl (the highest concentration in the measurements of $[\eta]$) and of more concentrated solutions plotted against the expansion coefficient yielded dependences similar to the recalculated results by Streeter and Boyer¹² (Fig. 3). A somewhat larger scatter of the results in our case is due to a slightly lower accuracy of the viscosity measurements at higher solvent viscosities. It can be seen that at lower concentrations (1.6 g/dl) viscosity only increases with the expansion coefficient. This finding agrees well with what we visualize, namely, that under the conditions when the spheres of macromolecules do not yet overlap, and the individual macromolecular coils behave at flow as independent hydrodynamic particles, only expansion of coils plays its part, owing to the influence of the increasing thermodynamic quality. This leads to a subsequent change in the radius of gyration in Eq. (1) and an increase in viscosity.

At higher concentrations there occurs overlapping of macromolecular spheres and entangling of coils; the entanglements formed make the flow mechanism of such system much more complex. Bueche^{13,14} assumes that the entanglements participate in energy dissipation at flow in such a way that on the one hand, the moving macromolecule tries to pull the other surrounding particles with it, and on the other, the segments of the molecule try to get out of the entanglements, thus separating themselves from the other segments. He includes these effects into two factors, Γ_1 and Γ_2 , when calculating the viscosity. For the melt of an amorphous polymer, he derives the relationship

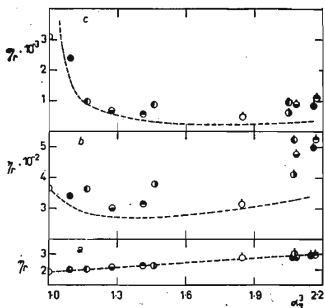


FIG. 3

Relative Viscosity as a Function of α_n^3 for Polystyrene Solutions

Temperature 25°C, polymer concentration: a 1.6 g/dl, b 9.13 g/dl, c 20.2 g/dl. Solvents: ○ decalin (19°C), ● decalin, ⊕ dimethyl phthalate, ⊖ butyl acetate, ⊙ butyl propionate, ⊗ dibutyl phthalate; pipped: ○ 1-butyl naphthalene, ⊕ cyclohexanone, ⊙ *p*-xylene, ⊖ ethylbenzene, ⊙ toluene, ● tetralin. Broken line: dependence calculated acc. to (4) and (7).

$$\eta = (N/6) (\overline{S}_r^2/M) (Z/v_2) \Gamma_1 \Gamma_2 \zeta \quad (3)$$

the factor Γ_2 being proportional to the number of entanglements on the polymer chain, λ ; apart from λ , Γ_1 also contains the parameter s' as a measure of the strength of the entanglements varying within the range 0 to 1. The value $s' = 0$ represents entanglement not restricting the motion of the macromolecule; $s' = 1$ indicates connection through a permanent bond. Owing to the complexity of the function Γ_1 and some adjustable parameters, Bueche's expression cannot be used for direct calculations of the melt viscosity from molecular data. Since, however, it comprises the strength parameter of the macromolecular chain bonds, we believe that it can help to elucidate the behaviour of concentrated solutions, at least from the qualitative point of view. The bond strength of the polymer entanglements in solutions is in the first place determined by the thermodynamic quality of the solvent. In poor solvents in the surroundings of the Θ -temperature the strength of the polymer-polymer contacts is considerable, which is reflected in a higher value of the parameter s' , a higher Γ_1 and a higher viscosity. The increasing quality of the solvent means a larger affinity of the polymer to the solvent, and thus also a decrease in the strength of the polymer entanglements; s' will then be lower and the viscosity will fall off.

It seems that the effect of the thermodynamic quality of the solvent upon the viscosity of moderately concentrated solutions is a superposition of two counteracting contributions: on the one hand, weakening of the strength of mutual contacts between the polymeric chains, and on the other, an increase in the radius of gyration of the polymeric chain by expansion in a thermodynamically better solvent. Starting from the Θ -conditions, a strong decrease in viscosity first prevails when the solvent quality is being improved, owing to the rapidly decreasing strength of the polymer entanglements; in this region, too, the macromolecules expand, but in this stage the expansion has no decisive influence upon viscosity. Only when the change in the bond strength becomes small, the increase in the radius of gyration becomes important, and the viscosity increases.

It is evident from comparing the curves in Fig. 3 that the steepness of the η_r vs α_n^3 dependence in the surroundings of $\alpha_n^3 = 1$ increases with concentration, which is in accordance with our idea of the increase in the number of entanglements and the degree of penetration of the polymeric chains in moderately concentrated solutions. At the same time the influence of the expansion of the macromolecular coil falls off. At an adequately high polymer concentration the viscosity in the Θ -solvent may be as high as in a thermodynamically very good solvent. This fact was indicated by the η_r vs c dependences of polystyrene in decalin and tetrachloromethane (Fig. 1b), calculated from the literature data⁹.

The existence of a minimum on the η_r vs. α_n^3 curves also ensues from the following calculation based on semiempirical relationships. The relationship between the viscosity and concentration of a polymer in the region of moderately concentrated solutions³ can be satisfactorily represented by Baker's equation¹⁵

$$\eta_r = (1 + [\eta] c/n)^n \quad (4)$$

with the parameter n depending on the polymer-solvent system. Heller¹⁶ expanded Baker's expression into a series and compared it with Huggins' equation. He thus obtained a relationship between the parameter n and Huggins' interaction constant, k_H :

$$n = 1/(1 - 2k_H) \quad (5)$$

According to Imai¹⁷, Huggins' constant is a function of the expansion coefficient and thus also of the thermodynamic quality of the solvent:

$$k_H = k_H^0/\alpha_n^4 + C'_0(1 - 1/\alpha_n^2), \quad (6)$$

where the interaction constant at the Θ -temperature $k_H^0 = 0.5$ and $C'_0 = 0.30$. By substituting this expression into relationship (5) we obtain the dependence of the parameter n on the expansion coefficient

$$n = 1/(0.4 + 0.6/\alpha_n^2 - 1/\alpha_n^4); \quad (7)$$

this dependence can be used in Baker's relationship (4) to obtain the η_r vs α_n^3 dependence. For the Θ -temperature the above dependence is reduced to become

$$(\eta_r)_\Theta = \lim_{|n| \rightarrow \infty} (1 + [\eta] c/n)^n = \exp [\eta] c. \quad (8)$$

The η_r vs α_n^3 dependences calculated using the relationships derived for the corresponding polystyrene concentrations (intrinsic viscosity $[\eta] = [\eta]_\Theta \alpha_n^3 = K_\Theta M^{1/2} \alpha_n^3$, where $K_\Theta = 7.7 \cdot 10^{-4}$) are plotted as curves in Fig. 3. At the lowest polymer concentration, 1.6 g/dl, the experimental points virtually coincide with the calculated curve. At 9.13 g/dl — although the qualitative agreement with the exception of the value obtained at the Θ -temperature is not perfect any more — the curve still retains its characteristic minimum, similarly to the sequence of the experimental points. However, at the highest α_n^3 the relative viscosities measured are fairly higher than the calculated ones. At the highest concentration 20.2 g/dl the minimum of the calculated curve is flat, and at the highest α_n^3 the increase in η_r is very small. If there is an agreement between the calculated and the experimental dependences η_r vs. α_n^3 , at a concentration 1.6 g/dl it means that the values of Huggins' constant calculated according to (6) are correct. A discord between the experimental and calculated dependences at higher concentrations, as well as a larger scatter of the points does not mean, therefore, that incorrect values of k_H and n have been used; it rather indicates that the description of the dependence η_r vs c in terms of Baker's equation at higher concentrations and larger expansions of the macromolecular coil is not as accurate as expected.

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