

CONTRIBUTION TO THE STUDY OF THE EFFECT OF SOLVENT VISCOSITY ON THE NON-NEWTONIAN BEHAVIOUR OF DILUTE POLYSTYRENE SOLUTIONS

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The dependence of intrinsic viscosity on shear stress in a range of 0.5 to 1300 dyn/cm² was investigated for solutions of polystyrene fractions (M_{η} 1.8 · 10⁶ to 4 · 10⁶) in a number of solvents greatly differing by their viscosities (η 0.006 to 0.62 P) and only insignificantly by their solvent power. The experimental results indicate that the effect of solvent viscosity on the $[\eta]$, vs parameter β_0 dependence for molecular weights of polystyrene $M_{\eta} < 5 \cdot 10^6$ may be neglected: they are confronted with the values predicted from Cerf's theory of the non-Newtonian flow.

A number of molecular theories have been suggested to explain the non-Newtonian behaviour of dilute solutions of macromolecular compounds¹. With one exception² they all agree in that under the Θ -conditions the non-Newtonian decrease in relative intrinsic viscosity $[\eta]_r$ is an unequivocal function of the parameter β_0 defined by

$$\beta_0 = [\eta]_0 M \eta_0 G / RT, \quad (1)$$

which besides the velocity gradient G , molecular weight M , and intrinsic viscosity of the polymer at zero shear stress, $[\eta]_0$, also includes solvent viscosity, η_0 . This means that the dependence of relative intrinsic viscosity ($[\eta]_r/[\eta]_0$) on β_0 should be common for solvents of different viscosity. However, according to Cerf's theory² which considers the so-called internal viscosity (related to the flexibility of the polymer chain) one may expect that the shape of the $[\eta]_r$ vs β_0 curve will depend on solvent viscosity.

Only occasional remarks on this topic can be found in the literature³, so that the first and so far only one systematic study are papers by Wolff⁴⁻⁶. According to this author, in the case of polystyrene the effect of solvent viscosity on the $[\eta]_r - \beta_0$ dependence may be observed only at molecular weights of 10⁷, while at lower molecular weights it cannot be perceived. However, in this region Wolff's measurements do not go into much detail, which led us to an investigation of the effect of solvent

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viscosity in this particular range of molecular weights. We measured the dependences of intrinsic viscosity on the velocity gradient for a wide range of viscosities, η_0 0.006 to 0.62 P, with polystyrene fractions having molecular weights M_η of $1.8 \cdot 10^6$ to $4 \cdot 10^6$.

EXPERIMENTAL

Polymer. Polystyrene obtained by thermally initiated bulk polymerization up to high conversion was fractionated by gradual precipitation with methanol from benzene solutions having a concentration of approximately 0.2%; the fractions were reprecipitated and dried at 50°C *in vacuo* over phosphorus pentoxide. Their molecular weights were determined from intrinsic viscosity (benzene solutions, 25°C) according to equation⁷ $[\eta_0] = 1.23 \cdot 10^{-4} \cdot M_\eta^{0.72}$ (Table I). Further measurements were carried out with fractions so chosen as to have their molecular weights within an interval limited on one side by the threshold value of the non-Newtonian behaviour and on the other by a value at which a perceptible flow degradation of polystyrene takes place.

TABLE I
Characterization of Solutions
 η_0 in P, $[\eta]_0$ in dl/g.

Fraction (M_η)	Solvent	η_0	$[\eta_0]$	α_η^3	$\varphi \cdot 10^3$
$1.85 \cdot 10^6$	benzene	0.006	3.12	3.55	2.420
	ethyl butyrate	0.006	1.80	1.73	0.563
	dibutyl phthalate	0.161	1.76	1.68	0.533
$1.95 \cdot 10^6$	octyl benzoate	0.057	1.99	1.86	0.700
	tricresyl phosphate	0.618	2.10	2.00	0.820
	dioctyl phthalate	0.557	0.95	0.88	-0.047
$2.98 \cdot 10^6$	dioctyl phthalate	0.557	1.21	0.91	-0.028
	tricresyl phosphate	0.618	2.89	2.20	0.886
$4.00 \cdot 10^6$	dibutyl phthalate	0.161	2.94	1.95	0.534
	ethyl butyrate	0.006	2.93	1.91	0.530

Solvents, commercial products, were purified by distillation; octyl benzoate was prepared by Perkin synthesis from benzoyl chloride and octanol in the presence of pyridine.

Solutions of the highest concentration (1 g/dl) were prepared by shaking at an elevated temperature (60°C), solutions of lower concentrations were obtained by diluting the initial solution. The solution of polystyrene in dioctyl phthalate was prepared by adding dioctyl phthalate to benzene solution and removing benzene by distillation. Before measurements all solutions were filtered through a glass fritted disc, density S3.

Viscometry. All measurements were carried out at 25°C: determinations of the molecular weights of fractions and of solvent viscosities, measurements of solution viscosities at zero and higher shear stresses (τ 8 to 1300 dyn/cm²) and treatment of experimental data were performed according to Quadrat⁸. Intrinsic viscosities at constant shear stress, $[\eta]$, were calculated according to Heller's procedure⁹. All calculations of the corrected values of apparent relative viscosity, t'_r , recalculation to η_r by numerical differentiation of the $\log t'_r$ vs $\log \tau$ dependence, and extrapolation in order to obtain intrinsic viscosity by the least squares method were carried out with a National Elliott 803 B.

RESULTS AND DISCUSSION

Cerf's theory is based on the assumption that the distribution of segments around the gravity centre of the polymer chain may be described by the Gaussian function. Strictly speaking, it should therefore be confronted with the experimental results obtained under the Θ -conditions. Since Θ -solvents for polystyrene with sufficiently different viscosities are not known, "good" solvents had to be used. In order to eliminate the effect of solvent power, we used solvents having very close values of solvent power.

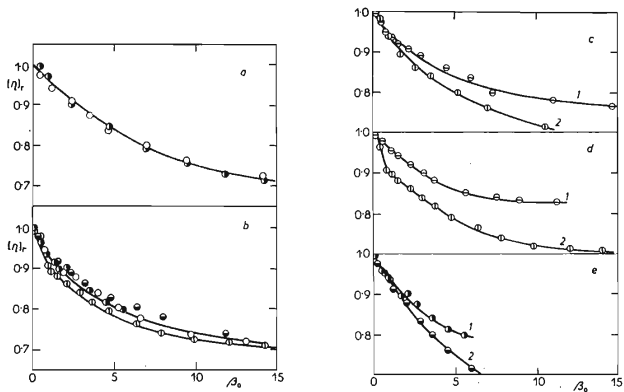


FIG. 1

Effect of Solvent Viscosity (*a, b*) and Solvent Power (*c—e*) on the $[\eta]_r$ vs β_0 Dependence

Polystyrene fractions, $M_n \cdot 10^6$: *a* 4.00, *b* 1.85 and 1.95 *c* 2.98, *d* 1.95, *e* 1.85. Solvents: ○ dibutyl phthalate, ● ethyl butyrate, ⊙ octyl benzoate (in Fig. 1e benzene), ⊕ tricresyl phosphate, ⊙ benzene, ⊕ dioctyl phthalate.

TABLE II

Influence of Solvent Viscosity on Non-Newtonian Effect

$$E_{\beta_0=7} = (1 - [\eta]_c)_{\beta_0=7}; [\eta]_0 \cdot \eta_0 \text{ in P} \cdot \text{ml} \cdot \text{g}^{-1}.$$

Fraction (M_η)	Solvent	$E_{\beta_0=7}$	$[\eta]_0 \cdot \eta_0$
$1.85 \cdot 10^6$	benzene	0.300	1.871
	ethyl butyrate	0.230	1.116
	dibutyl phthalate	0.223	28.28
$1.95 \cdot 10^6$	octyl benzoate	0.207	11.37
	tricresyl phosphate	0.247	130.1
	dioctyl phthalate	0.158	52.80

The ratio

$$\varphi = (\alpha_\eta^5 - \alpha_\eta^3) / M_\eta^{1/2}, \quad (2)$$

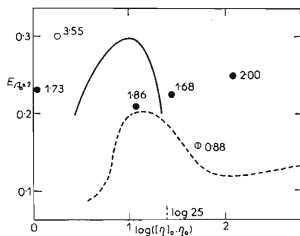
was used as the measure of solvent power. According to the Flory theory¹⁰, this ratio should be constant at a given temperature and for a given polymer-solvent system (especially at high molecular weights). The viscosity expansion factor, α_η^3 , was calculated from intrinsic viscosity values at zero shear stress, $[\eta]_0$, according to¹¹

$$\alpha_\eta^3 = [\eta]_0 / K_\theta M_\eta^{1/2} \quad (3)$$

where for polystyrene $K_\theta = 7.6 \cdot 10^{-4}$ (Table I).

FIG. 2
Correlation of Non-Newtonian Effect $E_{\beta_0=7}$
and of the Product $[\eta]_0 \cdot \eta_0$

Cerf's theory (hydrodynamic interaction):
— weak, - - - strong. Values of the expansion coefficient α_η^3 for individual experimental points of polystyrene fractions with M_η $1.85 \cdot 10^6$ and $1.95 \cdot 10^6$.



Ethyl butyrate, octyl benzoate, dibutyl phthalate, and tricresyl phosphate were chosen as solvents for polystyrene having close solvent power and different viscosity (Fig. 1). For the sake of comparison, we also performed measurements in solvents with close viscosities and different solvent powers; ethyl butyrate and tricresyl phosphate were complemented by benzene and dioctyl phthalate respectively for this purpose (Fig. 2, Table I).

The dependences of viscosity η and intrinsic viscosity $[\eta]$ on shear stress (and consequently also the $[\eta]_r$ vs β_0 dependences) decreased monotonically in all cases and over the whole range. At shear stresses below 8 dyn/cm² intrinsic viscosity decreased linearly with increasing shear stress. Hence, intrinsic viscosities at zero shear stress, $[\eta]_0$, were obtained by linear extrapolation of $[\eta]$ from this region to zero shear stress.

A comparison of the $[\eta]_r$ vs β_0 dependences for polystyrene fractions in solvents with very close φ values and large differences between viscosities did not reveal any pronounced influence of solvent viscosity on this dependence. For a fraction having M_n 4 · 10⁶ practically perfect agreement has been found in ethyl butyrate and dibutyl phthalate, although the solvent viscosities differ by a factor of twenty five. For fractions with M_n 1·85 · 10⁶ and 1·95 · 10⁶ (for which the difference in molecular weights may be neglected) the course of the $[\eta]_r$ - β_0 dependence is almost identical for four solvents with viscosities ranging from 6 · 10⁻³ to 6·2 · 10⁻¹ P. The coincidence is not so perfect as for the fraction with M_n 4 · 10⁶, but the maximum difference between the values of $[\eta]_r$ is 0·03, i.e. approx. 4%, and is probably not important.

To verify the predictions of Cerf's theory², it was suggested⁵ to plot $E = (1 - [\eta]_r)_{\beta_0=7}$ against $\log([\eta]_0 \cdot \eta_0)$; according to the theory, the plot should pass through a maximum and at $([\eta]_0 \cdot \eta) < 25$ decrease to zero as a consequence of the total flexibility of the macromolecule at a high solvent viscosity. Fig. 2 shows this dependence obtained by our measurements (Table II). For reasons of comparison the Figure also includes schematic theoretical curves corresponding after Cerf's theory to two extreme cases of a weak and strong hydrodynamic interaction; both dependences exhibit a maximum. On the other hand, no sign of a maximum can be seen for our points for four solvents having close α_n^3 values and $[\eta]_0 \cdot \eta_0$ lying in the 1 - 100 interval, while the E values coincide within the limits of experimental error. Thus, although according to Wolff⁵ the effect of the expansion factor on E should be negligible at $[\eta]_0 \cdot \eta_0 > 25$, our data seem to suggest that - similarly to $[\eta]_0 \cdot \eta_0 < 25$ - in this region too the expansion factor plays an important role.

The results of this paper demonstrate that for polystyrene at $M_n \leq 5 \cdot 10^6$ the effect of solvent viscosity on the $[\eta]_r$ - β_0 dependence may be neglected.

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