

VISCOMETRIC PROPERTIES OF THE CONCENTRATED POLYMER SOLUTIONS. II.*

DEPENDENCE OF THE NON-NEWTONIAN VISCOSITY ON THE THERMODYNAMIC QUALITY OF THE SOLVENT AND ON ITS VISCOSITY

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The dependence of the viscosity of moderately concentrated polystyrene solutions in solvents whose viscosity and thermodynamic quality differ considerably can be unified by plotting relative viscosity νs the product of the velocity gradient and Rouse relaxation time. By shifting along the x -axis of the common experimental function this plot is made to coincide with the theoretical Graessley's curve.

A decrease in viscosity with increasing velocity gradient in polymer solutions having a concentration which gives rise to entanglements of molecules can be explained by a change in the density of chain entanglements due to flow. On this basis, Graessley^{1,2} has derived a theoretical dependence of the decrease in η/η_0 on a universal parameter representing the product of the velocity gradient G and Rouse relaxation time $\tau_R = (6/\pi^2)(M\eta_0/cRT)$, where η and η_0 are viscosities of the solution at a given and zero gradient, respectively, M is molecular weight of the polymer, c is its concentration, T is absolute temperature and R is the gas constant. Comparison of the theoretical dependence with the results of measurements of polystyrene solutions in butylbenzene has showed³ that the plot $\log(\eta/\eta_0) \nu s \log(\tau_R G/2)$ for different concentrations and molecular weights is not uniform. By shifting along the x -axis the experimental curve coincides with the theoretical one, but the length of the shift depends on the molecular weight and concentration of the polymer. The ratio of τ_R to the relaxation time τ_G corresponding to the length of the shift increases with increasing value of the product of concentration and molecular weight, *i.e.* a quantity expressing the density of entanglements.

It was interesting to find out to what extent the effect of the thermodynamic quality of the solvent (or its markedly different viscosity) would be reflected in the plot $\log(\eta/\eta_0) \nu s \log(\tau_R G/2)$. For this purpose, we used solutions of unfractionated polystyrene ($\bar{M}_n = 2.7 \cdot 10^5$) in eleven solvents having a concentration 20.2 g dl^{-1} . Their viscosities and the viscosity expansion factor for a given molecular weight defined as $\alpha_n^3 = [\eta]/[\eta]_0$ ($[\eta]$ being intrinsic viscosity in the solvent used and $[\eta]_\theta = K_\theta M^{1/2}$,

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TABLE I

Solvent Viscosities (η_s in cP) and Expansion Coefficient of Solutions of a Polystyrene Sample at 25°C

Solvent	η_s	α_η^3	Solvent	η_s	η_η^3
Diocetyl phthalate	51.1	0.794	Dibutyl phthalate	16.05	1.463
Decalin ^a	2.57 ^b	1 ^b	Tricresyl phosphate	62.6	1.542
Decalin	2.27	1.092	1-Butylnaphthalene	4.44	1.847
Dimethyl phthalate	12.4	1.167	Cyclohexanone	1.98	2.076
Butyl acetate	0.688	1.277	Ethylbenzene	0.637	2.086
Butyl propionate	0.757	1.415	Tetralin	1.91	2.158

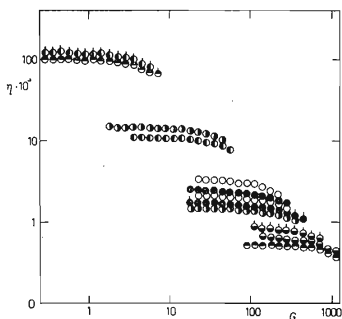
^a Ref.⁵, ^b For 19°C.

FIG. 1

Dependence of the Viscosity η on the Velocity Gradient G of Polystyrene Solutions at 25°C

$\bar{M}_\eta = 2.7 \cdot 10^5$, polymer concentration 20.2 g/dl. Solvents: \circ decalin (19°C), \bullet decalin, \odot butyl propionate, \ominus dibutyl phthalate, \oplus butyl acetate, \ominus dimethyl phthalate; pipped: \circ 1-butyl naphthalene, \bullet tetralin, \oplus tricresyl phosphate, \ominus cyclohexanone, \oplus ethylbenzene, \ominus dioctyl phthalate.

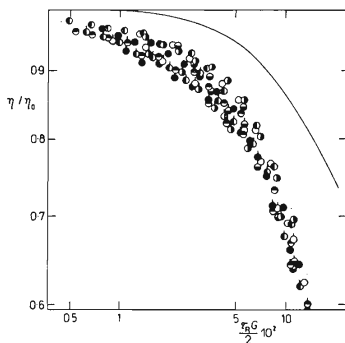


FIG. 2

η/η_0 as a Function of $\tau_R G/2$
Points designated as in Fig. 1.

where $K_{\theta} 7.6 \cdot 10^{-4}$) and used as a measure of their thermodynamic quality are listed in Table I. The measurement was carried out by means of Weissenberg's cone-plate rheogoniometer. The preparation of samples at an elevated temperature by stirring with steel balls has been described in an earlier paper⁴.

Large differences in viscosity at zero velocity gradient η_0 (Fig. 1) follow mainly from different viscosities of the solvents. The effect of the thermodynamic quality of the solvent upon this quantity is not great⁴. Experimental results represented in the correlation η/η_0 vs $\tau_R G/2$ form a common set of points whose scatter of the η/η_0 values is 5% max. (Fig. 2) (regardless of the thermodynamic quality and viscosity of the solvent used). It follows therefrom that the magnitude of the non-Newtonian decrease in viscosity with the velocity gradient at a constant polymer concentration is determined only by the viscosity at zero gradient, η_0 , proportional to the degree of entanglements of the macromolecules and to the strength of these entanglements. The shift of Graessley's theoretical curve to the right corresponds to the ratio $\tau_G/\tau_R = 0.3$, which is in agreement with the results of measurements of polystyrene solutions in butylbenzene³ at a low molecular weight and polymer concentration.

In conclusion, it should be pointed out that although the above results were obtained by measurements performed in only one moderately concentrated polystyrene solution, no marked changes in the dependence of the non-Newtonian behaviour on the thermodynamic quality of the solvent are likely to occur if a higher molecular weight (letting alone higher concentration) is used.

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