NON-NEWTONIAN BEHAVIOUR OF DILUTE SOLUTIONS OF POLYMER. VI.*

"UPTURN EFFECT" OF THE NON-NEWTONIAN DEPENDENCE OF INTRINSIC VISCOSITY FOR POLYISOBUTYLENE SOLUTIONS IN A LOW-VISCOSITY SOLVENT

O.Quadrat

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6*

Measurements performed with solutions of two polyisobutylene fractions in benzene (Θ-solvent) have shown that the intrinsic viscosity of the fraction with a higher molecular weight ($4 \cdot 5 . 10^{6}$) was increasing with shear stress after the initial decrease, while that of the fraction with a molecular weight of $2 \cdot 0 . 10^{6}$ went on decreasing over the whole range of the shear stresses used. The experimental curves resembled the theoretical curves calculated by Peterlin ("upturn effect") for chains having a large kinetic flexibility assuming a change in the hydrodynamic interaction between segments during the flow expansion of polymer coils.

One of the most interesting although so far unexplained phenomena of the rheology of dilute polymer solutions consists in the so-called "upturn effect", *i.e.* the occurrence of a minimum or even maximum on the curves representing the dependence of relative intrinsic viscosity, $[\eta]_r$, on shear stress τ, or the parameter β_0,

$$[\eta]_r = [\eta]/[\eta]_0 \qquad (1)$$

and

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

where $[\eta]$ and $[\eta]_0$ are intrinsic viscosities at a given and zero velocity gradient, M is molecular weight of the polymer, η_s is viscosity of the solvent, G is velocity gradient, τ is shear stress, R is universal gas constant, and T is temperature. The effect has been theoretically predicted by Peterlin[1-4] who assumed that a deformation of the macromolecular coil in the hydrodynamic field is accompanied by a change in the intramolecular hydrodynamic interaction. The calculation was performed for a Gaussian coil under the Θ-conditions. According to theory a sufficient length of the polymer chain and its low kinetic rigidity are conditions of this effect.

To suppress kinetic rigidity of real polymer chains, solvents having high viscosity were mainly used for the experimental investigation of this effect. In solvents of this type, Burow, Peterlin, and Turner[5] observed the effect for poly(methyl methacrylate) and polystyrene in aroclor ($\eta_s = 10-100$ P) while Bianchi and Peterlin[6] observed it for polyisobutylene in polybutene ($\eta_s = 5$ P). In low-viscosity solvents, the minimum on the $[\eta]_r$ vs β_0 curves has as yet been found only for high-molecular weight polystyrene in decalin[7,8].

When investigating the influence of the thermodynamic quality of the solvent on the non-Newtonian behaviour of dilute polyisobutylene solutions in benzene we obtained $[\eta]_r$ vs β_0 curves with a minimum which were similar to the curve predicted by Peterlin. Since the system involved is a system with a low-viscosity solvent, a more detailed analyzis of the results seems called for here.

EXPERIMENTAL

Polyisobutylene Oppanol B 100 was divided into six fractions. The fractionation was carried out by gradual precipitation of a 0·5% benzene solution with acetone. The fractions were isolated by evaporating frozen benzene solutions *in vacuo*. Their molecular weight was determined viscometrically in benzene solutions at 25°C while using a relationship suggested by Fox and Flory[9], $[\eta] = 0.83 \cdot 10^{-3} M^{0.53}$. The non-Newtonian measurements were carried out by using two high-molecular weight fractions having molecular weights $2·0 \cdot 10^6$ and $4·5 \cdot 10^6$. Solutions in benzene (anal. purity grade, redistilled after drying with sodium) were filtered through a fritted disc, density S 2, prior to the measurements. The viscometric measurements in capillary viscometers provided with a manostat, as well as the method of correction and extrapolation used to obtain intrinsic viscosities by an Elliott 4100 computer were similar to the preceding paper[10].

RESULTS AND DISCUSSION

An experimental investigation of the "upturn" effect is made difficult by two factors: negative thixotropy, on the one hand, and degradation of the high-molecular weight polymers due to flow, on the other. Both phenomena occur in the region of elevated shear stresses, where according to Peterlin's theory a new rise in viscosity can be expected. Degradation of the polymer at high shear stresses can lead to a reduction or total suppression of the effect. Negative thixotropy caused by the formation of intermolecular bonds due to flow and observed during the measurements of solutions in capillary viscometers is reflected — similarly to the "upturn" effect — in a minimum on the η_{sp}/c vs τ curves. However, this phenomenon becomes less pronounced if the solutions are diluted and disappears completely at infinite dilution. In this respect it differs from Peterlin's "upturn" effect which is preserved also on the $[\eta]$ vs τ curves. Negative thixotropy is supported by the high molecular weight of the polymer, poor thermodynamic quality of the solvent, and its high viscosity. With respect to the fact that it seems appropriate to try to prove the "upturn" effect under the above conditions (best in the Θ-solvent), both effects are rather difficult to distinguish; they depend on the reliability of the extrapolation of the η_{sp}/c values to zero concentration. However, the course of the η_{sp}/c curves is not always the same for negative thixotropic solutions; *e.g.*, for poly(methyl methacrylate) solutions in cyclohexanone with isopropanol in the surroundings of the Θ-temperature, where strong negative thixotropy could be observed and the curves of the dependence of reduced viscosity on shear

stress were characterized by a minimum and maximum, a monotonously decreasing $[\eta]$ vs τ curve was obtained reliably after extrapolation of reduced viscosity to zero concentration[11]. On the other hand, the dependences of reduced viscosity on concentration for a decaline solution of polystyrene, where a weak negative thixotropy was observed, has an unusual course[12]; although they were represented by straight lines at elevated concentrations, the reduced viscosity deviated to lower values at the lowest concentration. As a consequence, it was impossible to decide in this case to what extent both effects participate in the rise of $[\eta]_r$ with β_0.

No concentration anomalies could be observed for polyisobutylene solutions in benzene at the Θ-temperature even at the highest values of shear stress; the η_{sp} vs c dependences were straight lines, so that the extrapolation was easy on the whole. The minimum on the $[\eta]_r$ vs β_0 curves remained also after extrapolation to infinite dilution (Fig. 1). We infer therefrom that we have here the "upturn" effect and not negative thixotropy (*cf.* above). It can be seen from Fig. 2 that relative intrinsic viscosity with the parameter β_0 increases only in the case of a solution of the polyisobutylene fraction with a higher molecular weight at the Θ-temperature (24°C). An increase in temperature to 40°C made the effect disappear, *i.e.* led to a gradual decrease in $[\eta]_r$ with β_0. The fraction with a lower molecular weight did not exhibit any increase in $[\eta]_r$ even at the Θ-temperature.

The fact that a mere decrease in the molecular weight to one half of its original value is sufficient to suppress the effect explains why Passaglia, Yang, and Wegemer[13] did not find any minimum on the $[\eta]_r$ vs τ dependence under the same conditions
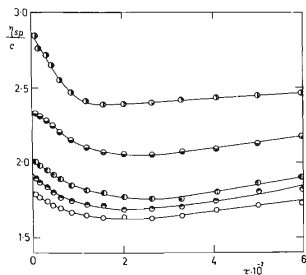

Fig. 1

Dependence of the Reduced Viscosity η_{sp}/c (dl g^{-1}) on the Shear Stress τ (dyn cm^{-2}) of Polyisobutylene Solution ($M = 4\cdot5 \cdot 10^6$) at 24°C

Concentration: $\bullet$ $c = 0\cdot314$, $\ominus$ $0\cdot168$, $\bullet$ $0\cdot085$, $\ominus$ $0\cdot045$, $\circ$ $c = 0$.
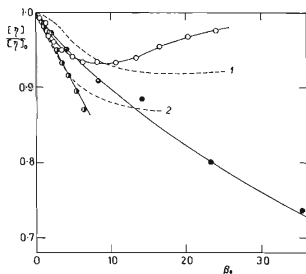
Fig. 2

Dependence of the Relative Intrinsic Viscosity $[\eta]/[\eta]_0$ on the Parameter β_0

$\circ$ $M = 4\cdot5 \cdot 10^6$ (24°C), $\bullet$ $M = 4\cdot5 \cdot 10^6$ (40°C), $\circ$ $M = 2\cdot0 \cdot 10^6$, (24°C); broken line: *1* Fixman's theory, *2* Chikahisa's theory.

for a polymer with the molecular weight $1.59 \cdot 10^6$. This behaviour is in qualitative agreement with the assumed dependence of the intensity of the effect on the length of the polymer chain in Peterlin's theory. On the other hand, the effect of the thermodynamic quality of the solvent on the shape of the curves differs from Peterlin's theory, similarly to Wolff[7,8]; while the theory[3] predicts, for a thermodynamically good solvent, a smaller initial decrease in intrinsic viscosity and its steeper rise after attaining the minimum than under the Θ-conditions, the experiments have shown that the steepness of the initial decrease in $[\eta]_r$ only increases with improving solvent quality. However, taking into account that the theory mentioned above considers only one of a number of effects contributing to the non-Newtonian flow, the disagreement between experiments and theory need not mean that the theoretical prediction is wrong.

The depth of the minimum ($[\eta]_r = 0.93$) on our curve can be compared with the values found by Wolff[7,8] for polystyrene solutions in decalin. It is considerably smaller than the value found in the minimum by Bianchi and Peterlin[6] for polyisobutylene solutions in polybutene ($[\eta]_r = 0.6$), and also than the value approximately equal to 0.7 offered by Peterlin's theory. The coordinate of the β_0 minimum is practically identical with the result obtained by Wolff and with theory; for solutions in polybutene the minimum lies at values which are approximately ten times higher. The remarkable similarity between our experimental results and those obtained by Wolff can be explained by the fact that a low-viscosity solvent was used in both cases.

It has been shown in the preceding paper[10] that the $[\eta]_r$ vs β_0 dependence for polystyrene solutions at the Θ-temperature is close to the dependence according to Chikahisa's theory[14], and that on the other hand, functions derived by Fixman are better fitted for thermodynamically good solvents[15]. Also both theoretical curves at the Θ-temperature have been plotted along with the experimental results for polyisobutylene solutions in Fig. 2. The initial course of Chikahisa's curve coincides with the experimental points for the polymer with the lower molecular weight, for which intrinsic viscosity went on decreasing monotonously over the whole measured range of shear stresses. On the other hand, the initial decrease in $[\eta]_r$ vs β_0 for the polymer with the higher molecular weight is somewhat milder, without however attaining the course corresponding to Fixman's theory. It follows therefrom that also the non-Newtonian behaviour of polyisobutylene solutions at the Θ-temperature is better described by a function based on Chikahisa's theory.

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