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VISCOSITY AND HEATS OF ACTIVATION OF CONCENTRATED POLYMER SOLUTIONS AS A FUNCTION OF CONCENTRATION, TEMPERATURE, AND THE NATURE OF THE SOLVENT

(Presented by Academician V. A. Kargin on 22 II 1962)

The dependence of the viscosity of concentrated solutions on concentration, the molecular weight of the polymer, and temperature has been studied in a number of works ([1–5]). The influence of the nature of the solvent on the rheological properties of concentrated polymer solutions has been investigated only in a comparatively narrow range of concentrations ([6–9]). The aim of the present work was to study the influence of the nature of the solvent on the viscosity of concentrated polymer solutions and on the magnitude of the activation barriers over a broad concentration range, in order to reveal structural features of concentrated solutions. The objects of the investigation were a highly elastic polymer–polyisobutylene with molecular weight $1.2 \cdot 10^6$–and a glassy polymer –polystyrene (mol. wt. $2.8 \cdot 10^5$).

The viscosity coefficients, as a function of solution concentration, were determined by flow from a capillary, using a rotational viscometer and a shear plastometer ([4]). Since the investigations were carried out at very low shear rates, the obtained values of the viscosity coefficients are close to the values of the viscosity coefficients at zero shear rate. Viscosity measurements were carried out at 20, 35, and 50°. On the basis of the dependence $\lg \eta = f(1/T)$, which was linear in the temperature interval studied, the heats of activation of viscous flow were calculated. The data obtained were compared with the thermodynamic affinity of the polymer for the solvent, and with the heats and entropies of dissolution.

Figures 1 and 2 show the dependence of the logarithm of viscosity on the concentration of polymer in the solution, expressed in volume fractions (φ_2), for solutions of polyisobutylene and polystyrene. The form of the curves obtained is very characteristic: the curves of the dependence $\lg \eta = f(\varphi_2)$ for solutions of polyisobutylene in all solvents have a very steep rise in the initial concentration region and a gentler slope at higher values of φ_2. For polystyrene solutions, on the contrary, a very sharp increase in viscosity is observed in the region of higher concentrations. This difference is not accidental–the form of the curves obtained by us for polyisobutylene solutions is analogous to the form of the curve obtained in work (4), while the character of the curves in Fig. 2 is analogous to the curves obtained for solutions of polystyrene and polymethyl methacrylate (3,10). This is associated with the difference in the physical state of the polymers studied. Polyisobutylene and its concentrated solutions, in the temperature range of the study, are in the highly elastic state; polystyrene and its concentrated solutions are glasses. Therefore, at high values of the polymer volume fraction, the viscosity of polystyrene solutions increases considerably more than that of polyisobutylene solutions.

In solutions of both polymers, a large difference in viscosity is observed depending on the nature of the solvent. If one takes into account that the curves $\lg \eta = f(\varphi_2)$ at $\varphi_2 = 1$ must converge to a single point, it becomes obvious that there is a concentration region in which the difference in the viscosities of solutions in different solvents is especially pronounced. It is most natural to explain the differences in the viscosity of solutions by the different viscosity of the solvents themselves, as was done in (6). Indeed, the higher the viscosity of the solvent itself, the greater the viscosity of the solution (for example, decalin and toluene). However, the viscosities of the solvents differ by a factor of 4–5, whereas the viscosity

solution by 12 (for polyisobutylene solutions) and by 1400 times (for polystyrene solutions). Consequently, the difference in the viscosity of polymer solutions is connected with the viscosity of the solvent, but is not reduced to it.

The reason for the large differences in the viscosity of concentrated polymer solutions, as also of dilute ones, should be sought in the different interaction of the components. In contrast to dilute solutions, in which the chains are coiled into balls, at high polymer concentrations its chains are apparently more or less straightened and arranged in bundles. Such solutions must be regarded, similarly to solutions of low-molecular substances, as a single multicomponent system in which, during flow, solvent molecules and polymer chains (or bundles) are displaced. Therefore it is of interest to compare the viscosity data with the data on the heats of activation, presented in Figs. 3 and 4. The figures show the general character of the regularity: the heat of activation increases with the solution concentration from values of 2–4 kcal/mol for the solvents to 16 kcal/mol for polyisobutylene and 23 kcal/mol for a polystyrene solution with volume fraction $\varphi_2 \cong 0.6$. The heat of activation of the solution depends on the heat of activation of the solvent itself; however, the difference in the heats of activation of the solution is considerably greater than the difference in the heats of activation of the solvents. The influence of the nature of the solvent is especially pronounced in the values of the heats of activation in polyisobutylene solutions in the concentration range from $\varphi_2 \cong 0.3$ to $\varphi_2 \cong 0.6$, and in polystyrene solutions at $\varphi_2 > 0.6$.

Fig. 1. Dependence of the logarithm of the viscosity of polyisobutylene solutions on the volume fraction of polymer at 20°:
1 –toluene, 2 –isooctane, 3 –carbon tetrachloride, 4 –butyl propionate, 5 –

Fig. 1

Figure 1: Fig. 1

Fig. 2. Dependence of the logarithm of the viscosity of polystyrene solutions on the volume fraction of polymer at 20°: 1 —ethyl acetate, 2 —ethylbenzene, 3 —benzene, 4 —carbon tetrachloride, 5 —decalin

Figure 2: Fig. 2. Dependence of the logarithm of the viscosity of polystyrene solutions on the volume fraction of polymer at 20°: 1 —ethyl acetate, 2 —ethylbenzene, 3 —benzene, 4 —carbon tetrachloride, 5 —decalin

cyclohexane, 6 —decalin

From a comparison of Figs. 1 and 3 (2 and 4) it is seen that there is a correlation between the values of viscosity and the heats of activation of flow: the greater the heat of activation, the greater the viscosity of the solution. Consequently, the viscosity of concentrated polymer solutions, just like the viscosity of low-molecular liquids, is determined by the heat of activation, i.e., by the activation barrier that is overcome during the mutual displacement of chains and solvent molecules.

The magnitude of this barrier and the viscosity of the solution do not depend directly on the energy of interaction of the polymer with the solvent, as follows from the absence of a correlation between the indicated quantities and the heats of dissolution of the polymer in different solvents. For example, over the entire concentration range the viscosity of polyisobutylene solutions in isooctane (an athermal system) is the same as in carbon tetrachloride (an endothermic system). The viscosity of concentrated polymer solutions

also is not directly related to the thermodynamic affinity of the polymer for the solvent. Thus, from the experimental data (Fig. 1) it follows that in the concentration range from $\varphi_2 = 1$ to $\varphi_2 \cong 0.5$ the viscosity of polyisobutylene solutions in isooctane, carbon tetrachloride, and butyl propionate is the same, whereas the thermodynamic affinity of polyisobutylene for these solvents is different. Carbon tetrachloride and isooctane are good solvents for polyisobutylene (high absolute values of the difference in chemical potentials $\Delta\mu_1$ over the entire concentration range). Butyl propionate is a poor solvent for polyisobutylene.

Fig. 2. Dependence of the logarithm of the viscosity of polystyrene solutions on the volume fraction of polymer at 20°: 1 —ethyl acetate, 2 —ethylbenzene, 3 —benzene, 4 —carbon tetrachloride, 5 —decalin

We established a correlation between the viscosity of a solution and the values of the entropy of mixing upon its formation: the greater the value of ΔS, the lower the heat of activation and the viscosity of the solution. Large values of the entropy of mixing ΔS indicate that the polymer chains in the given solvent assume a larger number of conformations than in the condensed polymer phase.

Fig. 3

Figure 3: Fig. 3

A strong increase in entropy is observed in the athermal system polyisobutylene —isooctane, i.e., it may also occur with unchanged thermodynamic flexibility of the chain. When polyisobutylene is dissolved in other solvents, the value of ΔS may be greater or smaller than when it is dissolved in isooctane, which indicates a different flexibility of the polymer chain that it assumes in different solvents. The more flexible the chain becomes, the easier it is for it to move in parts, the smaller the independent segment of the chain (segment), and the lower the heat of activation and the viscosity of the solution. Conversely, in a solvent in which the chain cannot assume a large number of conformations, the flow segment is large, and the heat of activation and the viscosity of the solution are high.

Of course, comparison of such quantities as viscosity and entropy of mixing is not always correct, since the first quantity is a kinetic characteristic of the solution, whereas the second is a thermodynamic one. However, since for polyisobutylene the kinetic and thermodynamic segments coincide^(11), such a comparison is legitimate. For polystyrene solutions this is less correct. But the main conclusion that follows from such a comparison seems to us sufficiently convincing. The viscosity of concentrated polymer solutions is determined both by the viscosity of the solvent and by the flexibility of the polymer chain in the given solvent. The lower the viscosity of the solvent and the more flexible the polymer chain in the given solvent, the lower the viscosity of the solution. These two factors may exert an influence either in the same or in opposite directions.

The addition of a low-viscosity component of the solvent to a high-viscosity component (polymer) in itself increases the fluidity of the system^(12) to a greater extent, the lower the viscosity of the added component. But in addition to that

the fluidity of the system increases as a result of irreversible changes in the arrangement of the chains to a greater degree, the more flexible the chain molecule is.

The experimental material presented in this work indicates that for concentrated polymer solutions, as well as for the polymers themselves, the characteristic values of the heats of activation of flow are not small but very large. Large values of the heats of activation, exceeding those for low-molecular liquids by a factor of 8–20, indicate that the independently moving segments are very large in their dimensions,

Fig. 3. Dependence of the heat of activation of flow of polyisobutylene solutions on the volume fraction of polymer: 1 —toluene, 2 —isooctane, 3 —carbon tetrachloride, 4 —cyclohexane

Fig. 4. Dependence of the heat of activation of flow of polystyrene solutions on

Fig. 4

Figure 4: Fig. 4

the volume fraction of polymer: 1 —ethyl acetate, 2 —ethylbenzene, 3 —carbon tetrachloride, 4 —decalin

i.e., the chains or bundles moving during flow are more rigid than has been assumed up to the present time.

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