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Abstract

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THE INFLUENCE OF THE MOLECULAR WEIGHT OF POLYISOBUTYLENE ON THE VISCOSITY AND ACTIVATION HEATS OF ITS CONCENTRATED SOLUTIONS

(Presented by Academician V. A. Kargin on 18 II 1963)

Over the last ten to twelve years it has been established that the dependence of the logarithm of viscosity on the logarithm of the molecular weight of a polymer is expressed by two straight lines having different tangents of the angle of inclination (^{1,2}). For the flow of chemically diverse polymers of high molecular weight, the equation

$$\lg \eta = 3.4 \lg M - C, \tag{1}$$

is fulfilled, where η is the viscosity, M is the molecular weight of the polymer, and C is a constant depending on its chemical nature and temperature. There are data indicating the applicability of equation (1) to concentrated polymer solutions ($^{2-5}$). However, these conclusions were drawn on the basis of fragmentary studies, which were carried out either over a narrow interval of molecular weights or at one or two solution concentrations and at a constant temperature. It was of interest to carry out such a study over a wide range of molecular weights and concentrations at different temperatures.

Seven samples of fractionated and unfractionated polyisobutylenes with molecular weights from 10^3 to $2.8 \cdot 10^6$ were taken as the objects of the study; hydrogenated polyisobutylene dimer—iso-octane (2, 2, 4 trimethylpentane)—was used as the solvent. In such a system, the intermolecular interaction and thermodynamic flexibility of the polyisobutylene chain are the same as in the polymer itself.

The Newtonian viscosity of the solutions was measured at 20, 35, and 50°. The measurement procedure is described in (^{6}). On the basis of the obtained depen-

Fig. 1. Dependence of the logarithm of viscosity on the volume fraction of polyisobutylene in solution at 20°. 1 –molecular weight $0.9 \cdot 10^3$, 2 –$2.0 \cdot 10^4$, 3 –$1.1 \cdot 10^5$, 4 –$2.4 \cdot 10^5$, 5 –$6.4 \cdot 10^5$, 6 –$1.2 \cdot 10^6$, 7 –$2.5 \cdot 10^6$

Figure 1: Fig. 1. Dependence of the logarithm of viscosity on the volume fraction of polyisobutylene in solution at 20°. 1 –molecular weight $0.9 \cdot 10^3$, 2 –$2.0 \cdot 10^4$, 3 –$1.1 \cdot 10^5$, 4 –$2.4 \cdot 10^5$, 5 –$6.4 \cdot 10^5$, 6 –$1.2 \cdot 10^6$, 7 –$2.5 \cdot 10^6$

dence $\lg \eta = f(1/T)$, which is linear in the temperature interval studied, the activation heats of viscous flow were calculated.

Figure 1 gives the dependence of the logarithm of viscosity on polymer concentration (viscosity was expressed in poises, concentration in volume fractions). It follows from the figure that, in solutions of polymers of higher molecular weight, a sharp increase in the viscosity coefficient is observed in the region of low concentrations. In this case, the higher the molecular weight of the polymer, the greater the steepness of the curve $\lg \eta = f(\varphi_2)$. For solutions of polymers of low molecular weight, a sharper increase in viscosity is observed in the region of high concentrations. On the basis of the data of Fig. 1, the dependence of the logarithm of the viscosity of polyisobutylene solutions on the logarithm of the molecular weight of the dissolved polymer was constructed; it is presented in Fig. 2. Noteworthy is the fact that, over the entire concentration range, the dependence $\lg \eta = f(\lg M)$ is expressed, just as for polyisobutylene itself (1), by two intersecting straight lines. In the region of higher molecular weights, the tangent of the angle of inclination of the straight lines does not depend on the concentration of the solution and is equal to 3.4; that is, for solutions of polyisobutylenes of high molecular weight, equation (1) is fulfilled. For solutions of polymers of low molecular weight, the tangent of the angle of inclination of the straight lines $\lg \eta = f(\lg M)$ is considerably smaller, and its value depends on the concentration of the solution.

It is seen from Fig. 2 that the position of the point of intersection of the straight lines depends on

concentration of the solution: the lower the concentration, the greater the value of the molecular weight M_c corresponding to the point of intersection. This is shown clearly in Fig. 3, which gives the curves $\lg M_c = f(\varphi_2)$ for two temperatures. A change in temperature does not affect the form of the dependence $\lg \eta = f(\lg M)$, but as the temperature is raised the point of intersection of the straight lines shifts into the region of higher molecular weights (Fig. 3).

Figure 4 presents the dependence of the activation heats of viscous flow of solutions of different polyisobutylene samples on concentration. Curve (1) shows the change in activation heat with the concentration of a solution of polyisobutylene having molecular weight $\sim 10^3$. With an increase in molecular weight from 114 (isooctane) to 1000, a sharp increase is observed in the value of the activation heat from 1.9 kcal/mol to 14.5 kcal/mol. Upon

Fig. 2. Dependence of the logarithm of viscosity on the logarithm of the molecular weight of dissolved polyisobutylene at 20°. The numbers by the curves are the concentrations of the solution in volume fractions.

Figure 2: Fig. 2. Dependence of the logarithm of viscosity on the logarithm of the molecular weight of dissolved polyisobutylene at 20°. The numbers by the curves are the concentrations of the solution in volume fractions.

Fig. 1. Dependence of the logarithm of viscosity on the volume fraction of polyisobutylene in solution at 20°.
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passing from the sample with $M = 1000$ to the sample with $M = 20\,000$, the activation heat increases by only 1.5 kcal/mol (from 15.5 to 16 kcal/mol). A further increase in molecular weight up to $M = 1.2 \cdot 10^6$ does not affect the value of the activation heat.

The very fact that the activation heat of viscous flow is independent of the molecular weight of the polymer has long been known. The present results only refine the value of the molecular weight beginning from which ΔH remains constant, i.e., the value of the flow segment, which is somewhat higher than 1000. Of greatest interest is the circumstance that the independence of the activation heats from the molecular weight of the polymer in this same range of molecular weights is retained for solutions up to a concentration of $\varphi_2 \simeq 0.35$. In the region of more dilute solutions, the activation heat of flow proves to depend on the magnitude of the molecular weight of the dissolved polymer (curve 2 splits). Constancy of the value of ΔH is observed beginning with a molecular weight equal to $\sim 2.4 \cdot 10^5$.

The experimental material presented, testifying to general regularities in the flow processes of polymers and their concentrated solutions, should be considered from the standpoint of modern concepts of the structure of polymers.

At present, the existence of complex supramolecular structures may be regarded as proven not only in plastics, but also in rubber-like polymers (7), to which polyisobutylene belongs. Apparently, these structures do not arise instantaneously upon transition to the solid state, but are prepared in solutions. In passing from dilute solutions, in which individual isolated molecules assume various conformations, up to compact coils, to concentrated solutions, the formation of more complex structures should be expected (8). Obviously, in the transition from the polymer to its concentrated solutions and upon further dilution, the breakdown of these structures should be observed. What the structures in solutions are, how they are formed and destroyed, and how they move during flow—these are

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

the questions to which studies of the properties of concentrated solutions must provide answers. From this standpoint, the experimental material presented above is also of interest.

Fig. 3. Dependence of the logarithm of the critical molecular weight on the volume fraction of polyisobutylene in solution.
1 –at 50°, 2 –at 20°

Let us begin with Fig. 2. At a certain value of the molecular weight of the polymer, a sharp bend is observed in the curve $\lg \eta = f(\lg M)$, i.e., the mechanism of flow changes. From Bueche' s theory (8) it follows that this bend in the curve $\lg \eta = f(\lg M)$ is explained by the presence in solutions of structures that break down at molecular-weight values smaller than M_c. Bueche' s theory predicts a shift of the critical value M_c, with decreasing solution concentration, toward higher molecular weights, and the constancy of the product $M_c \cdot C$. All this is confirmed by the data we obtained over a wide concentration range. For example, at a polymer molecular weight of $1.8 \cdot 10^6$, the structures persist down to a concentration of the order $\varphi_2 \simeq 0.05$, whereas at $M = 2.8 \cdot 10^4$ they break down at a concentration $\varphi \simeq 0.5$. The product $M_c \cdot C$ is constant and equal to 10^4, which agrees well with Ref. (9).

However, Bueche' s theory is based on old ideas about structure formation in solutions caused by entanglement of molecular chains. From the standpoint of these ideas, it is difficult to understand the experimental fact observed by us: the shift of the critical molecular weight toward larger values with increasing temperature (Fig. 3). This fact, it seems to us, is easily explained by the reversible breakdown of such statistical–

Fig. 4. Dependence of the heat of activation of flow of polyisobutylene solutions on the volume fraction of polyisobutylene in solution.
a –molecular weight $0.9 \cdot 10^3$,
b –$2.0 \cdot 10^4$,
v –$1.1 \cdot 10^5$,
g –$2.4 \cdot 10^5$,
d –$6.4 \cdot 10^5$,
e –$1.2 \cdot 10^6$

formations such as bundles, which are analogues of swarms in low-molecular liquids. The existence of organized and ordered formations in polymer solutions is also indicated by data on activation heats. The experimental curves for the dependence $\Delta H = f(\varphi_2)$, shown in Fig. 4, coincide with Hirai' s theoretical curves $^{(10)}$, calculated under the assumption that associates formed by bundles of chains are present in the solutions. It is precisely this assumption that leads to the independence of the activation heats from the molecular weight of the polymer in the region of high concentrations and to the splitting of the curve in the concentration region $\varphi_2 < 0.35$. It is interesting to note that the product of the molecular weight by the concentration (Fig. 4) in the concentration region below $\varphi_2 = 0.35$ does not exceed the same value, 10^4.

Thus, the data presented indicate the presence of organized structures in concentrated polymer solutions, which disintegrate and form at concentrations that are lower the higher the molecular weight of the polymer.

The formation of low-molecular structures is accompanied by a sharp increase in the viscosity of the solution, observed at concentrations that are lower the higher the molecular weight of the polymer (Fig. 1). Evidently, in concentrated solutions and in the polymer itself these supramolecular structures of the bundle type prove to be kinetic units moving during flow. This assertion is in good agreement with previously published data $^{(6)}$ on the identical viscosity of polyisobutylene solutions in a good solvent—iso-octane—and in butyl propionate, in which polyisobutylene swells only to a limited extent, i.e., in which the supramolecular structures do not disintegrate.

All the material presented indicates that the flow segment of polyisobutylene, equal to 1000 or a somewhat larger value (Fig. 3), is equivalent not to a section of chain, as was formerly supposed, but to a certain aggregate of links arranged in bundles.

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