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Abstract

Full Text

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RHEOLOGICAL PROPERTIES AND SUPRAMOLECULAR STRUCTURE OF RUBBER-LIKE POLYMERS

Rheological properties are of primary importance for polymer-processing operations. Of particular interest is the dependence of a polymer' s viscosity on shear stress. Thus, when the shear stress is varied from values close to zero to several kilograms per 1 cm^2, the viscosity of many linear polymers decreases by several orders of magnitude. In technology this makes it possible to carry out processing operations at comparatively small true shear stresses.

In the work of Bartenev and Vishnitskaya (^{1}) it was suggested that the decrease in the viscosity of polyisobutylene (PIB) with increasing shear stress and shear-strain rate is associated with the destruction of the supramolecular structure characteristic of linear polymers at high temperatures (above the glass-transition temperature or the melting temperature). New experimental data obtained by us for polyisobutylenes confirm this assumption and indicate the essential role of supramolecular structures in the mechanism of polymer flow.

Fig. 1. Curves of shear-stress change at 80° during deformation of polyisobutylene at prescribed shear-strain rates: 1 –0.013; 2 –0.025; 3 –0.117; 4 –0.230; 5 –1.06 $\sec^{-1}$

Polyisobutylenes with molecular weights (by Flory) of 200 thousand, 900 thousand, and higher were studied in the temperature range 60–120° and at shear-strain rates from 0 to 1 $\sec^{-1}$ on a rotational viscometer (^{2}), operating under conditions of constant shear-strain rate, $\dot{\gamma} = \text{const}$. In what follows the data are given for PIB with mol. wt. 900,000, since analogous results were obtained for polyisobutylenes of other molecular weights.

Usually, in linear polymers, as the shear-strain rate increases, the shear stress

Fig. 2. Rheological curves of polyisobutylene with molecular weight 900,000 at 80°: 1 –for the steady-state flow regime; 2 –for the maximum stress

Figure 2: Fig. 2. Rheological curves of polyisobutylene with molecular weight 900,000 at 80°: 1 –for the steady-state flow regime; 2 –for the maximum stress

also increases. In polyisobutylene, in a certain range of rates anomalous behavior is observed, as is seen from the shear-stress curves shown in Fig. 1. Here, as is usual for all systems, at low strain rates no maximum is observed on the curves, whereas at high rates it is observed the more distinctly, the greater the shear-strain rate. Accordingly, in the region of low shear-strain rates the maximum and steady-state stresses coincide, while at high rates they differ (Fig. 2). From the curves shown in this figure, the anomalous effect is clearly seen in the form of an increase in shear stress after a certain critical stress P_k has been reached.

It may be supposed that the effect of a drop in stress above a certain critical value P_k is associated with the transition from "physical" flow to "chemical" flow, in which the molecular weight must be irreversibly reduced

of the polymer, since in the region of high temperatures one should expect that oxygen attaches to the macroradicals formed in the process of "chemical" flow. However, control experiments showed that no decrease in molecular weight is observed.

The molecular weight was monitored by viscosity; the experiments were performed as follows: the control viscosity was taken to be the viscosity of the polymer measured at 80° and at a low shear-deformation rate of 0.013 sec^{-1}, which corresponded to a shear stress of 0.6 kg/cm^2 and a viscosity of $4.5 \cdot 10^7$ poise. The polymer was tested for a long time in a viscosimeter at a shear-deformation rate of 0.117 sec^{-1}, then unloaded and allowed to rest at 80° for 2 h. After this, the viscosity was again measured at a shear-deformation rate of 0.013 sec^{-1}. Similar tests were carried out at rates of 0.23 and 1.06 sec^{-1}. In all these experiments the control viscosity practically did not change ($4.4 \cdot 10^7$ –$4.7 \cdot 10^7$ poise).

In addition, the activation energy of viscous flow was measured by a precise method ([3]). At low and high deformation rates the activation energy proved to be the same. Its constancy is connected with the fact that the mechanism of flow of PIB at low and high deformation rates was identical. Thus, it has been shown that over the entire investigated range of shear-deformation rates, "physical" flow of the polymer is observed.

Fig. 2. Rheological curves of polyisobutylene with molecular weight 900,000 at 80°: 1 –for the steady-state flow regime; 2 –for the maximum stress

According to data ([4]), supramolecular structures are characteristic not only of solid amorphous polymers, but also of highly elastic polymers, melts of crystalline polymers, etc. At high temperatures (in the viscofluid state), polymer

Figure 3

Figure 3: Figure 3

bundles become unstable because of the weak intermolecular forces between polymer chains and intensive thermal motion, as a result of which they break up. However, weak ordering processes remain even at high temperatures. Thus, instead of long fibril-bundles, short ordered bundle-like swarms, or “microbundles,” are formed. They have the same fluctuation nature as regions of short-range order in liquids, but differ in relatively greater stability and greater ordering.

In connection with the above, a linear polymer may be regarded as a network whose temporary junctions are microbundles. The chain segments not entering at a given moment into microbundles change their conformation at the rate of thermal motion and, during the lifetime of the microbundles, manage to change their conformation many times. Since the lifetime of the microbundles is considerably greater than the time for free segments to pass from one equilibrium position to another, the rate of viscous flow depends chiefly on the average number of microbundles per unit volume of polymer. In the process of flow, destruction of the microbundles takes place. The process of destruction proceeds the faster and the farther, the greater the stress and the rate of flow.

The observed anomalous decrease in stress with increasing shear-deformation rate (Fig. 2) is apparently explained by the process of destruction of supramolecular structures, which below the critical stress P_k proceeds slowly, and above P_k rapidly. In this connection one can low-

one may consider that P_k is a quantity in some way connected with the strength of the supramolecular structures.

Similar anomalous rheological curves (Fig. 2) are also observed for polymer solutions, as well as for disperse systems (^{5}). Since supramolecular structures exist in polymer solutions, for them too such an anomaly is explained by the abrupt destruction of supramolecular structures upon reaching the critical stress.

Fig. 3. Rheological curves of polyisobutylene with molecular weight 900,000 at 80° in the steady flow regime: 1 $-\dot{\gamma} =$ const, readings after 15 min; 2 —the same after 1-2 h; 3 $-P =$ const

The character of the rheological curves for the steady process of viscous flow is preserved at all temperatures, but with increasing temperature the anomaly becomes less pronounced, while the critical stress P_k gradually decreases (it is equal to 1.35 kg/cm^2 at 60°; 1.18 at 80° and 0.95 at 120°). At very high temperatures the rheological curve degenerates into a straight line characteristic of Newtonian flow, and the anomaly disappears together with the supramolecular structure, which is completely destroyed under intensive thermal motion.

For polyisobutylene one more anomaly of the rheological properties is observed. It is clearly seen from comparison of the rheological curves (Fig. 3) obtained on

Figure 4

Figure 4: Figure 4

a rotational viscometer under two test regimes, $\dot{\gamma} = \text{const}$ and $P = \text{const}$. The rheological curves coincide at stresses lower than the critical stress and diverge with increasing shear deformation rate.

Both rheological curves correspond to an apparent "steady" flow regime, when the curve $P(t)$ or $\dot{\gamma}(t)$ is observed to pass into a section practically parallel to the time axis t. However, in longer observations it was found that the parallelism of the sections of the curves to the time axis is not obeyed quite strictly. With time the stress (Fig. 1) gradually and very slowly decreases, tending toward an equilibrium value. In this case rheological curve 1 in Fig. 3 approaches curve 2. In the $P = \text{const}$ regime, the shear deformation rate in the "steady" regime increases stepwise with time, and consequently curve 3 (Fig. 3) shifts to the left with time.

Fig. 4. Changes in shear stress under different deformation regimes of a linear polymer: 1 —in the regime $\dot{\gamma} = \text{const}$; 2 —in the regime $P = \text{const}$; 3 —in the regime $P' = \text{const}$, where $P' > P$

From the data presented it follows that curve 3 (Fig. 3), obtained at $P = \text{const}$, in reality does not correspond to the true "steady" process, since in long experiments further destruction of the supramolecular structure occurs and the rheological curve shifts leftward toward curve 2, which is close to the "equilibrium curve."

All these phenomena are connected not only with the destruction of supramolecular structures, but also with the features of the $\dot{\gamma} = \text{const}$ regime at high deformation rates, when a maximum appears on the curves $P(t)$ at $P > P_k$. At that

at the same time, the testing regime $P = \text{const}$ does not have this feature (Fig. 4).

The destruction of the supramolecular structure with increasing stress obeys a sharply increasing nonlinear law, as follows from works (1, 6). Therefore, the destruction of the supramolecular structure at the maximum will be the strongest.

Figure 4 shows the curves: 1—for $\dot{\gamma} = \text{const}$ and 2—for $P = \text{const}$, where $P > P_\text{k}$. Curve 1 corresponds to such a shear-strain rate at which the shear stress after the maximum in the "steady-state" regime would coincide with $P = \text{const}$ for curve 2 (section BB). Since the supramolecular structure in the regime $\dot{\gamma} = \text{const}$ (at the maximum) is destroyed to a greater extent than in the regime $P = \text{const}$, the shear-strain rate on the section of curve BB for the second regime will be lower. In order, in the "steady-state" flow process in the regime $P = \text{const}$ (curve 1), to reach the specified value $\dot{\gamma} = \text{const}$, the shear stress must be increased to

$P' =$ const (curve 3, Fig. 4). This explains the divergence of curves 1 and 3 in Fig. 3.

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Note: Figure translations are in progress. See original paper for figures.