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Transition of Linear Flexible-Chain Polymers from the Fluid to the High-Elastic State, Spurt Effect, and Superspurting Modes of Their Motion

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SUMMARY

It is typical of high-molecular linear flexible-chain polymers with a narrow molecular-weight distribution to flow in a broad range of shear stresses similarly to Newtonian liquids. There exists a critical stress at which a spurt effect in the capillary or a jumpwise increase in volume output occurs. It corresponds to the transition of the polymers from the fluid into the rubbery (high-elastic)state. Under supercritical conditions the polymers break at the entrance to the capillary with the result that flowing through the latter is a stream formed by the polymers torn into pieces. For the first time, the regularities of supercritical motion of flexible chain linear polymers have been established.

INTRODUCTION

Transition from the fluid to high-elastic state is a relaxation process typical of high-molecular linear polymers whose molecular weight (M) is much greater than M_c. The value of M_c is determined by a rather sharp change of the dependence of initial viscosity on molecular weights (VINOGRADOV and MALKIN 1980). According to BOYER and MILLER (1978) M_c is in direct correlation with a cross-section of macromolecules and characterises their kinetic flexibility. At $M > M_c$ there appears a network of fluctuating macromolecular entanglements and the polymers become susceptible to considerable recoverable strains.

With increasing shear rate and stress the entanglement network may break down. Depending on the molecular weight (or, to be more precise, on M/M_c), the molecular weight distribution (MWD), and temperature, this process takes different courses.

High-molecular linear polymers are capable of passing to the high-elastic (rubbery) state under the effect of high shear rates. This transition is of relaxation nature and occurs at temperatures that may exceed T_g. It takes place upon reaching the critical shear stress (τ_s) which is an important characteristic of all high-molecular representatives of the polymer-homologous series. The transition under consideration occurs when condition $\dot{\gamma}_s$= const. is also met.As will be shown later the flow of polymers with narrow MWD up to $\tau = \tau_s$ proceeds at constant viscosity. Then,the critical deformation rate $\dot{\gamma}_s$ corresponding to τ_s, becomes inversely proportional to the initial viscosity of the polymer and is temperature-dependent, just as viscosity. It should be emphasized that the condition τ_s = const. applies not only to the abrupt transition of monodisperse polymers to the rubbery state but also to the smooth transition of polydisperse ones exhibiting non-Newtonian flow.

Transition of a linear polymer to the high-elastic state causes the spurt effect: as a result of loss of fluidity the polymer detaches itself from the wall of a capillary and starts sliding over it.

The decreasing resistance to the polymer movement produces an abrupt, ten-, hundred-, and even thousand-fold, increase in the volume rate of polymer flow through the capillary.

The above behavior was studied in a series of experiments (VINOGRADOV 1973) conducted at the laboratory of Polymer Rheology of the Institute of Petrochemical Synthesis of the USSR Academy of Sciences. The quantitative aspects of supercritical modes of polymer motion still remained to be studied, although as far back as 1972 it was established by polarization- optical studies (VINOGRADOV at al.1972,VINOGRADOV and MALKIN 1980) that under supercritical conditions the polymer becomes discontinuous at the entrance to the capillary with the result that flowing through the latter is a stream formed by the polymer torn into pieces.

EXPERIMENTAL

The experiments were carried out using a constant-pressure capillary viscometer (VINOGRADOV and PROZOROVSKAY 1964) with a set of cylindrical polished capillaries. The variation factor of the flow rate corresponding to a given pressure did not exceed ± 10% at a result reliability of 95%.

The experiments involved 1,4-polybutadienes (PB) with a narrow molecular weight distribution, obtained by anionic polymerization, 1,4-polyisoprene (PI) and a fluorine rubber SKF-32 all for wide MWD were investigated as well.

RESULT AND DISCUSSION

Consider now the experimental results involving the series of PB with narrow (M_w/M_n = 1.1-1.2) and wide MWD, strained in the broad range of shear rates and stresses. Fig.1 illust-

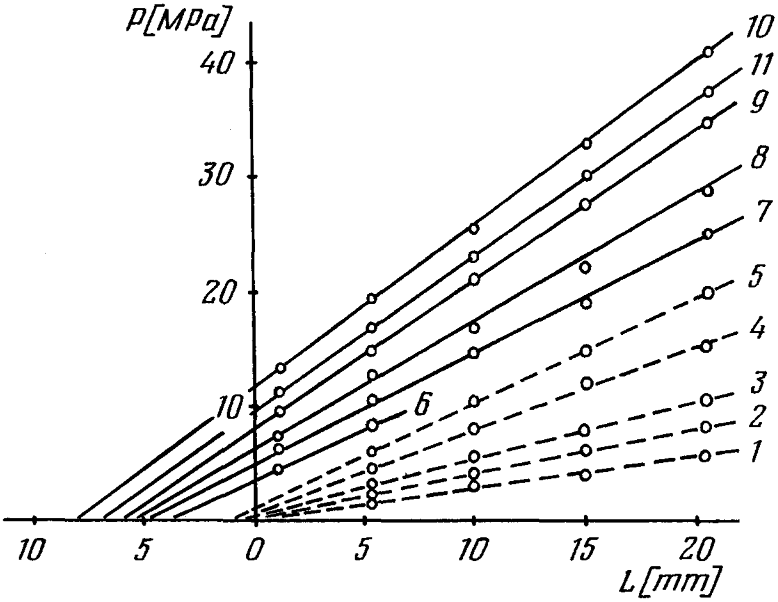


Fig.1. Total pressure P versus capillary length L at 20°C and a capillary diameter of 1.0 mm for PB with narrow MWD ($M_w = 2.6\cdot10^5$) at different flow rates (log Q,m^3/s): -11.2(1);-11.0(2);-10.8(3);-10.6(4);-10.4(5);-8.8(6);-8.4(7);-8.2(8);-7.8(9);-7.4(9);-7.2(10);-7.0(11).

rates the results of determining the pressure losses at the inlet of a capillary 1.0 mm in diameter for PB with $M_w = 2.6 \cdot 10^5$ at 20°C. It shows two sets of lines of total pressure (P) versus capillary length (L) corresponding to laminar flow (dashed lines) and supercritical polymer motion (solid lines). Characteristic of the laminar flow are small pressure losses at the capillary inlet (P_0 = P at L = 0), commensurate with the pressure change in the capillary over a length equal to the capillary diameter. In the supercritical mode, P_0 increases rapidly with the speed of polymer motion. Data concerning the relationship between P_0 and the flow rate, obtained for PB with narrow and

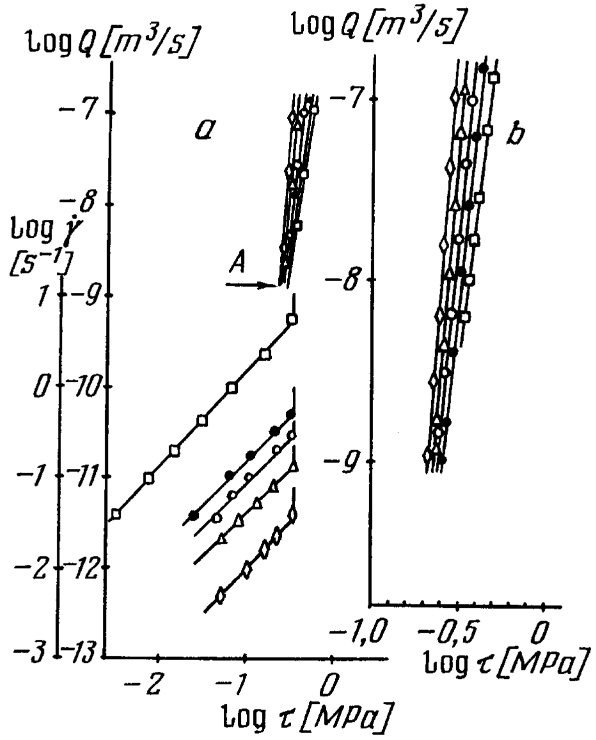


Fig.2a,b. Flow rate and shear rate versus shear stress at 20°C and a capillary diameter of 1.0 mm for PB with narrow MWD and M_w: □ - $1.1 \cdot 10^5$; ● - $2.0 \cdot 10^5$; ○ -$2.6 \cdot 10^5$; ◇- $4.7 \cdot 10^5$. △-$3.4 \cdot 10^5$

wide MWD as well as for polymers chemically different from PB, such as PI and fluorine rubber (SKF-32), suggest that under supercritical conditions the significant increase in the pressure at the capillary inlet is due to processes involving breaking of the polymers.

Fig.2 a,b represents flow rate (Q) versus shear stress in a broad range of values of Q for PB with different M and narrow MWD. The shear stress at the capillary wall was determined from the formula $\tau = \frac{(P - P_o)\cdot R}{2L}$, where R and L are, respectively, the capillary radius and length. It can be seen that high-molecular polymers with a narrow MWD at $M/M_c > 10$ and $T/T_g \gg 1$ are represented by straight lines with a slope equal to unity in a broad range of shear stresses, i.e. they behave like Newtonian liquids (lower part of Fig.2a). This specific behavior can be explained as follows: the fluctuating entanglement network of polymers with a narrow MWD is characterised by high density and uniformity. The high uniformity of the entanglement network provides for even distribution of stresses over a large number of nodes with the result that weak forces act upon each node. Under such conditions there is no upsetting of the dynamic equilibrium of the processes of entanglement network node breakdown under the effect of shear stress and formation of new nodes under the effect of heat motion. This means that the polymer structure remains virtually unchanged, and the polymer flows like a Newtonian liquid.

If the dynamic equilibrium is upset with increasing shear stress, the breakdown rate of network nodes starts exceeding the rate of their formation, forces acting upon the remaining nodes increase greatly, and the breakdown of the entanglement network becomes avalanche-like with the result that the spurt effect occurs (the vertical portions in Fig.2a). It corresponds to a jump of the volume output from the highest shear stress end of the flow curves up to point A where the supercritical motion of the polymers begins (the upper part of the Fig.2a). The same data concerning supercritical motion are presented in an enlarged scale in Fig.2b.

The pressure drop in the capillary (in the case of constant flow rate), defined as $P - P_o$, and, consequently, the associated force of friction are linearly dependent on the capillary length, that is the contact area (Fig.1). Hence, in the supercritical mode of motion the polymers behave as a quasi-solid body, being governed by the Amontons-Coulomb law of friction. In this mode, when the polymer slides over the capillary walls, the flow rate is strongly dependent on the shear stress: 1.5-fold increase in τ results in a more than 100-fold increase in the flow rate. It should be pointed out that the determination of the value of $P - P_o$ (or τ from the above formula) and the errors, involved primarily in the determination of P_o, describe the above behavior of the polymer as a quasi-solid body only by way of a rough approximation. Thus, the method of capillary viscometry may provide only approximate data concerning the friction of polymers.However, in spite of this limitation, a clearly defined difference in the behavior of PB of various molecular weights is observed. To achieve the same flow rate, a lower shear stress is required for a more high-molecular polymer. In the rubbery state region, the dissipation loss modulus of polymers decreases with increasing M, which facilitates external friction.

Fig.3 shows the effect of temperature on the behaviour of PB with narrow MWD and $M_w = 2.6 \cdot 10^5$.In the supercritical mode, the temperature no more affects the relationship between the flow rate and shear stress. Note that τ_s is almost independent of temperature since the latter does not produce any tangible effect on the node density of the fluctuation entanglement network (the activation energy of the entanglement network formation process is as low as 8 kJ/mole for flexible-chain nonpolar polymers.

Shown in Fig.4 is the rather small effect of MWD and the chemical nature of polymers on the supercritical motion. It can be seen that polymers widely differing in nature slide in a similar manner under supercritical conditions. The differences in the stresses necessary to achieve the same flow rate are small, being not more than two-fold in extreme

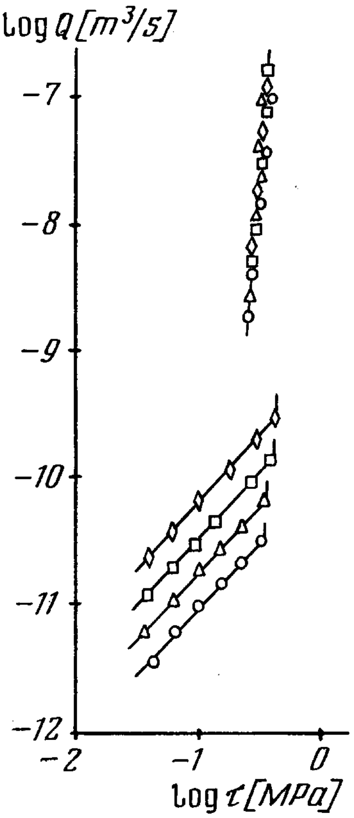


Fig.3. Flow rate versus shear stress at capillary diameter of 1.0 mm for PB with narrow MWD and $M_w = 2.6 \cdot 10^5$ at temperatures of: ○ -20°C; △ - 40°C; □ - 60°C; ◇ - 80°C.

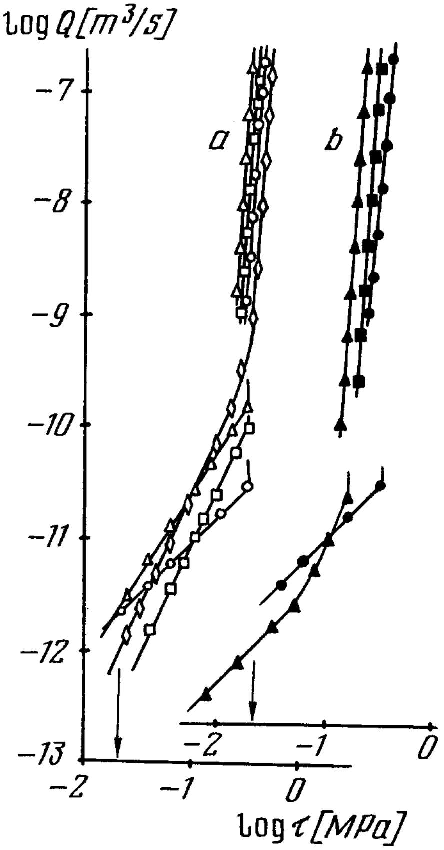
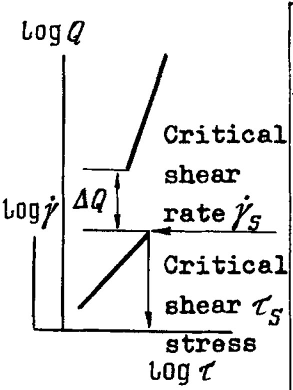


Fig.4 Flow rate versus shear stress at a capillary diameter of 1.0 mm for (a) PB with different MWD at 20°C: △ - $M_w/M_n=1.44$ ($M_w=2.7.10^5$); □ - $M_w/M_n=2.73$ ($M_w=2.6.10^5$); ◇ - $M_w/M_n=1.42$ (1.4-cis-PB with $M_w=$ $2.2 \cdot 10^5$ (b) various polymers: ● -PB with narrow MWD and $M_w=$ $2.6 \cdot 10^5$ (20°C); ▲ - PI with narrow MWD and $M_w=3.4 \cdot 10^5$ (20°C); ■ - fluorine rubber SKF-32 (103°C).

cases. Note that the flow of SKF-32 could be realized only at a flow rate not lower that 2.10^{-10} m^3/s. Fig.5 summarizes the data concerning the influence of different factors on the magnitude of the spurt, i.e. increase in the volume output ΔQ during this process.



Factors affecting the spurt	Value of ΔQ
L/D of capillary	Increases strongly with L/D ($\Delta Q \sim L$)
Mol. weight of polymer	Increases strongly with M ($\Delta Q \sim M^{3.4}$)
MWD of polymer	Decreases with the broadening of M_w/M_n
Temperature	Does not show any noticeable change

Fig.5. Generalized representation of the influence of different factors on the value of volume output ΔQ at the spurt.

CONCLUSIONS

It is known that such elastomers as polybutadienes are difficult to process, primarily because of their tendency to enter readily into the quasi-cross-linked state, resulting in a spurt with subsequent slippage and breakdown. The rubbers in a quasi-cross-linked state do not lend themselves to mixing on a molecular level with other types of rubber and carbon black.

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