

Ultimate regimes of deformation of linear flexible chain fluid polymers

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At temperatures far from the glass transition temperature linear flexible chain high polymers of narrow *MMD* when being deformed may undergo a transition from the fluid to the forced high elastic (and the glass) state. In simple shear, uniaxial extension and in the triaxial stressed state the transition of polymers to the forced high elastic state is accompanied by their rupture. Of decisive importance for this transition is the combination of the rate and amount of deformation. On the other hand, such a transition occurs at stresses which vary by 10–20 times for the various homologous series of linear flexible chain polymers. We have established unexpectedly simple relations connecting the parameters that characterize the rheological properties of polymers at deformation rates and stresses tending to zero with their ultimate strength and long term durability. This is determined by the fact that the polymers under consideration behave like linear bodies until they are fractured (in terms of the theory of linear viscoelasticity). From this it may be inferred that the selection of the simplest (as to composition) polymers having a highly homogeneous entanglement network plays a decisive role in the elucidation of the fundamental specificity of the rheological properties of polymeric systems.

INTRODUCTION

Two types of limiting regimes of deformation of polymeric systems are possible. The first type includes conditions under which the stresses, deformations, and rates of deformation are insignificantly different from zero. Such conditions are experimentally not feasible. Therefore the functional relations between the quantities indicated have to be extrapolated to their zero values. It is necessary to note at this point that the sensitivities of the various parameters (viscosity, high elasticity modulus, the coefficient of the first normal stress difference, etc.) to deformation conditions are generally different. This circumstance deserves attention because to the practically constant viscosity (within the accuracy limits of its measurement), which may be taken as initial, there often correspond recoverable deformations, which amount to tens of per cent.

The second limiting state of polymers and their concentrated solutions corresponds to the impossibility of their deformation as continuous media i.e. their fracture, which determines the ultimate strength and long term durability of polymeric systems. However, the process of destruction, say, the rupture of polymers, is usually considered with respect to polymers in the solid or high elastic states (cured rubbers). A question arises in this connection: how does the fracture of polymers occur in the fluid state?

Low viscosity inelastic polymer solutions may undergo a specific process involving their rupture called cavitation. This is attributed to the low extensibility of low viscosity liquids. The processes of cavitation will not be discussed here. The present work is entirely devoted to the problem of fracture of polymeric systems as a result of their forced transition from the fluid to the high elastic (rubbery) state on deformation.

Previously it has been shown¹ that at very high rates of deformation (on impact) viscous liquids (solutions of rosin

in oil) may break, like glass. In the case of polymers of high molecular mass, as the rate of their deformation increases they must pass from the fluid state first to the forced high elastic state (*FHES*). When the rate of deformation increases considerably, they assume the forced glass state (*FGS*). The processes of transition of polymers from the fluid state (*FS*) to *FHES* and *FGS* are not equivalent; not only are the conditions of transition from one state to another significantly different but also the ultimate strength and long term durability of polymers in *FHES* and *FGS*. Immediately the following question arises: what are the conditions of these transitions from the standpoint of both their deformation regimes and the structure of polymeric systems? This question as well as the entire concept of the transition of polymeric systems from *FS* to *FHES* were first formulated by the author in his lecture at the IUPAC symposium on macromolecules in Leiden². Later these problems were systematically elaborated in the work carried out in the Polymer Rheology Laboratory of the Institute of Petrochemical Synthesis of the USSR Academy of Sciences^{3–10}.

Let us define the concept of the forced high elastic state of polymeric systems. In this state, the fluidity and, accordingly, the possibility of accumulation in the polymer of infinitely large irrecoverable deformations is suppressed. The *FHES* is characterized by the tendency towards accumulation and reverse donation of a considerable energy as a result of uncoiling and coiling of macrochains. These processes take time.

Recoverable deformations are invariably limited and hence, the fracture of polymeric systems in the course of continuous deformation becomes inevitable when they assume the *FHES*. Not only the stresses and rates of deformation but also the amount of deformation (therefore, the time of deformation) may be important. Therefore, the time of deformation is included in the characteristics of the processes under consideration not only in the form of the rate

of deformation but directly, as the long term durability of polymeric systems. On transition from *FHES* to *FGS* the leathery state is first attained and only a very considerable increase of the deformation rate converts polymer systems into the glass brittle state. In this process, the greater the transition of polymeric systems from the high elastic and the leathery state to *FGS*, the less is the deformation preceding their brittle fracture.

At this point there arises an important question. If we assume the concept of the existence of a network of fluctuating entanglements in polymer systems, it may happen that in polymers which are in *FHES* this network functions like a network formed by chemical bonds in cured elastomers. If this is so, then for polymers in *FHES* there must be valid relationships typical of the fracture of cured elastomers and a failure envelope can be obtained for them, which is one of the most important characteristics¹¹ of systems of this kind. On transition from *FHES* to the leathery state the largest recoverable deformation is attained. A change of the law governing the durability of polymer systems, namely, the change from the power durability/rupture stress relation typical of cured rubbers¹² to the exponential law characteristic of *FGS*¹³ must correspond to this transition.

Let us now consider the conditions and specific features of the transition of polymer systems from *FS* to *FHES*. This is a relaxation transition which is most distinctly pronounced in high polymers of narrow molecular mass distribution (*MMD*).

HIGH POLYMERS OF NARROW *MMD*

The intensive development of the anionic polymerization process has made high polymers of narrow *MMD* readily available. High polymers are compounds in which the high elastic state is most distinctly prominent. This state begins to reveal itself when the molecular mass exceeds the critical value of M_c . It corresponds to the region of the sharp change of the relation between initial viscosity and molecular mass, which is usually associated with the formation of a network of entanglements. High polymers are thus defined here as polymers in which $M > 5M_c$. They are characterized by a developed, sufficiently homogeneous network of entanglements.

In the fluid state when the temperature exceeds the melting point and is much higher than the glass transition temperature and the deformation rates are low, the ruptures of the entanglement network may be compensated for by the formation of new entanglements. Then, at least in principle, a polymer may be deformed as long as desired. This reservation is important for extension processes since when the specimens being deformed become thinner the process loses its stability.

In linear flexible chain high polymers of narrow *MMD* the network of entanglements is highly dense and homogeneous. The parameters characterizing the viscoelastic properties of polymers of this type remain constant up to high stresses. This refers primarily to viscosity. It remains constant, at a first approximation, up to stresses of the order of several hundreds of MN/m^2 . This course is followed by the deformation of high polymers when the nodes of entanglement networks remain statistically equally stressed. It is necessary, however, to note that the constancy of viscosity equal to its initial value (within the error of measurement) does not mean that the polymer behaves in the same manner as in the undeformed state since at the high stresses

indicated above, the recoverable deformations may amount to 100% and higher.

With further increase of stresses and deformation rates the effect of the amount of recoverable deformation becomes increasingly more important. When a certain combination of the deformation rate and stress, on the one hand, and the amount of recoverable deformation, on the other, (and, hence, the time of deformation) is reached, the breakdown of the entanglement network is not compensated by recovery; and the load on the nodes left increases progressively. The fracture of the network may become avalanche-like. The time-dependent ultimate strength is reached. Since the rate of recovery of the entanglement network is determined by the Brownian motion of macromolecular segments, it depends significantly on temperature.

EFFECT OF TEMPERATURE ON THE CONDITIONS OF DEFORMATION OF HIGH POLYMERS OF NARROW *MMD*

The difference of the polymer state from the glass temperature is of great importance since this determines the intensity of thermal motion and the rate of rebuilding of the fluctuating network of entanglements and, hence, the rate of recovery of the ruptured network nodes. As the polymer approaches the glass temperature the rate of formation of entanglements decreases. Therefore, when the temperature decreases and the stress increases, the entanglement network becomes more sparse and less homogeneous. The decrease of the number of entanglements leads to a decrease of the resistance of the polymer system to deformation; the rate of deformation increases disproportionately to the stress, and the flow becomes non-Newtonian⁸.

An important example to illustrate what has been said above refers to data on the viscous properties of polybutadiene (PB) of molecular mass 1×10^5 and narrow *MMD* ($M_w/M_n = 1.1$) reported in the literature⁸. At room and higher temperatures the polymer behaves as a Newtonian liquid up to shear stresses of 0.2 MN/m^2 . But at -50°C it is a typical non-Newtonian body, for which at a shear stress of 0.1 MN/m^2 the exponent in the power equation describing the flow of systems of this kind is equal to 0.575.

Thus, high polymers of narrow *MMD*, depending on the ratio of the test temperature to T_g , on the one hand, and of M to M_c , on the other, may behave differently on deformation over a wide range of stresses. An extreme case is the case of sharp transition from Newtonian flow with the initial viscosity (at a certain, but rather high approximation) to the fracture of the samples or to the detachment from the confining walls. This may happen at $T \gg T_g$ and $M \gg M_c$.

In experiments on capillary viscometers a more general case is often observed: the smooth transition from the flow of the polymer with the initial viscosity to the distinctly pronounced non-Newtonian flow ends up with an increase of the flow rate as if the stress derivative of the shear rate tends to infinity. Flow curves of this kind are recorded for polydisperse polymers. Such flow curves however, are also encountered with polymers of narrow molecular mass distribution at low values of M/M_c and T/T_g . This refers primarily to polystyrenes (PS), which is of particular importance, for, since the 1960s, they have become widely available and have been studied by many investigators.

Polystyrenes are characterized by a high value of M_c

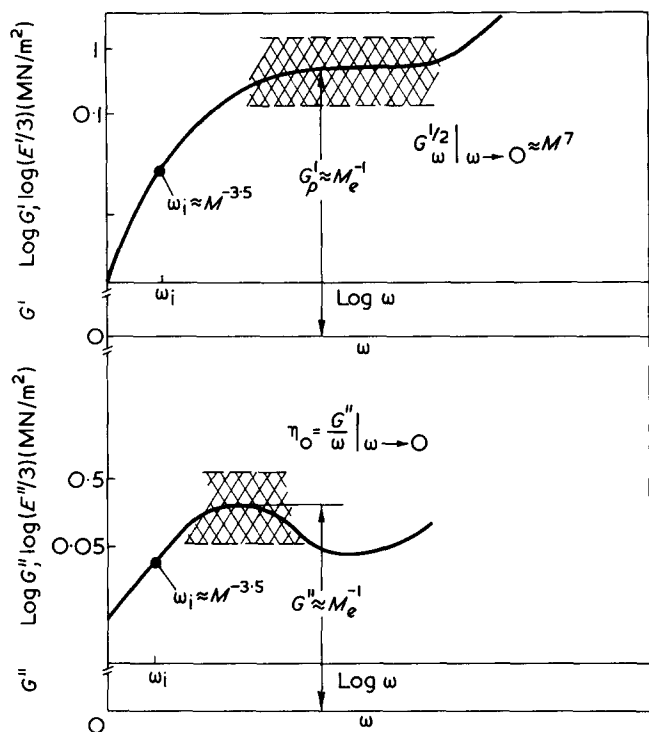


Figure 1 The frequency dependence of the components of the complex shear modulus for linear flexible chain high molecular mass polymers of narrow MMD. $T \gg T_g$; $M \gg M_e$; $M_w/M_n \approx 1$

(about 4×10^4) which is more than six times as high as the M_c of PB. Therefore, in most cases, PS samples with a relatively low ratio of M/M_c were used. If the high value of T_g is also taken into account, then it is easy to understand why the flow curves for PS usually given in the literature have a smooth transition from Newtonian to the sharply pronounced non-Newtonian flow. An enormous increase of flow rates at shear stresses exceeding 0.1 MN/m^2 corresponds to the transition of PS via the ultimate strength. The smoothness of such a transition has precluded its correct interpretation.

HARMONIC REGIMES OF CYCLIC DEFORMATION AND STEADY FLOW OF HIGH POLYMERS OF NARROW MMD

Let us consider the frequency relationships (Figure 1) for the components of the complex shear and uniaxial extension moduli in the linear region of deformation when the storage (G') and loss (G'') moduli do not depend on the deformation amplitudes. We shall discuss here only simple shear since uniaxial extension is equivalent to it. The position of the steeply falling left hand branches of the curves in question describes the behaviour of polymers in the terminal zone, which corresponds to the fluid state of the polymer. It is characterized by the initial values of viscosity η_0 and high-elasticity coefficient $A_{G,0}$ (or simply the elasticity coefficient), and by their dependence on temperature and molecular mass:

$$\eta_0 = \lim_{\omega \rightarrow 0} (G''/\omega) \approx M^{3.5} \exp(E/RT)$$

$$A_{G,0} = \lim_{\omega \rightarrow 0} (G'/\omega^2) \approx M^7 \exp(2E/RT)$$

The initial value of the elasticity coefficient is related

simply to the initial value of the normal stress coefficient, which is given by the relation between the first difference of normal stresses and the shear rate: $\sigma_{11} - \sigma_{22} = \sigma_w = \zeta_0 \dot{\gamma}^2$, namely, $\zeta_0 = 2A_{G,0}$.

The transition through the maximum and the attainment of the plateau region for the $G''(\omega)$ and $G'(\omega)$ curves correspond to the transition of the polymer to FHES. The heights of the maximum and the plateau determined by the values of G''_{max} and G'_{pl} are independent of the molecular masses and vary very slightly with temperature (proportional to absolute temperature). They are related in a simple manner³: $G''_{max} = 0.4 G'_{pl}$.

According to the literature data⁴ for the polymers of narrow MMD under consideration, the curvilinear portion of the $G''(\omega)$ dependence, which corresponds to the transition from the terminal zone to the maximum, has an extent of the order of ten-fold (or slightly higher) variation of ω and G'' . A considerable fall of temperature brings about a broadening of the curvilinear portion on the $G''(\omega)$ relation. The position of the maximum point, which is characterized on the frequency scale by the value of ω_{max} , is determined by the relationship between the initial viscosity of the polymer and temperature and molecular mass.

The values of G'_{pl} and G''_{max} are used to determine the parameter M_e , which, along with M_c , characterizes the density of the entanglement network. The value of M_c exceeds by several times the value of M_e . The ratio M_c/M_e probably depends on the nature of the polymer¹⁶.

The hatched zones in Figure 1 show that the values of G''_{max} and G'_{pl} vary only within the limits of 10–20 times for the various homologous series of linear flexible chain polymers. We shall show below that this is of great practical importance for the estimation of deformability and the ultimate strength and long term durability of polymers.

Various models of the linear behaviour of a viscoelastic polymer even under the conditions of unimolecular approximation describe satisfactorily the results of direct measurements of the functions $G'(\omega)$ and $G''(\omega)$ for polymers of narrow MMD^{4,15,17}.

The similarity of the $G'(\omega)$ and $G''(\omega)$ graphs for linear flexible chain polymers of the various homologous series enables us to construct master curves for carbon chain polymers and polysiloxanes. Such master curves are reported in the literature²⁴. The storage moduli are normalized with respect to their values of G'_{pl} , while loss moduli are normalized with respect to their values of G''_{max} . The viscoelastic functions are reduced for all polymers to the temperature $T_0 = T_g + 100^\circ\text{C}$. The molecular masses are normalized with respect to the values of M_z ($M_z = M_e/M_0$, where M_0 is the molecular mass of the monomer). Master dimensionless viscoelastic functions are thus obtained, which are shown in Figure 2.

CORRELATION OF THE CHARACTERISTICS DETERMINED UNDER DYNAMIC LOW AMPLITUDE AND STEADY FLOW CONDITIONS

The linear theory of viscoelasticity, generalized for large deformations, as in the literature^{18,19}, leads to the equalities $\tau = \sigma_{12} = G''$; $\sigma_w = \sigma_{11} - \sigma_{22} = 2G'$, where τ and σ_w are, respectively, the shear stress and the first difference of normal stress under steady flow conditions. It is assumed that ω is numerically equal to the shear rate in steady flow. Experiments with high molecular mass polybutadienes (PB)

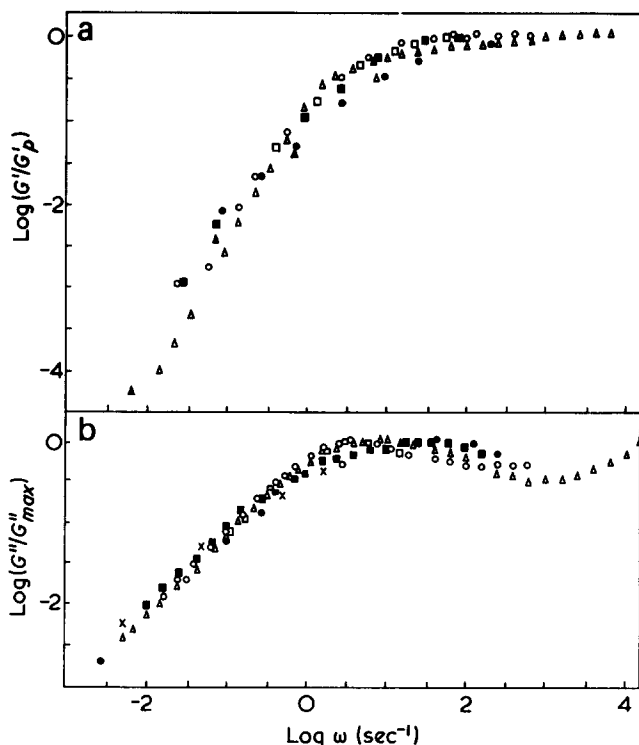


Figure 2 The frequency master curves of the components of the complex shear modulus for linear flexible chain high molecular mass polymers of narrow *MMD*: ○, PB; △, PS; ■, PMPHS; □, P1; x, PMMA; ▲, PVAC; ●, PDMS

and polyisoprenes (PI) of narrow *MMD* have shown that the correlation under consideration is valid for values of τ numerically equal to G''_{max} and that $\dot{\gamma}$ is about three times as low as ω_{max} . With polydisperse polymers the correlation of the parameters determined under steady flow and low amplitude deformation conditions is reliable only in the region of low values of ω and $\dot{\gamma}$ (strictly speaking, as their values tend to zero).

At $\dot{\gamma} > \omega_{max}$ the correlation of the functions $G''(\omega)$ and $\tau(\dot{\gamma})$ becomes impossible since under conditions, where $\omega > \omega_{max}$, the dynamic characteristic is sloping and cannot be equivalent to the steady flow conditions; the shear stress decreases with increasing rate of shear, which determines the instability of the deformation regime. The problem of the attainment of the critical regime of deformation of high molecular mass linear polymers can be tackled from a different standpoint as well.

The maximum of the function $G''(\omega)$ represents the transition of polymeric systems to *FHES*. In this state, polymeric systems always have a limited deformability. Therefore, if the deformation (or deformation amplitude) and the time of deformation are sufficiently great, a fracture of the polymeric system occurs, which on shear leads to the detachment of the polymer from the confining walls (since the ideal homogeneity of the stress field is practically unattainable and a higher stress will be observed at any of the walls). The critical values of stresses, deformations, rates of deformation (their amplitudes) and also of the deformation time will hereafter be designated by the respective asterisk-marked quantities. They determine the ultimate strength and long term durability of polymeric systems.

The quantities τ^* , just as G''_{max} , must be independent of the molecular masses for the high molecular samples belonging to each homologous series of linear flexible chain polymers. The values of $\dot{\gamma}^*$ as well as ω_{max} are governed by the

initial viscosity of the corresponding samples and, hence, by its dependence on the molecular masses and temperature.

SPURT OF POLYMER STREAMS IN DUCTS

The flow of polymers at high stresses is most simply realized in ducts. The attainment of the critical values of stresses and rates of deformation indicated above corresponds to the transition of polymers to *FHES* and to a sharp decrease of the fluidity of polymeric systems. In ducts, the highest stress is observed in the wall layers. Here the polymer system either ruptures or detaches from the wall. The processes subsequent to a break in the continuity of polymeric systems in the wall layers take place differently, depending on the deformation conditions.

Let us first examine what happens at given constant pressure gradients in ducts. The detachment of the main mass of the polymer from the walls causes a sharp decrease of the resistance and unloading of the polymer. The polymer is ejected at a high velocity from the duct; a spurt of the stream occurs. The flow rate may increase hundreds and thousands of times. The unloading of the freely ejected stream is responsible for the absence not only of the swelling effect but also of its periodical surface ruptures at the exit of the duct^{22,23}. Therefore, from the duct there is ejected a smooth stream, whose cross-section corresponds to the cross-section of the duct. The length of the smooth portion of the stream is equal to that of the duct.

A considerable decrease of the resistance of the stream in the duct causes a highly increased rate of deformation at the entrance zone and an extremely high concentration of stresses at the mouth of the duct. As a result, the polymer is fractured and is no longer a continuous medium. This is accompanied, on the one hand, by the above-mentioned highly increased flow rates, and, on the other, by the laminar flow being replaced by the chaotic motion of the mass broken into pieces.

It should be noted that under spurt conditions, at the given constant pressure on the plunger which pushes the polymer from the reservoir into the duct, the constancy of the pressure gradient in the duct may be spoken of only with certain reservations.

With increasing pressure gradients in the post-critical region the flow rates begin to exceed their highest value, which corresponds to the critical conditions responsible for the appearance of a spurt. A third, upper branch of the curve appears, showing the dependence of flow rates on pressure gradients. It should be stressed that these are the conditions of chaotic motion of the polymer broken into fragments. They have nothing to do with the laminar flow of polymeric systems and the spurt conditions have no relation to the proper flow curve.

The spurt of the stream under conditions of 'constant pressure gradients' in ducts completes the development of the process of elastic turbulence which reveals itself sharply in high polymers of narrow *MMD*, beginning from shear stresses approximately 5 times lower than the critical spurt stress. The elastic turbulence and spurt are processes of the same nature. If the spurt is due to the transition of polymers from *FS* to *FHES* starting at the entrance zone and spreading over the entire length of the duct, the regular distortions of the shape of the stream leaving the duct are caused by the events that happen at the edges in the entrance zone where the local stresses attain the critical values of spurt.

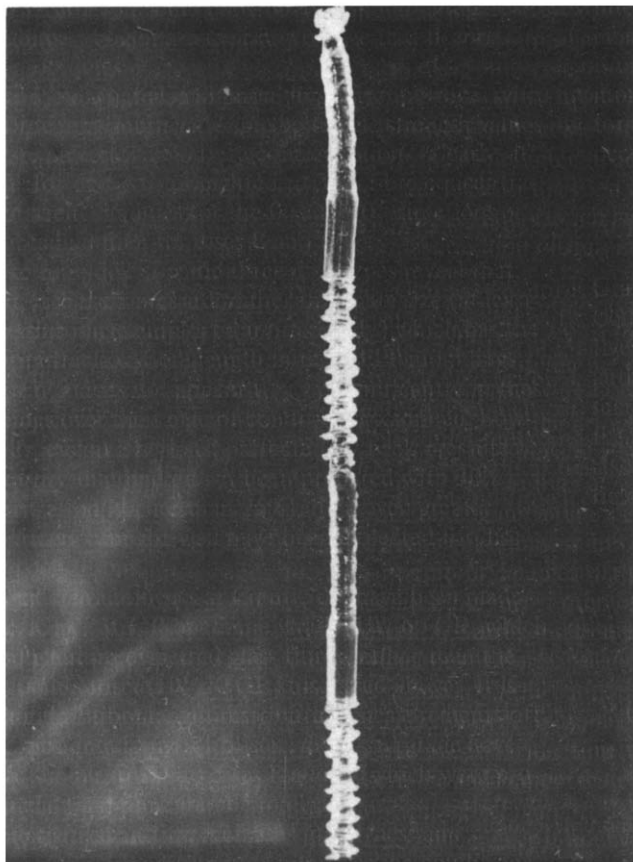


Figure 3 The shapes of the streams emerging from the capillary under spurt conditions at a constant velocity of the plunger for a high molecular mass polybutadiene of narrow *MMD*

We shall now consider what takes place if we specify the constant velocity of the plunger pushing the polymer out of the duct. When the rate of deformation of the polymer in the wall layer in the duct reaches the critical value, the polymer breaks away from the wall. A smooth portion of the polymer stream is ejected from the duct. Its cross-section and volume correspond to those of the duct. The spurt of the stream is accompanied by a sharp decrease of the resistance to polymer movement and a corresponding decrease of the pressure gradient in the duct. The spurt of the stream speeds up the flow of the polymer at the mouth of the duct, which is accompanied by a break in the continuity, i.e. ruptures in the polymer. Therefore, the smooth portion of the stream is followed by a portion of irregular form similar to that observed under the critical and after critical conditions of motion of polymeric systems considered above.

The continuous movement of the plunger retards the decrease of the pressure gradient. It reaches a minimum and then begins to increase rapidly. When the pressure gradient reaches a level at which intensive elastic turbulence develops, characteristic regular disturbances appear in the stream, which correspond to elastic turbulence. Therefore, under the conditions leading to the appearance of a spurt, with the constant velocity of the plunger being predetermined, three characteristic portions are observed in the stream: a smooth portion, a portion of irregular form and a portion with regular distortions of the surface of the stream. When the velocity of the plunger increases, the smooth and regularly distorted portions contract, and, finally, the entire stream assumes an irregular form.

The development of elastic turbulence and spurt is

accompanied by vibrational processes (of flow rate and pressure, depending on the conditions of deformation of the polymer). Formally these vibrations may be accounted for by the compressibility of the polymers²⁵⁻²⁸. In principle, however, these are processes caused by the reversible transitions of polymers from the fluid to the high elastic state, and back to the fluid state. The relation between the shape of the stream leaving the duct and the regimes of deformation of polymers under spurt conditions is shown in Figure 3.

The spurt effect is due to the transition of polymeric systems from *FS* to *FHES*. Since the correlation of low amplitude oscillating deformations and steady flow is applicable to linear flexible chain polymers of narrow *MMD*, it follows that the critical shear stress at which a spurt is observed (τ_s), just as that of G''_{max} , must have, within each polymer homologous series, a constant value independent of the molecular masses and (at a sufficient approximation) temperature, i.e., is an important rheological characteristic of each polymer homologous series. As regards the critical shear rate, $\dot{\gamma}_s$, at which the spurt occurs, at a first approximation $\dot{\gamma}_s \approx \omega_{max}$ and $\dot{\gamma}_s$ must be proportional to $M^{-3.5}$ and vary with temperature in accordance with the activation energy of flow typical of a given polymer homologous series. That the quantity τ_s is independent of the molecular mass and temperature is nicely confirmed by the data presented in Figure 4. It will be shown later that the validity of the conception developed above makes it possible to arrive at an important conclusion.

The hatched bands in Figure 1 for the relations $G'(\omega)$ and $G''(\omega)$ correspond to the critical values of $G' = G'_{pl}$; $G'' = G''_{max}$ and $\dot{\gamma} = \dot{\gamma}_s$; $\tau = \tau_s$. This means that for all the polymers under discussion, at shear stresses higher than 0.05–1 MN/m² a spurt must occur and hence no laminar flow is possible. This is the limit of intensification of the extrusion process. On the contrary, the after critical conditions of polymer motion can be efficiently used in moulding.

An essential disadvantage in the investigation of the spurt process and, in general, of the ultimate strength and long term durability of polymer systems in capillary rheometers is that we have to deal with the high inhomogeneity of the stress fields. This makes it extremely difficult to estimate the conditions under which the ultimate strength of polymer systems is attained.

Valuable information can be gained in experiments using rheometers, where a high homogeneity of the stress fields and shear rates is provided. For example, rheometers with coaxial cylinders can be employed for this purpose. Let us now briefly consider the results obtained by experiments on rheometers of this type^{20,21}.

LARGE AMPLITUDE OSCILLATING SHEAR

Under linear deformation conditions, where the deformation amplitudes (γ_a) and deformation rate amplitudes ($\dot{\gamma}_a = \omega\gamma_a$) are low, the deformation of polymers does not result in their fracture. In all the three states, the fluid, high elastic and glass states, their durability is practically infinite. On the other hand, in the forced high elastic and forced glass states, which are estimated by the low amplitude deformation, such critical values of deformation amplitudes (γ_a^*) and deformation rate amplitudes ($\dot{\gamma}_a^*$) must be attained, at which the fracture of polymers will take place. It must reveal itself

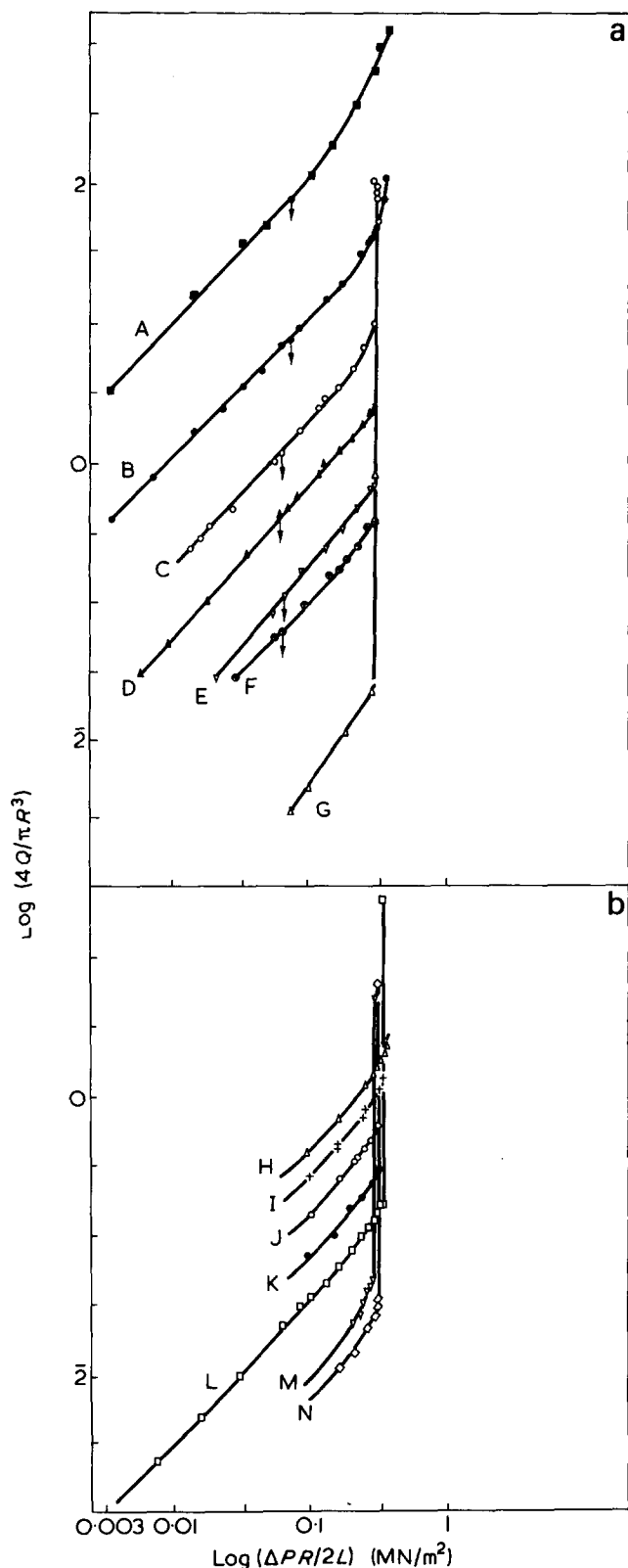


Figure 4 (a) The flow curves, spurt effect and appearance of elastic turbulence (marked with arrows) for polybutadienes of narrow *MMD*. Experiments have been performed on a capillary rheometer at 25°C. Curves A–G refer to polymers of the molecular masses 3.8, 6.75, 10, 15, 20, 24 and 58 × 10⁴ respectively; M_w/M_n from 1.1 to 1.22 (for the lowest molecular mass sample). Length/diameter = 25. (b) Flow curves and the spurt effect for PB of molecular mass 3.2 × 10⁵ and narrow *MMD* at different temperatures: H; –5°C; I, 0°C; J, 25°C; K, 40°C; L, 60°C; M, 80°C; N, 100°C. Length/diameter = 10

through the spurt effect. In rotational devices, the spurt reveals itself in a sharp decrease of the amplitudes of torques and of the corresponding stress amplitudes (τ_a^*). A very important problem is the effect of the increase of deformation amplitudes on the transition of polymers from *FS* to *FHES*, i.e., the possibility of the polymers being fractured, their spurt under the influence of increasing deformation amplitudes in the region of frequencies corresponding to the condition $\omega < \omega_{max}$ on low amplitude oscillating shear.

First we shall discuss the effect of the various combinations of amplitudes and frequencies on the spurt process for high molecular mass polymers of narrow *MMD*. This is shown in *Figure 5* based on the data reported in the literature¹⁰. Here the *Figures 5a* and *5b* show the relation $G''(\omega)$, which has been obtained at low amplitudes of deformations under linear regimes of polymer deformation. Below them are given the relations $\tau_a(\gamma_a)$; $\gamma_a^*(\omega)$; $\dot{\gamma}_a^*(\omega)$. The polymers under discussion behave like linear bodies (the stress is directly proportional to the deformations) up to the critical deformation conditions, to which there corresponds a spurt, a sudden fall of the stress (torque), which is shown by arrows in *Figure 5c* for the sake of clarity. The critical stress amplitudes are practically independent of the frequency.

Of importance is the fact that the critical deformation amplitude, γ_a^* , does not depend on the frequency if it exceeds the value of ω_{max} , which corresponds, at a low amplitude deformation, to the transition of the polymer from the fluid to the high elastic state. On the other hand, at frequencies lower than ω_{max} , the value of γ_a^* increases with decreasing frequency. The occurrence of a spurt at frequencies lower than ω_{max} signifies that the transition of polymers from the fluid to the forced high elastic state shifts to the region of ever decreasing frequencies. Hence, the transition of polymers from *FS* to *FHES* depends not only on the rate of deformation (frequency) but also on the amount of deformation.

Figure 5d shows the frequency dependence of critical deformation amplitudes. From this curve it follows that the critical deformation amplitudes sharply decrease (at a first approximation, by a power law) with increasing frequency up to a value equal to ω_{max} . On transition to the region of the high elastic state, which is assessed by the low amplitude deformation, the critical deformation amplitude has a low

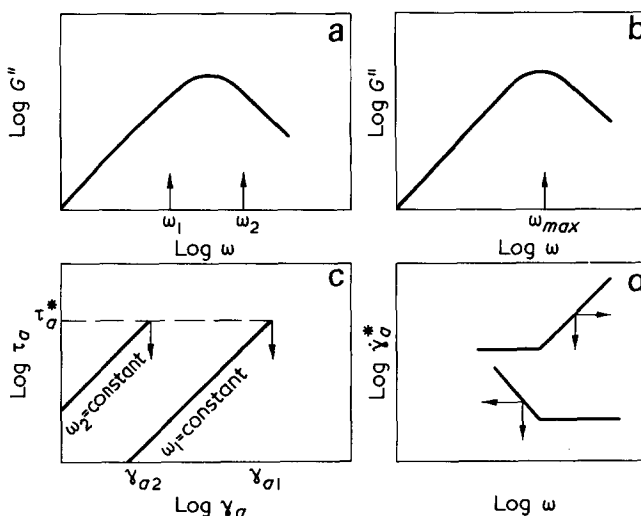


Figure 5 The most important specific features of the deformation behaviour on oscillating low and high amplitude shear of high molecular mass polymers of narrow *MMD*

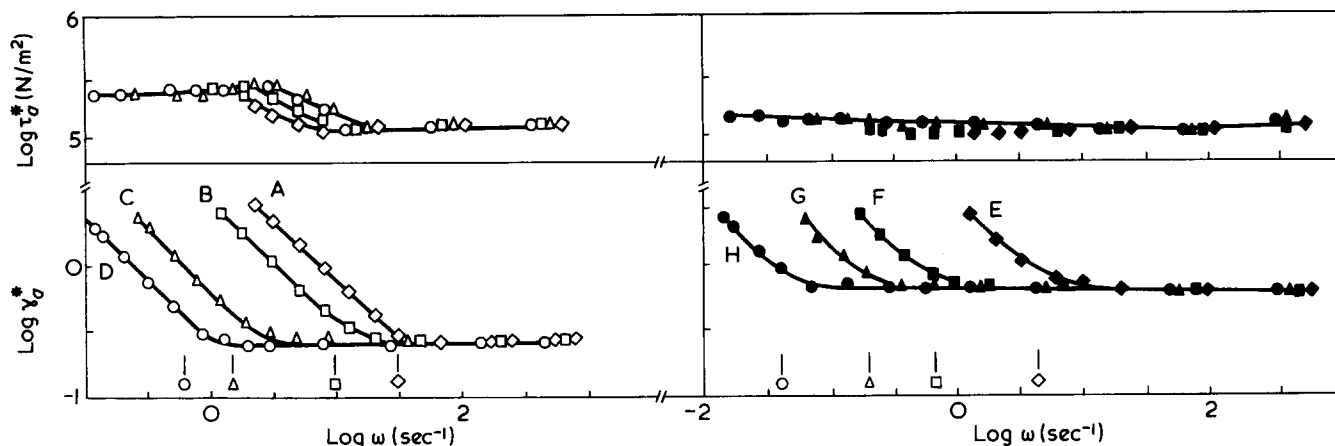


Figure 6 The frequency dependences of the critical amplitudes of shear stresses and deformations (corresponding to spurt) for polybutadienes (Δ , \square , \circ) and polyisoprenes (\blacktriangle , \bullet , \blacksquare). Experiments have been performed at 25°C. Curves A–H correspond to polymers of molecular masses: 7.6×10^4 ; 1.4×10^5 ; 2.3×10^5 ; 3.2×10^5 ; 1.5×10^5 ; 3.8×10^5 ; 5.75×10^5

value independent of the frequency. The relation $\dot{\gamma}_d^*(\omega)$ can easily be transformed into the frequency dependence of the critical values of deformation rate amplitudes since $\gamma_d^* = \omega \dot{\gamma}_d^*$. In Figure 5d the deformation rate amplitudes are related to the right hand ordinate.

Now we shall consider experimental data for polybutadienes and polyisoprenes of narrow *MMD*. They are presented in Figure 6. This figure shows data for polybutadienes, and for polyisoprenes. All the points on these graphs correspond to the spurt. The vertical strokes along the abscissa indicate the values of ω_{max} for the corresponding polymers. Each stroke splits the frequencies into two regions: the low frequency region corresponds to the fluid state, and the high frequency region represents the high elastic state (low amplitude deformation). For polybutadienes the critical stress amplitudes differ somewhat for these two regions. The cause of this difference is not clear.

The deformability of polybutadienes in the region of the high elastic state (estimated by the low amplitude deformation) is lower than that of polyisoprenes. This difference in behaviour of the polymers under discussion is accounted for by the higher rigidity of polybutadienes, which is determined by the higher density of the entanglement network.

There exists a quantitative correspondence between the deformation conditions under which a spurt appears in capillary viscometers and in rotational devices at large deformation amplitudes. This follows from the coincidence of the molecular mass dependences of the critical values of $\dot{\gamma}_d^*$ and $\dot{\gamma}_s$. This is shown in Figure 7, which confirms the statement that the parameters $\dot{\gamma}_d^*$ and $\dot{\gamma}_s$ depend on *M* in the same way as ω_{max} .

The spurt in rheometers with coaxial cylinders is caused by the fracture of the polymer in the zone of the highest stress near the inner cylinder. Observation of the behaviour of polymers in polarized light makes it possible to follow the course of the process of rupture of the polymer²¹. Under the spurt conditions the inner cylinder can easily be taken out of the clearance. The polymer is left on the outer cylinder. The critical values of deformation amplitudes and stresses corresponding to the spurt conditions do not depend on the rigidity of the dynamometer at its high values, on the machining quality of the working surfaces of the cylinders or the material they are made of. This means that the spurt conditions are determined by the bulk characteristics of polymers.

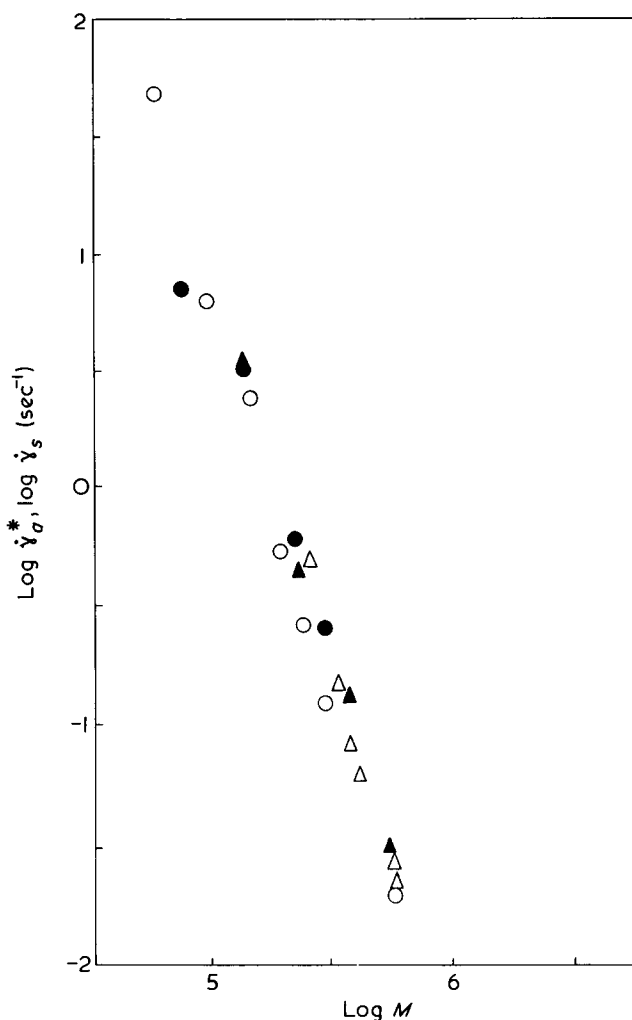


Figure 7 The dependences of the critical amplitude of deformation rate $\dot{\gamma}_d^*$ (\blacktriangle , \bullet) and critical rate of deformation $\dot{\gamma}_s$ (Δ , \circ) on the molecular mass of the polymer at 25°C. \circ , \bullet = PB, Δ , \blacktriangle = PI

UNIAXIAL EXTENSION

For high molecular mass linear polymers of narrow *MMD*, whose behaviour is described by the theory of linear viscoelasticity, there must exist a simple relation between their

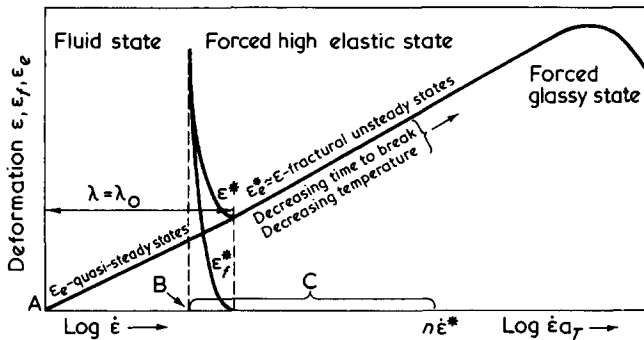


Figure 8 A diagram showing the principal specific features of the deformation behaviour of high molecular mass flexible chain polymers of narrow *MMD* in uniaxial extension. $T \gg T_g$; $M \gg M_c$; $M_w/M_n \approx 1$. A, initial values of fundamental parameters λ_0, E_e, E_f^1 ; B, $\dot{\epsilon}_0^* \approx \lambda_0^{-1} \approx M^{-3.5}$; $\dot{\epsilon}_0^* \lambda_0 \approx P^* = \text{constant}$; $\tau_s \approx (P^*/3) = 0.05\text{--}0.5 \text{ MN/m}^2$; $\epsilon_e = \epsilon_{e0}^*$; C, $t^* = B[P^*(\lambda_0)]$; $\dot{\epsilon} = \text{constant}$; $c = -2$; $P = \text{constant}$; $c = -3$; $\dot{\epsilon}_e \approx \epsilon^* = f[P^*(\lambda_0)]$

properties on simple shear and uniaxial extension. Moreover, in both cases, there must be a strict correspondence between the conditions of the transition of polymers from the fluid to the high elastic state. The spurt on simple shear is expected to correspond to the rupture of polymers in uniaxial extension. An important question arises: could the ultimate strength and long term durability characteristics of the polymers under discussion be described within the framework of the theory of linear viscoelasticity generalized for large deformations^{18,19}?

Figure 8 based on the data reported in the literature^{9,30,31} shows schematically the most important features of the behaviour of the polymers in question upon uniaxial extension.

The ordinate in Figure 8 represents the Hencky deformation. Here ϵ is the total deformation; ϵ_f is the irrecoverable deformation; ϵ_e is the recoverable part of total deformation; λ_0 is the initial value of longitudinal viscosity. The abscissa represents the logarithms of the rate of total deformation or its value multiplied by the reduction coefficient, according to the principle of temperature/rate superposition. The vertical broken line is the boundary between the fluid state and the forced high elastic state.

In the fluid state, the accumulation of total deformation and irrecoverable deformation is, in principle, unlimited. In practice, the limitation of extension may be caused by the thinning of the samples and the surface tension effect with subsequent increase of the instability of the extension process. For this reason, the 'steady' flow upon extension of the polymers should be regarded as a quasi-steady process. In this state, the recoverable deformation measured by elastic recoil after the unloading, increases monotonically with increasing deformation rate. In the case of high molecular mass linear polymers of narrow *MMD*, longitudinal viscosity is constant and equal to its initial value.

When the critical rate of deformation $\dot{\epsilon}^*$ represented by the vertical broken line is reached, the accumulation of irrecoverable deformation begins to fall sharply. The critical rate of deformation is inversely proportional to the initial viscosity and therefore depends very strongly on molecular masses and temperature. The product of the critical deformation rate and initial viscosity is equal to the critical value of true tensile stress σ_{11}^* . Each polymer homologous series is characterized by a certain value of σ_{11}^* , which is practically independent of the temperature and molecular mass.

The critical rate of deformation and stresses are the lowest values at which the rupture of the polymer samples can be recorded. There is some arbitrariness in the determination of the critical parameters since they depend on the length of observations (the long term durability of polymers will be discussed below).

High molecular mass polymers of narrow *MMD* behave as linear bodies until they are fractured. Therefore, over a wide range of deformation rates the Trouton relation between longitudinal viscosity and shear viscosity is fulfilled. From this follows a simple relation between the critical shear stress at which a spurt appears and the critical true tensile stress which corresponds to the rupture of polymers on extension. An important conclusion can be drawn from what has been said above concerning the hatched bands in Figure 1. Hence, in uniaxial extension it is impossible to exceed a stress of the order of 1 MN/m^2 without rupture of the polymer being deformed. In other words, a quasi-steady flow cannot be realized at stresses equal to or higher than 1 MN/m^2 . This circumstance has been noted in the literature³¹. An explanation for it is given here for the first time.

When the rates of deformation or stresses exceed their critical values, the accumulation of irrecoverable deformation decreases catastrophically. The total deformation diminishes. There is a minimum on the curve of total deformation *versus* rate of deformation. This is important for an explanation of the peculiarity of failure envelopes for uncured polymers.

Of great importance is the confirmation of the possibility of application of the principle of temperature/rate reduction, not only under quasi-steady conditions but also at deformation rates exceeding the critical values. What has been said is illustrated in Figure 9. Here the unfilled signs correspond to quasi-steady flow, the filled signs represent deformation leading to the rupture of samples. Polyisoprenes of narrow *MMD* ($3.75, 5.75, 8.3$) $\times 10^5$ have been investigated at temperatures from -25° to 75°C . It should be stressed that very high degrees of extension are attained in the forced high elastic state; they may amount to 15–20.

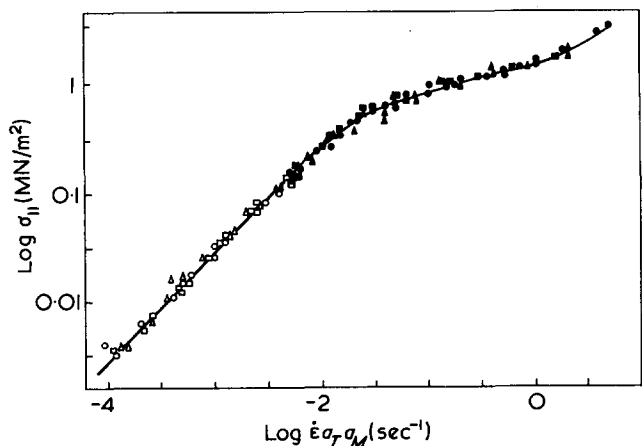


Figure 9 The flow curve and the dependence of the ultimate strength on the reduced rate of total deformation for high molecular mass polyisoprenes of narrow *MMD* at different temperatures:

| Flow | Fracture | $M \times 10^{-5}$ |
|-----------|------------------|--------------------|
| Δ | \blacktriangle | 3.75 |
| \circ | \bullet | 5.75 |
| \square | \blacksquare | 8.3 |

$$a_T = f[\lambda_0(T)]; a_M = \mathcal{J}(M^{3.6})$$

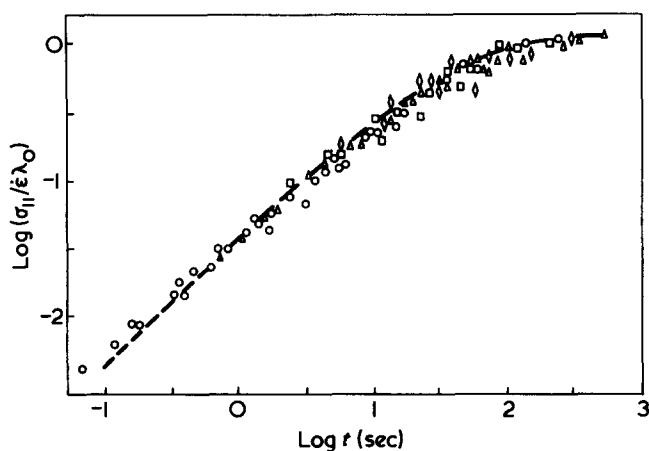


Figure 10 The temperature-invariant relation between the reduced extension time and the true stress normalized with respect to viscosity and rate of extension deformation. Polyisoprenes of molecular mass 5.75×10^5 at temperatures from 0–75°C: ○, 0°C; △, 25°C; □, 50°C; ◇, 75°C

The polymers under discussion behave like linear bodies up to rupture. Therefore, at the specified constant rate of deformation, their deformation is described by the linear theory of viscoelasticity as follows:

$$\sigma_{11}(t)/(\dot{\epsilon}\lambda_0) = 3 \int_0^{\infty} \theta F(\theta) [1 - \exp(-t/\theta)] d\theta$$

Here $F(\theta)$ is the relaxation spectrum for simple shear. The expression given can be generalized³⁰ for the various temperatures, normalizing the function with respect to longitudinal viscosity (its value up to the rupture of polymers is constant). Further, let us introduce the reduced time $t_r = t[\lambda_0(25^\circ)/\lambda_0(t)]$. Here $\lambda_0(t)$ and $\lambda_0(25^\circ)$ are the longitudinal viscosities at temperature t and the reduction temperature, respectively; then the dependence of the dimensionless parameter $(\sigma_{11}/\dot{\epsilon}\lambda_0)$ on t_r has the form shown in Figure 10. The broken line in Figure 10 was calculated from the data for the relaxation spectrum obtained in dynamic experiments on shear deformation. An excellent agreement between the calculation results and extension experiments points to the possibility of using the theory of linear viscoelasticity for describing the processes of deformation and rupture of high molecular polymers of narrow *MMD*.

In Figure 8, on the right hand side each point on the curves of deformation *versus* rate of deformation corresponds to the rupture of the polymer samples. The long term ultimate strength increases with increasing stress and rate of deformation, and the time up to rupture t^* decreases. This time is simply related to the ultimate strength, the rupture stress. It is described at a good approximation of the power function. The value of exponent $c < 0$, depends on the deformation conditions. At constant stress the value of c is higher than at constant rate of deformation. This difference can easily be explained. Indeed, when a constant rate of deformation is specified, the stress increases from zero to a value corresponding to rupture. Such conditions are considerably 'milder' than the conditions under which a high stress operates all the time, from the onset of deformation up to the rupture of the polymer.

It is important to note that the power function describes the time up to the rupture of uncured polymers in just the

same way as for vulcanized rubbers¹². This is an indirect evidence that uncured polymers in the forced high elastic state behave as quasi-cured polymers.

The above-mentioned simple behaviour of polymers on extension is observed in the forced high elastic state when T/T_g is greater than 1.2 and the rates of deformation are such that the glass state is not attained.

One of the most important characteristics of vulcanized rubbers is the failure envelope¹¹. It determines the combination of stresses and deformations at which the polymer is ruptured. Based on the data reported in the literature^{9,29,30} it is possible to construct a failure envelope for uncured polymers. Figure 11 shows a failure envelope for high molecular mass flexible chain polymers. The envelope splits the plane of true stresses and total deformations into two parts (Figure 11). The hatched right-hand zone corresponds to the combination of true stresses and deformations at which the polymer is ruptured sooner or later. If the combination of true stresses and deformations corresponds to the unhatched region of the graph, the stress may relax without rupture of the polymer.

LONG TERM DURABILITY OF UNCURED POLYMERS

Now we shall consider the problem of long term durability, the time from the onset of deformation up to the rupture of the polymer. The relevant data are presented in Figure 12, and cover a wide range of deformation rates and temperatures. Curves A and B describe, respectively, the behaviour of polybutadienes and polyisoprenes. The graphs obtained show that the data on long term durability can be presented in the form of a master curve when use is made of the principle of temperature/time superposition: the time up to rupture depends on molecular mass and temperature in just the same manner as the initial viscosity. This is an extremely important fact. It indicates that the process of rupture is described by the linear theory of viscoelasticity in spite of the fact that the rupture occurs at very high deformations. On the other hand, from this it follows that the rupture is a relaxational process and the mechanical-chemical factors play no essential role. No less surprising is the fact that, though the rupture of polymers is a relaxa-

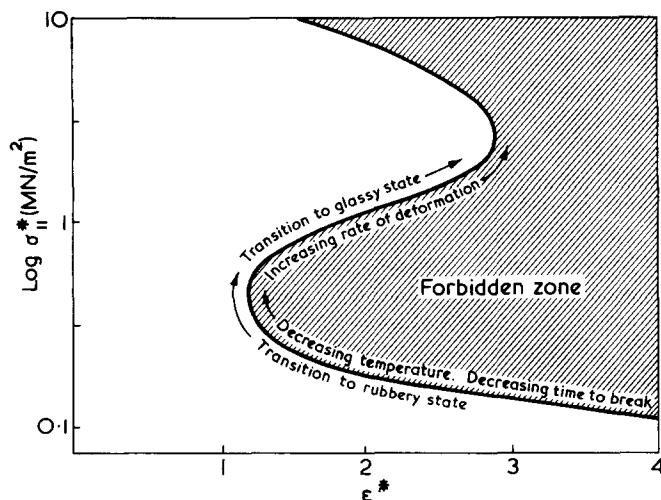


Figure 11 A diagram of the failure envelope for uncured high molecular mass linear polymers of narrow *MMD*

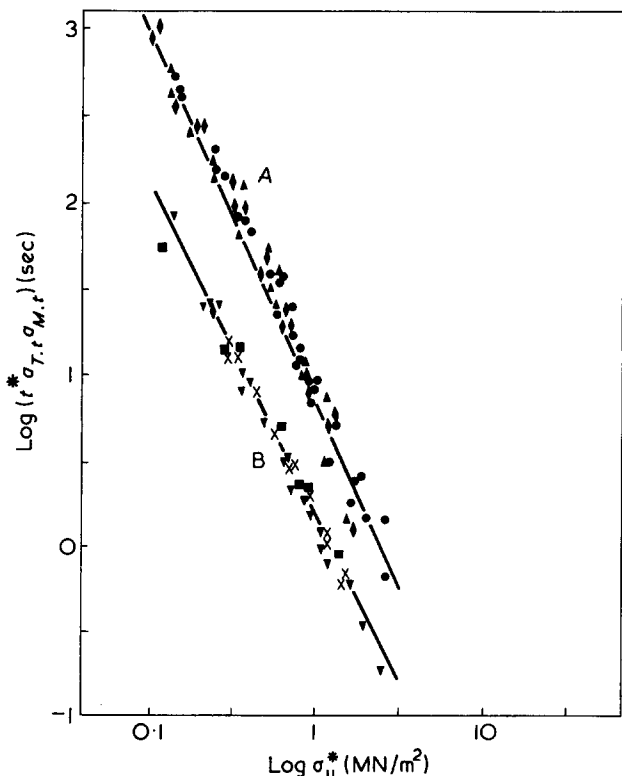


Figure 12 The long term durability of polybutadienes (A) and polyisoprenes (B) invariant with respect to temperature and molecular mass. A, molecular weights: \blacktriangle , 3.75×10^5 ; \bullet , 5.75×10^5 ; \blacklozenge , 8.30×10^5 . B, molecular weights: \blacksquare , 1.20×10^5 ; \times , 1.95×10^5 ; \blacktriangle , 2.90×10^5 . Temperature ranges -25° – 75° C

tional process, it definitely depends on the accumulation of defects in the samples. Therefore the relationships that can successfully be employed to describe the ultimate strength and long term durability of polymeric systems on the basis of the conceptions of summation of defects leading to their fracture, can be used for polymers in the forced high elastic state²⁹.

TRIAXIAL STRESSED STATE

This is the third simplest type of the stressed state. It can be realized by placing the sample between two discs or a disc and a flat ring. The thickness of the sample must be small as compared with its width. Experiments with polymers in the triaxial stressed state are very important to the problem of adhesion.

High molecular mass polybutadienes and polyisoprenes of narrow *MMD* have been studied by Sosin under the conditions of the triaxial stressed state. Experiments were carried out at specified constant stresses. The time to the rupture of the samples was measured. Three types of rupture were observed. At relatively low stresses there takes place a cohesive fracture of the polymers which develops inside the test samples. With increasing load the time up to rupture is shortened. The cohesive fracture obeys the same relationships that were considered above for uniaxial extension deformation; i.e., the determining factor is the relation between the ultimate strength and long term durability and the initial viscosity and its dependence on molecular masses and temperature. The conditions of the cohesive fracture are independent of the nature of the solid surfaces with which the polymer is in contact.

At a certain critical value of stress a mixed type of fracture is detected: the free surface of the solids in contact with the polymer appears. In this case, the time up to rupture is more strongly dependent on the stress than in the case of the cohesive fracture of the polymers. At still

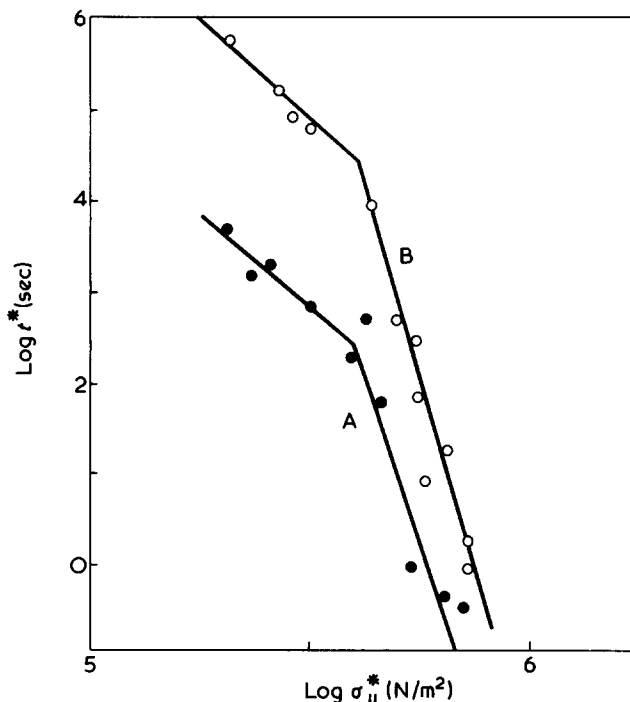


Figure 13 The long term ultimate strength of polybutadienes of narrow *MMD* ($M_w/M_n = 1.1$) in the triaxial stressed state (a layer of thickness about $100 \mu\text{m}$ between the Johanson blocks) at 20°C . The filled and unfilled circles refer to PB of molecular masses 1.5×10^5 (B) and 6.4×10^5 (A), respectively

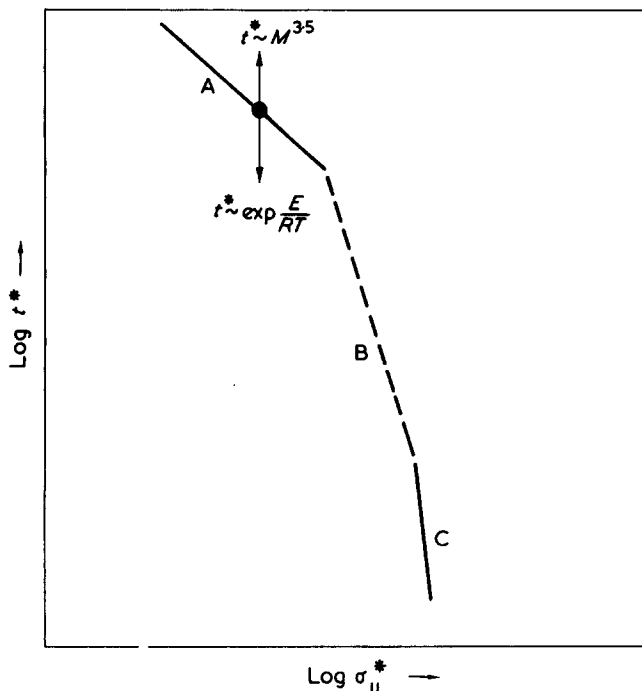


Figure 14 A diagram showing the processes of rupture and tearing-off of linear flexible chain high polymers in the triaxial stressed state. A, cohesive fracture; B, mixed cohesive–adhesive fracture; C, adhesive fracture, weak, complex dependence on temperature; independence of *M*

higher stresses the adhesive fracture is detected. It depends but slightly on temperature and molecular masses. The sharpness of transitions from the cohesive to the adhesive fracture greatly depends on *MMD*. Under the conditions of contact between PB and PI and polished metals the adhesive fracture occurs very rapidly and takes only a few fractions of a second. It is practically independent of the molecular masses of high polymers and varies with temperature less strongly than the cohesive fracture but in a complicated way (by an extremal law). The sharpness of the transition from the cohesive to the adhesive fracture depends greatly on *MMD*.

The dependence of the long term durability of two polybutadienes on the stress under the conditions of triaxial stressed state at room temperatures is shown in *Figure 13*. The upper branches of the curves refer to the cohesive fracture, and the lower to the mixed, cohesive–adhesive fracture. In a generalized form the long term durability of the polymers in the three dimensional stressed state is given schematically in *Figure 14*.

When comparing the polymers in the respective states, it is seen that their strength in the triaxial stressed state is about 1.5–2 times and the long term durability 2.5–3 times higher than in the case of uniaxial extension.

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