═══ **REVIEW** ═══

The Influence of Surface Phenomena on Molecular Mobility in Glassy Polymers

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Abstract—Literature data on molecular mobility in glassy polymers have been analyzed. It has been shown that, in the temperature range corresponding to the glassy state of a polymer, a large-scale (segmental) molecular motion is possible, with this motion being responsible for the physical (thermal) aging of the polymer. Heating of an aged polymer restores its initial state, and the aging process begins again (effect of "rejuvenation"). At the same time, aging processes may be initiated by a mechanical action on a glassy polymer. It is sufficient to subject an aged polymer to a mechanical action to transfer it to a state characteristic of a polymer heated above the glass-transition temperature. It should be noted that deformation of a glassy polymer is non-uniform over its volume and occurs in local zones (shear bands and/or crazes). It is of importance that these zones contain an oriented fibrillized polymer with fibril diameters of a few to tens of nanometers, thereby giving rise to the formation of a developed interfacial surface in the polymer. The analysis of the published data leads to a conclusion that the aging of a mechanically "rejuvenated" polymer is, as a matter of fact, the coalescence of nanosized structural elements (fibrils), which fill the shear bands and/or crazes and have a glass-transition temperature decreased by tens of degrees.

INTRODUCTION

Polymers are mainly distinguished from other substances by the chain structure of their molecules. This circumstance predetermines the physical reasons for a unique property of polymer molecules (macromolecules), namely, flexibility, i.e., the ability to vary their shape (conformation) under the action of an external stress and/or as a result of the thermal motion. Owing to this ability, the study of polymers long ago became an independent field of science, because the flexibility of macromolecules governs almost all their specific properties.

It is the flexibility that predetermines the ability of a macromolecule to be involved in several independent types of molecular motion, because not only a macromolecule as a whole, but also its separate groups and rather lengthy parts can be involved in the motion. These local modes of the molecular motion govern, to a large extent, the general mechanical properties of a polymer in different temperature ranges. For example, the study of dynamic mechanical properties enables one to obviously demonstrate the variety of molecular motions in polymers. Figure 1 schematically represents the temperature dependence of the mechanical loss tangent for a typical linear amorphous polymer. This dependence distinctly exhibits many relaxation transitions of the polymer in different temperature regions [1]. We shall not here analyze the molecular rearrangements (they have been studied in detail else-

where; see, e.g., [1, 2]) that are responsible for different peaks in the temperature dependence of the phase shift tangent. We would like only to note that the main relaxation transition (α-transition) that characterizes glass-transition temperature T_g of a polymer is due to defrosting of the large-scale (segmental) mobility of its macromolecules.

The properties of glassy polymers and the types of molecular motion responsible for them have been well studied and described in detail in numerous monographs and textbooks [1–6]. At present, diverse data are being accumulated in the scientific literature on
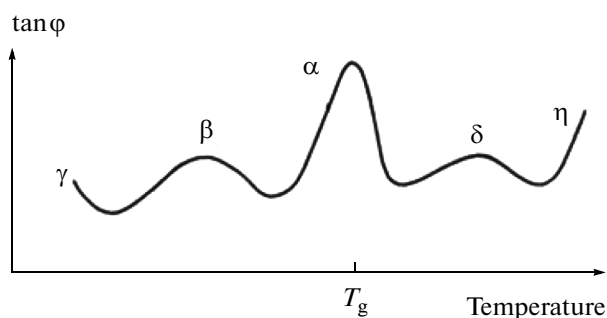

Fig. 1. Schematic representation of the temperature dependence of a phase shift tangent for a linear amorphous polymer [1].
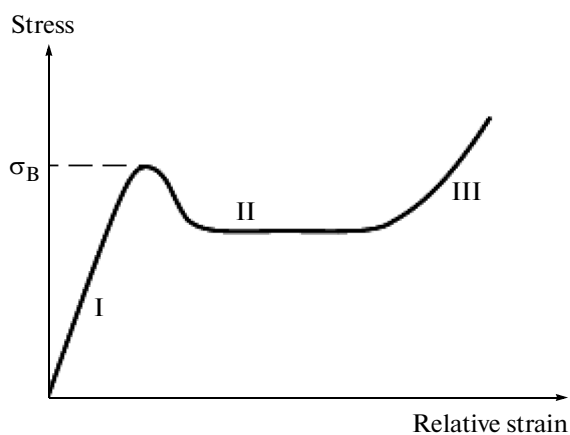
Fig. 2. Typical stress–strain curve for a glassy polymer. See text for explanations.

Fig. 3. Schematic representation of the temperature dependence of specific volume for an amorphous polymer. See text for explanations.

the influence of interfaces in polymer glasses on the features of their molecular motion and, as a consequence, on their fundamental physicochemical properties.

In this review, which is devoted to the peculiarities of molecular mobility in amorphous polymers, the main attention is focused on the large-scale types of the molecular motion that are revealed as α- and β-transitions predetermining, to a large extent, the mechanical, thermophysical, and other properties of polymers in the temperature range of their glassy state. At the same time, a large part of the review is devoted to analyzing the peculiarities of molecular motion at interfaces in glassy polymers and their influence on the basic macroscopic properties of such polymers.

ON THE TYPES OF MOLECULAR MOTIONS IN BULK GLASSY POLYMERS

The mechanical behavior of a glassy polymer is commonly illustrated by a stress–strain curve (Fig. 2). Such a curve comprises three main regions: (I) a so-called elasticity region, (II) a plateau region corresponding to neck development, and (III) a region of uniform deformation of the polymer part that has passed into the neck. We shall mainly discuss and analyze the phenomena and molecular processes relevant to the first two regions of the stress–strain curve. Polymers deformed to the aforementioned values are briefly characterized in textbooks as follows. "In the first region of the stress–strain curve, a polymer is subjected to an elastic deformation. A glassy polymer stretched to the strains corresponding to the second region of the curve cannot contract spontaneously. However, on heating above glass-transition temperature T_g, as soon as segments of macromolecules acquire the capability of thermal displacements, a sample contracts to a length close to the initial one" [3].
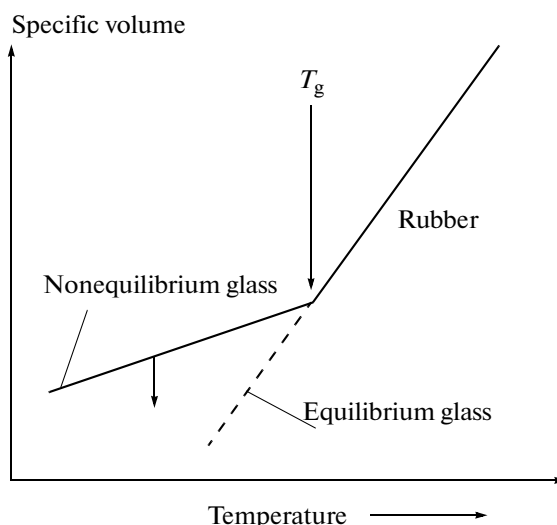
The above-cited concept of the glassy state of polymers as a state, in which the large-scale molecular motion is "frozen," is not quite correct. For several decades, experimental data have been accumulated in the scientific literature, which are outside the aforementioned framework. Let us consistently discuss the question of the possibility for the realization of some types of molecular motion (in particular, large-scale motion) in amorphous polymers at temperatures that conform to their glassy state.

Before proceeding to the direct consideration of the peculiarities of the molecular motion in amorphous polymers, we have to briefly recollect the mechanism of their glassy state development. Figure 3 schematically represents the temperature dependence of the specific volume of a linear amorphous polymer.

At relatively high temperatures (in the region of the rubberlike state), a polymer occurs in an equilibrium state; i.e., the rate of molecular rearrangements in it is rather high. As the temperature is reduced, this rate naturally decreases; at the same time, it remains rather high, so that the polymer is in a state close to the thermodynamic equilibrium. However, when T_g is reached, the polymer viscosity drastically rises, and further reduction in the temperature is not in correspondence with its equilibrium state, because the molecular dynamics of the polymer dramatically slows down; therefore, there is not enough time for macromolecules to acquire equilibrium conformations in the course of cooling. Thus, a glassy polymer obtained from a melt (solution) appears to be in a thermodynamically nonequilibrium state.

The equilibrium specific volume of a polymer, which could be reached provided that it was not vitrified, is denoted by the dashed line in Fig. 3 (at temper-

atures below T_g). The arrow indicates the direction in which the aforementioned molecular rearrangements "move" the glassy polymer toward the equilibrium state. The process of such "movement" is referred to as the physical or thermal aging of a polymer. This, in turn, means that the glassy polymer is not a system with a "frozen" molecular motion; hence, molecular rearrangements are possible in it at temperatures lower than T_g.

In order to understand the molecular processes that occur in glassy linear amorphous polymers, it is necessary to recollect the physical meaning of T_g, which is an important characteristic thereof. According to the principle of the temperature–time superposition (equivalence) [4, 5, 7], a fraction of a free volume of nearly 2.5% is reached in a polymer at T_g. This important circumstance suggests, in particular, that variations in the specific volume (Fig. 3) are, in fact, variations in the free volume with temperature. The attainment of the free volume value of ≈2.5% ensures the realization of a large-scale (segmental) molecular motion in an amorphous polymer, with this motion underlying almost all properties of polymers occurring in the rubberlike state. It must be noted that this motion is of a cooperative character; i.e., rotation of one kinetic unit (segment) requires the coordinated molecular motion of adjacent kinetic units.

Physical (Thermal) Aging of Glassy Polymers

In the most general form, the physical aging of glassy polymers comprises molecular processes that spontaneously proceed with time and lead to noticeable changes in the entire set polymer properties (density, enthalpy, permeability, as well as dynamic and static mechanical characteristics). These changes are realized under the conditions of isothermal annealing in the temperature range corresponding to the glassy state of a polymer. On the one hand, they suggest the possibility of a large-scale molecular motion in polymers occurring in the glassy state. On the other hand, they are of doubtless importance from the practical point of view, because there is the necessity to adequately predict the long-term properties of diverse items produced from glassy polymers.

It should be noted that, since the aforementioned changes in the polymer properties are of the fundamental character [8–10], the processes involved in the physical aging of polymer glasses are studied using a set of various experimental methods. For example, phenomena that accompany the aging of polycarbonate were studied by analyzing its mechanical behavior under the conditions of its uniaxial constant-rate stretching and creep [11, 12] with the help of dynamic thermal analysis [13–17], dynamic scanning calorimetry (DSC) [18–21], etc. The following methods of positron annihilation [22, 23], X-ray scattering [24],
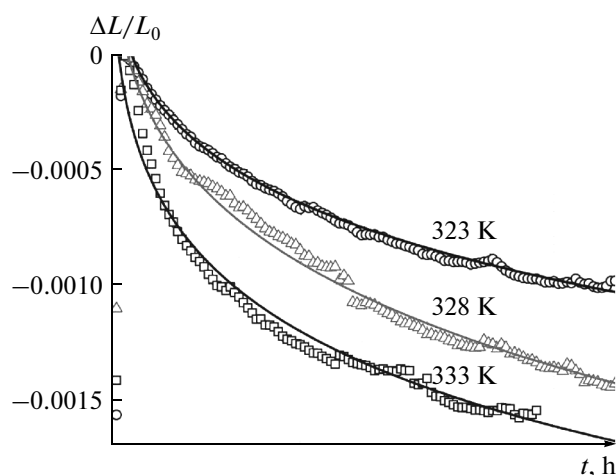
Fig. 4. Relative variations in linear sizes ($\Delta L/L_0$) of PET samples with aging time t at a constant temperature. Melted PET samples were quenched in ice-cold water and, then, heated at a rate of 10 K/min to temperatures denoted at the curves, at which they were subjected to isothermal annealing (PET glass-transition temperature is ~350 K) [30].

dilatometry [10, 25], FTIR spectroscopy [26, 27], and Raman spectroscopy [26, 27] seem to be especially promising. These and other methods for studying the physical aging of polymer glasses have been reviewed in [28].

Thus, a glassy polymer obtained from a melt by fast quenching to temperatures much lower than its T_g turns out to be in a nonequilibrium state; therefore, its properties (mechanical, thermophysical, etc.) are unstable.

Let us consider some typical manifestations of the processes relevant to the physical aging of polymer glasses. It appears that molecular rearrangements leading to noticeable changes in the entire set of the properties of an amorphous polymer may take place in it even at temperatures significantly lower than its T_g. Such rearrangements are, in particular, directly confirmed by a spontaneous increase in the density of a freshly molded and quenched amorphous polymer in the course of its aging [29]. An example of such increase in the density is presented in Fig. 4. It can be seen that the isothermal aging of the polymer is accompanied by a marked reduction in its volume, which unambiguously follows from the precise measurement of the linear sizes of the samples. It has been shown [30] that such variations really take place, and, which is of importance, the rate of the densification depends on the aging (annealing) temperature; the closer it is to T_g, the higher the process rate (Fig. 4). It should be emphasized once more that variations in the volume of a polymer during its aging are, in fact, variations in its free volume. The result obtained unambiguously indicates that the aging of polymer glasses is
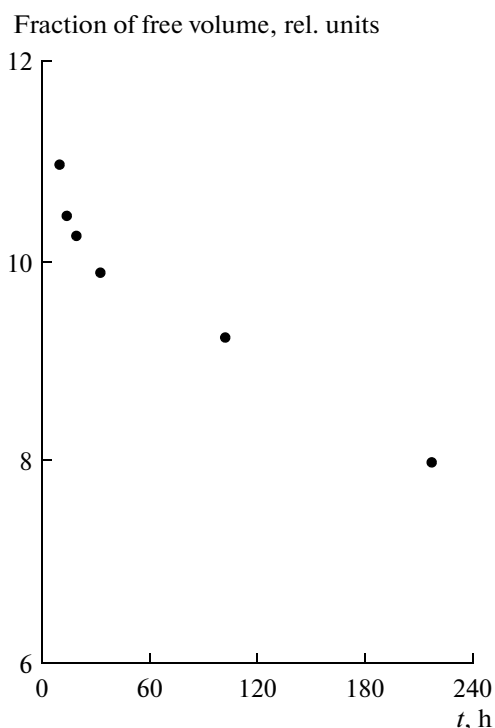
Fraction of free volume, rel. units

Fig. 5. Fraction of free volume in PET as a function of time *t* of its aging at 340 K [33].

Fraction of free volume, rel. units

Fig. 6. Temperature dependences of the fraction of free volume in PET at different times of polymer aging: (*1*) 0, (*2*) 96, and (*3*) 216 h [33].

accompanied by thermally activated molecular rearrangements.

The positron annihilation technique provides information on not only the free volume fraction in a solid, but also the effective sizes of so-called "free-volume holes." This technique enables one to directly assess the evolution of the free volume in a polymer during its physical aging. A typical example of such evolution is shown in Fig. 5. It is distinctly seen that the free volume in poly(ethylene terephthalate) (PET) drastically decreases during polymer aging, although the annealing temperature (340 K) is noticeably lower than its T_g (350 K).

The positron annihilation technique has been used to determine the parameters of the free volume for different glassy polymers, such as PET [29], polycarbonate [31], polystyrene [32], etc. An example of this determination is presented in Fig. 6, which shows that, first, in accordance with the principle of the temperature–time superposition, at T_g, the volume thermal expansion coefficient of a polymer changes jumpwise [33]. In other words, this dependence actually represents a method for determining polymer T_g. Second, the physical (thermal) aging of a polymer is accompanied by a marked growth in its T_g. Hence, the aging is accompanied by not only some densification (contraction) of a polymer, but also a change in its molecular dynamics, which is characterized by T_g.
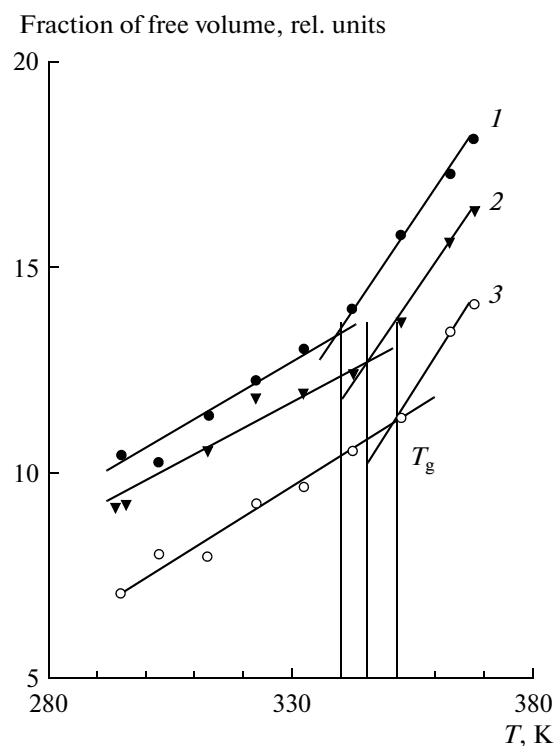
It is worth noting that the aging processes affect many properties of a glassy polymer, in particular, its thermophysical properties. In addition, this is unambiguously evident from the DSC data. Typical data of this kind are presented in Fig. 7. It is distinctly seen that, during the annealing, an endothermal peak arises and grows in the region of the glass-transition temperature. The existence of this peak enables us to determine the enthalpy of some process that occurs in a glassy polymer upon its physical aging [34]. The data presented in Fig. 7 indicate that physical aging is accompanied by not only some structuring, which is characterized by the endothermal peak, but also an increase in the T_g of the polymer, because this peak noticeably shifts toward higher temperatures. The value of this endothermal peak also depends on the time of the low-temperature annealing. The aforementioned variations in the DSC thermograms have been observed for various glassy polymers in a large number of studies [26, 29, 34–37].

Many mechanical and thermophysical characteristics of polymer glasses vary in the course of their aging. Figure 8 shows the dependences of the dynamic modulus, logarithmic damping decrement, and enthalpy on the time of the low-temperature annealing of amorphous PET. It is clearly seen that the dynamic mechanical characteristics (dynamic elasticity modulus and logarithmic damping decrement) and the ther-
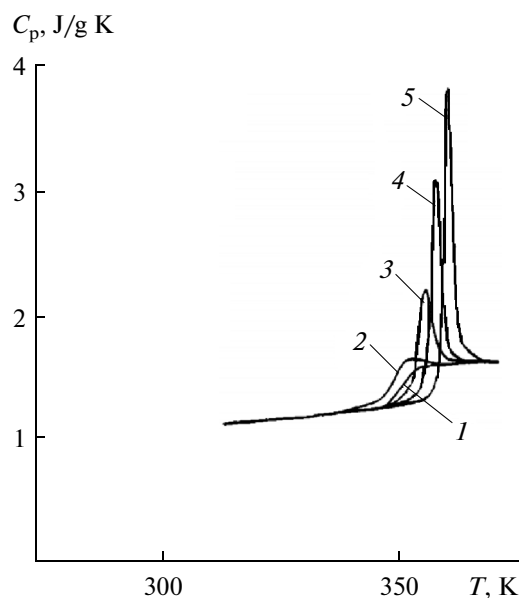
Fig. 7. DSC thermograms of PET samples annealed (aged) at 333 K for (*1*) 0, (*2*) 10^3, (*3*) 10^4, (*4*) 10^5, and (*5*) 10^6 s [34].

Fig. 8. Dependences of (*1*) dynamic elasticity modulus, (*2*) logarithmic damping decrement, and (*3*) enthalpy of amorphous PET on time of its annealing below T_g [27].

modynamic parameter (enthalpy) are in close correlation and testify that, in particular, in the course of the physical aging, the polymer becomes more rigid and less compliant [27]. In many works, the aging process has been related to variations in the set of macromolecule conformations upon polymer annealing below T_g.

Variations in the fraction of the free volume in an aging amorphous polymer must naturally affect its mechanical response in different regimes of deformation. Figure 9 illustrates the uniaxial compression curves for polystyrene samples obtained by quenching a melt (curve *2*) and resulting from a long-term annealing below T_g (curve *1*) [38]. It can be seen that molecular processes that accompany polystyrene annealing in the glassy state essentially increase the yield stress of the polymer (from 72 to 92 MPa) and the value of stress softening (the difference between the upper and lower yield stresses). As a whole, the uniaxial compression curve shifts toward higher stresses; however, at rather high strains, this difference gradually vanishes.

Variations in the fraction of the free volume during the physical aging noticeably affect the mechanical response of a polymer upon its deformation under creep conditions. This is evident from the data of work [5], in which poly(methyl methacrylate) (PMMA) samples were cooled from a temperature above the T_g to room temperature at different rates. Obviously, the higher the rate of polymer cooling upon its transition to the glassy state, the larger the free volume "captured" by the polymer. In turn, the larger the free volume of a polymer, the more easily molecular rear-
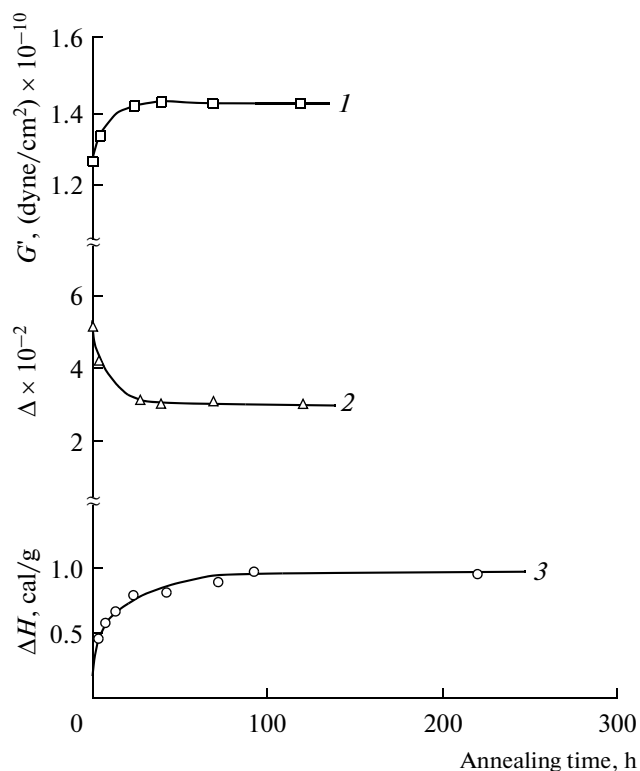
rangements take place in it. This circumstance strongly affects the mechanical response of the polymer. As follows from Fig. 10 [39], the relaxation rate of a polymer is, indeed, strongly dependent on its cooling rate and, hence, on the free volume that the polymer has "captured" upon transition into a glassy state.

As has been mentioned above, the free volume of a polymer determines its T_g, because the realization of the segmental cooperative molecular motion requires some space (free volume). Therefore, it is not surprising that an external hydrostatic pressure has a dramatic effect on T_g (Fig. 11a) [40]. The higher an applied hydrostatic pressure (uniform compression), the smaller the free volume in a polymer and the higher the temperature at which the free volume fraction sufficient for the realization of the large-scale (segmental) molecular motion is reached. In other words, the higher the hydrostatic pressure applied to a polymer the higher the temperature at which its T_g is reached (see experimental data in Fig. 11a).

The free volume determines not only the features of the molecular mobility in a glassy polymer, with T_g being, in particular, their measure, but also its important macroscopic characteristics, such as the yield stress and strength. Therefore, it is not surprising that the aforementioned characteristics also strongly depend on the applied hydrostatic pressure (Fig. 11b).
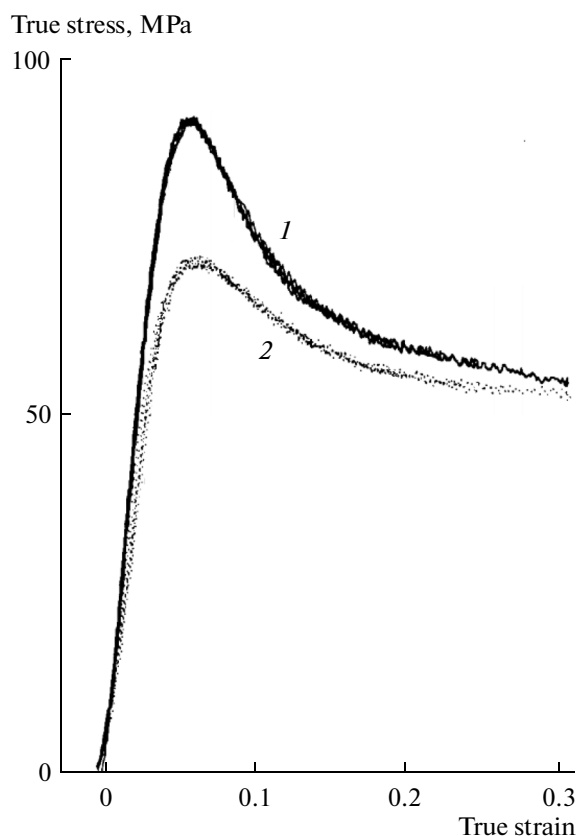
True stress, MPa

Fig. 9. Uniaxial compression curves for polystyrene at a deformation rate of 0.001 s^{-1} and a temperature of 295 K: (*1*) sample annealed at a temperature below T_g and (*2*) sample quenched in ice-cold water at a temperature 20 K higher than T_g [38].

Relative decrease in stress

Fig. 10. Curves of stress relaxation at 80°C for PMMA samples with different thermal prehistories: (*1, 2*) samples cooled from a temperature higher than T_g to 80°C at rates of (*1*) 5 and (*2*) 30 K/h, (*3*) sample cooled to room temperature in air, and (*4, 5*) samples quenched (*4*) at 25°C in oil and (*5*) with dry ice [39].

The yield stress of a polymer corresponds to the state in which its orientation occurs (begins) via displacements of large polymer chain fragments (segments). It is obvious that these displacements also require the existence of a rather large free volume, which, in turn, depends on the applied hydrostatic pressure. It is natural that both the yield stress (Fig. 11b, curve *1*) and the stress at break (Fig. 11b, curve *2*) are directly related to the hydrostatic pressure.

The data in Fig. 11b unambiguously indicate that a substantial free volume is necessary for realization of the large-scale molecular motion, which is responsible for the plastic deformation of a polymer. It is clear that hydrostatic pressure prevents the free volume of a polymer from increasing; therefore, the yield stress and the stress at break increase with this pressure (Fig. 11b).

The following important feature of the free volume as a structural element of a glassy polymer should be noted. As has been shown above, this volume may amount to a few percents of the total polymer volume and substantially vary with variations in temperature and/or hydrostatic pressure. Nevertheless, the free
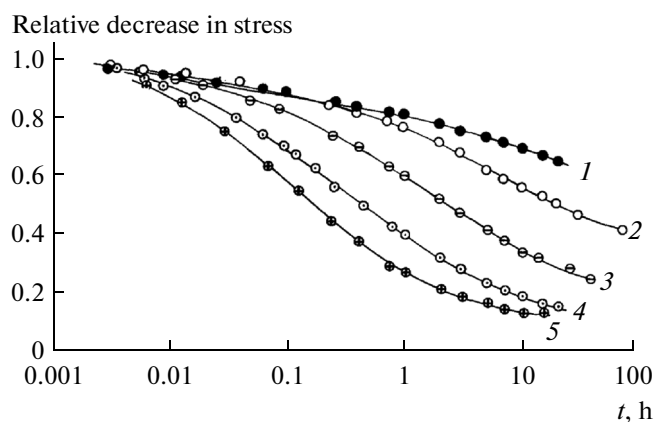
volume is of a fluctuation nature; hence, although it exists in the bulk of a real polymer, is has no stable physical (facial) boundaries and does not change the monolithic one-phase structure of a glassy polymer.

In conclusion of this section, it should be emphasized that the above-considered molecular rearrangements responsible for the physical aging of a polymer glass are explained by its thermodynamically nonequilibrium state. It should be noted that the processes relevant to aging proceed simultaneously in the entire polymer volume; i.e., they are of the affine character. The peculiarities of the molecular motion in glassy polymers free of internal interfaces have been reflected in this section; i.e., some bulk properties of polymers have been characterized.

Development of Large Interfacial Surfaces in Glassy Polymers

Thus, we have considered in detail the features of the molecular motion in monolithic (bulk) glassy polymers. The properties of glassy bulk polymers are determined by the aforementioned modes of the molecular motion that have been described in detail in monographs, textbooks, and handbooks and are traditionally believed to be the fundamental properties thereof. In accordance with the goal of this review, it is now necessary to consider the effect of a developed interfacial surface on the molecular mobility in glassy polymers.

In order to solve the above-formulated problem, we should, primarily, consider the methodology of the formation of highly developed interfacial surfaces in polymers. This goal is relatively easy to attain, because the self-dispersion of glassy polymers with the formation of a highly developed surface is a fundamental
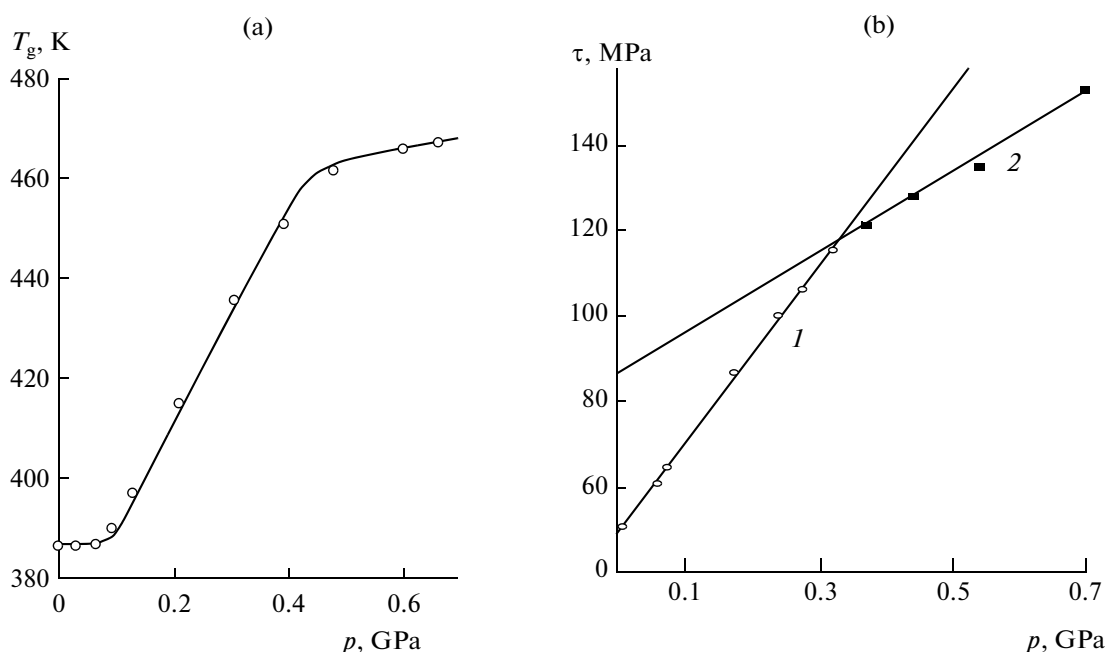
Fig. 11. Dependences of (a) glass-transition temperature [40] and (b) maximum shear stress τ at room temperature [4] on hydrostatic pressure p: (*1*) yield stress and (*2*) stress at break.

property thereof. In particular, mechanical loading of a glassy polymer to the values that conform to inelastic deformation (to strains corresponding to the region close to and/or higher than the yield stress) generates numerous structural heterogeneities with pronounced interfaces in a polymer volume [41].

In this connection, it is necessary to consider, at least cursorily, the data on the effect of mechanical loading on the structure of glassy polymers. Structural studies of deformed glassy polymers are numerous and have a long history. They have revealed the following experimental fact of great importance. It turns out that the affinity (uniformity) of the deformation is inherent in only amorphous polymers occurring in the rubber-like state (at a temperature higher than T_g) [42]. At the same time, numerous microscopic examinations have shown that the inelastic deformation of a glassy polymer is always realized nonuniformly over its volume [41]. In particular, the nonuniformity of the deformation over polymer volume is distinctly seen from the formation and propagation of a neck in a glassy polymer under conditions of its uniaxial stretching. However, structural nonuniformity of deformation is also observed before neck formation upon stretching and under conditions of uniaxial compression or rolling of a polymer, when no neck arises.

For example, Lazurkin was, seemingly, the first to show in his classical work [43] that, in the region of the yield stress, the deformation of a polymer occurs nonuniformly to yield a set of heterogeneities in a polymer. These heterogeneities are easily recorded with an opti-

cal microscope or, even, naked eye. These heterogeneities represent straight lines (bands) crossing over a polymer sample at angles of 45°−55° to the stretching axis. By analogy with low-molecular-mass solids, Lazurkin called them as shear bands and noted that the presence of microscopic heterogeneities (stress concentrators) is necessary for their formation.

The aforementioned shear bands are easily revealed by a microscopic examination. Figure 12 depicts an optical micrograph of a PET sample deformed at room temperature with neck formation [44]. It can be easily seen that the sample part that has not yet passed into the oriented state (neck) is permeated with the shear bands. The neck material is, at first sight, free of these bands; however, it "remembers" that it was formed from a polymer containing them (Fig. 13) [45].

If the neck of the PET sample is subjected to contraction in, e.g., a solvent, in which the polymer swells, a set of shears that can be recorded with an optical microscope arises in the material.

The nonuniform plastic deformation of a glassy polymer is also easily revealed at strains corresponding to the region below the yield stress. Figure 14a presents an optical micrograph of a glassy PET sample subjected to a constant load at a stress equal to nearly 0.7 of the yield stress value [46]. It is clearly seen that heterogeneities have appeared in the polymer. In addition to the set of shear bands oriented at an angle of ≈45° to the direction of the tensile stress, other zones of plastically oriented polymer propagating normal to the stretching axis can be seen. These are the so-called
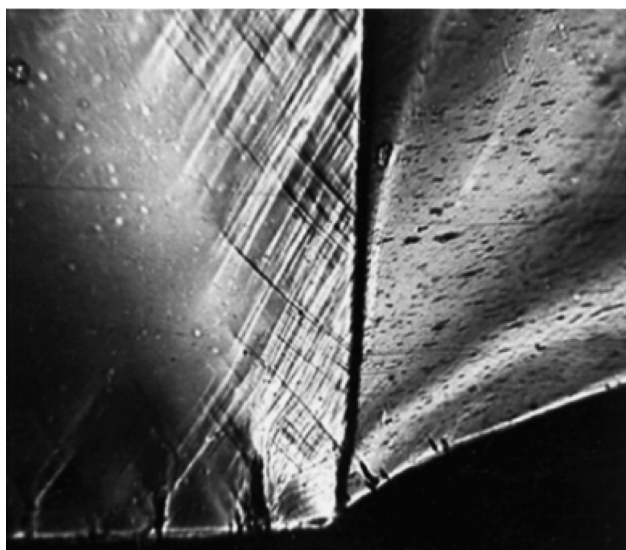
Fig. 12. Optical micrograph taken with crossed polaroids from a PET sample deformed at room temperature with neck formation. Materials of the neck and the undeformed part of the sample are shown in the right- and left-hand sides of the figure, respectively [44].

Fig. 13. Optical micrograph taken from a region of the neck after treatment with a solvent causing polymer contraction [45].

crazes, i.e., zones of deformed polymer that contain a substantial amount of microscopic voids [47−49]. An electron micrograph of the transition zone between the neck and the undeformed part of a PET sample is depicted in Fig. 14b [50]. Both shear bands and crazes are distinctly seen. The structure and properties of crazes will be considered in greater detail below; here, it should only be noted that the shear bands and crazes very often coexist upon mechanical loading of solid polymers.

The structural heterogeneity of a deformed glassy polymer is also unambiguously detected by small-angle X-ray scattering. It has been found [51] that intense diffuse X-ray scattering arise in polystyrene and poly(vinyl acetate) at 3−5% strains (a fortiori lower than corresponding yield stresses) and temperatures 10−20°C lower than corresponding T_g values. The result obtained unambiguously indicates that, under these conditions (in the so-called Hook region of the stress−strain curve), discontinuities and interfaces, which induce small-angle X-ray scattering, arise in glassy polymers.

Structural heterogeneities arise and develop not only upon the above-considered stretching of polymer films. Under the conditions of uniaxial compression of bulk polymers, bulky cylindrical samples are deformed in a manner such that they become barrel-shaped. Any heterogeneities are very difficult to register in such samples.

Nevertheless, the use of the methods well-known for the preparation of samples for microscopic examinations makes it possible to solve this problem. For
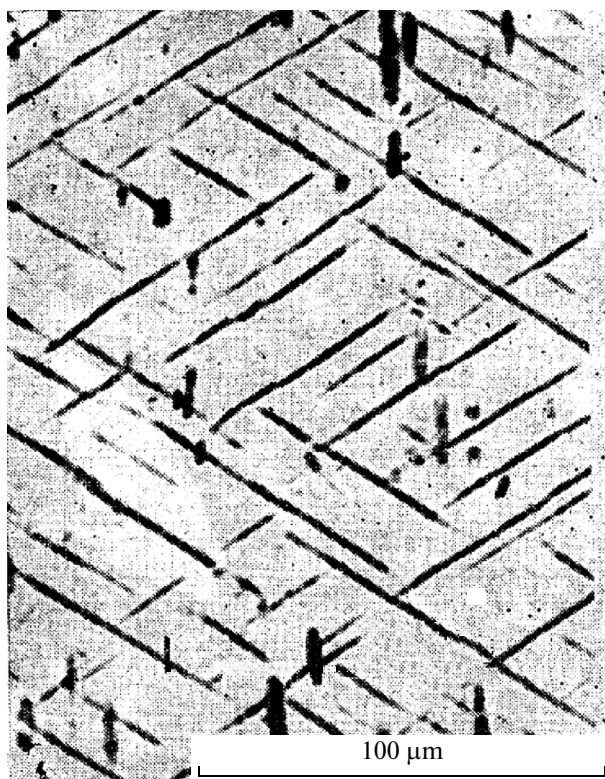
example, microsections were prepared in [52] from bulk samples of different glassy polymers deformed under the conditions of uniaxial compression. The obtained sections were examined with a polarization optical microscope. Deformed glassy polymers (polystyrene, polycarbonate, PET, and PMMA) appeared to contain rectilinear bands ~1 μm wide, which were characterized by a strong birefringence and separated by regions of an initial undeformed material.

A micrograph taken from a thin section of bulk polystyrene sample deformed under the conditions of uniaxial compression is shown in Fig. 15. It is clearly seen that the sample is actually saturated with shear bands. In other words, under these conditions, the polymer is deformed nonuniformly via the development of the shear bands. Note that the strong birefringence is observed for not only shear bands, but also crazes [48], thereby indicating that molecules of the material filling them are oriented.

Thus, the structure of a deformed polymer is very heterogeneous. It comprises microheterogeneities, which contain an oriented polymer and are located in the initial nonoriented polymer matrix. The question arises as to the area of the interfacial surface that arises in an initial monolithic polymer due to the formation of the aforementioned heterogeneities (shear bands and crazes). In connection to this, it is necessary to
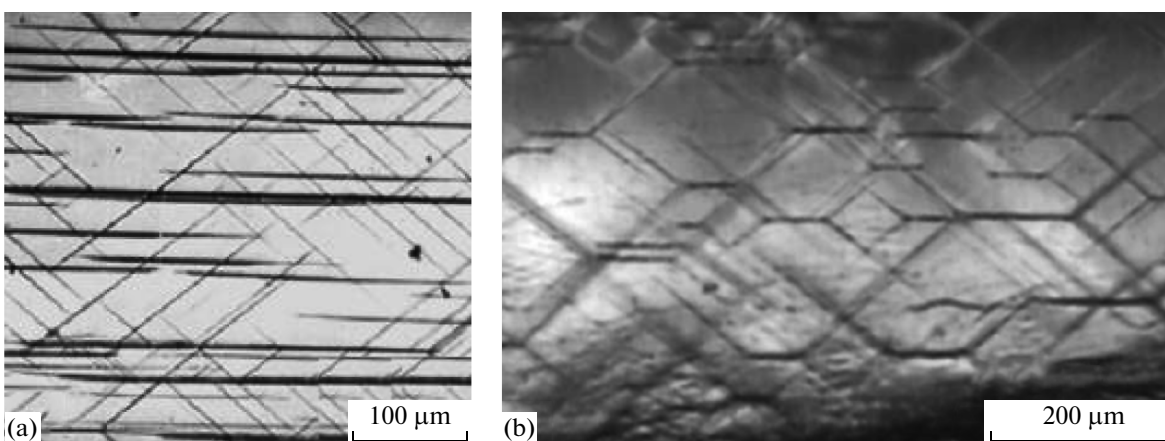
Fig. 14. Panel (a) optical micrograph taken from a PET sample deformed at room temperature under the action of a constant stretching load (~0.7 of the yield stress) for 2 h [46] and panel (b) electron micrograph taken from the transition region between the neck and the undeformed part of the PET sample [50]. The stretching axis is vertical in both cases.

consider their internal structure and properties in greater detail.

STRUCTURE OF CRAZES AND SHEAR BANDS RESULTING FROM DEFORMATION OF GLASSY POLYMERS

The development of crazes upon deformation of polymers in air and adsorption-active liquid media (AALMs) has been an object of many studied. Their structure has been studied and described in detail in numerous monographs and reviews [4, 5, 41, 53, 54].

Note that crazes have a fibrillar-porous structure; therefore, crazed glassy polymers are characterized by rather large "interfacial" surface areas (hundreds of square meters per gram) [48].

The structure of microheterogeneities of another type (shear bands) is less studied, although both shear bands and crazes frequently arise under the same conditions of polymer deformation and even compete with each other. Let us consider in greater detail the structural data that characterize mechanical loading of glassy polymers. Figure 16a depicts a photograph of a polymer sample in which a shear band is being initiated at the initial stage of stretching [55]. It is distinctly seen that, as well as in low-molecular-mass solids, this band grows through the sample at an angle of 45°−50° to the direction of the tensile stress. However, this is the only similarity between the shear bands in polymers and solids.

The shear bands in polymers appear to have a complex structure [56, 57]. They are filled with a finely dispersed oriented fibrillized material, which is quite analogous to the material that fills crazes [47, 48].

This important similarity is confirmed by direct microscopic observations. When a material containing shear bands is slightly stretched in the direction nor-

mal to the plane of the bands, the latter are opened (Fig. 16b) to exhibit a crazelike structure. The similarity with the craze structure turns out to be so striking that such opened shear bands have been called "shear band crazes" [56]. A "shear band craze" differs from a classical craze in the fact that its fibrils are tilted relative to the plane of the shear band (Fig. 16b).

The complex structure of shear bands in glassy polymers has a specific effect on the morphology of the surfaces resulting from their fracture. Figure 17a depicts a photograph of a polystyrene sample with a shear band initiated in it. A further deformation has resulted in the sample fracture along this shear band. It is clearly seen that a substantial amount of a polymer subjected to plastic deformation is, in this case, formed inside the shear band. The analysis of the
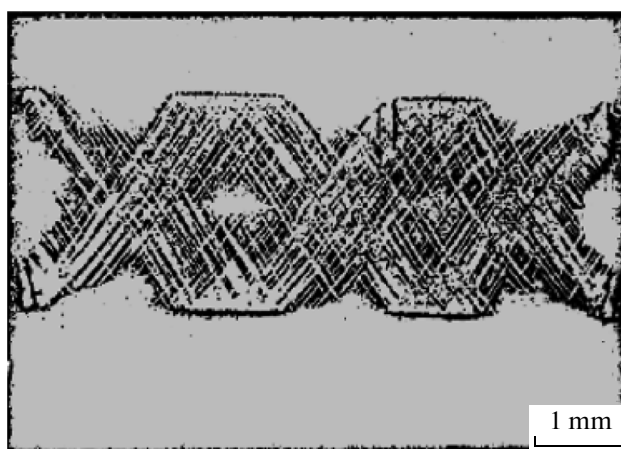

Fig. 15. Optical micrograph taken from a thin section of a polystyrene sample subjected to uniaxial compression. Compression axis is vertical [52].
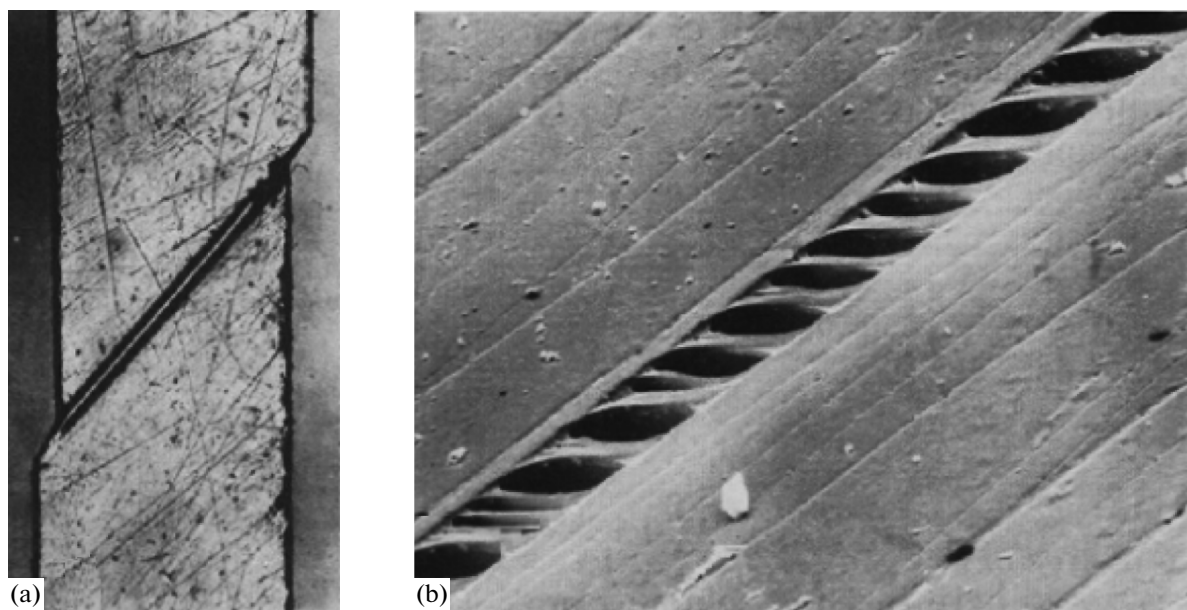
Fig. 16. Panel (a) appearance of a PET sample containing a shear band [55] and panel (b) electron micrograph of the shear band in polystyrene, with the band having been slightly stretched to show its internal structure [56].

micrographs taken at a high magnification (Fig. 17b) shows that this material consists of parallel plates composed of coalesced fibrils; i.e., its morphology is strikingly similar to the material of a craze [44]. This material can be easily separated from a sample with a pincer and studied by DSC [56]. The material of the shear bands has appeared to be responsible for the exothermal low-temperature (below T_g) effect, which is detected by DSC in deformed glassy polymers. At the same time, the material located between shear bands turns out to be undeformed and, therefore, identical to an initial bulk polymer. In particular, when being annealed, it exhibits no low-temperature exothermal effect.

The authors of [56] managed to realize both shear bands and crazes in the same polystyrene sample. Figure 18 shows an electron micrograph of such a sample, in which it is distinctly seen that a "shear band craze" differs from a classical craze only in the fact that its fibrils are tilted relative to the plane of the shear band. In other respects, the morphologies of these two structures are identical.

Another important aspect of the structure of the microheterogeneities (shear bands and crazes) that result from the deformation of glassy polymers is the presence of real microvoids in them (real interfaces). There is no doubt today that the crazes resulting from polymer deformation in air or AALMs have a microporous structure [47, 48]. Deformation develops in a polymer by the crazing mechanism at, at least, initial stages via an increase in its total porosity. At the same time, under the conditions of a shear flow, a substantial total contraction of a polymer being stretched

takes place and, in spite of the presence of the shear bands having real boundaries, the appearance of a real porosity in the polymer is not so obvious.

It has been shown [58] that methanol transport into PMMA samples subjected to uniaxial compression by 23—24% dramatically differs from its transport into initial undeformed PMMA. The rate of diffusion into deformed PMMA is two and five times higher at 40 and 25°C, respectively, than that into undeformed PMMA. These data indicate that the shear bands in glassy polymers contain some regions in which the material is so loosened that transport of low-molecular-mass substances is facilitated.

It can be easily shown how a polymer may be deformed under the same conditions either by the crazing mechanism or via the development of shear bands [59]. When a bulky PET sample is stretched in an AALM, crazes are nucleated on the surface of the sample and begin to grow into it. It is natural that, as they grow, the viscous drag to the AALM flow increases while moving toward their vertices. Finally, a situation arises in which the liquid cannot be supplied to the places of the orientational transformation of the polymer (craze vertices). Since the presence of an AALM in sites of active deformation is necessary for the development of crazes, the polymer "chooses" an alternative way of development of deformation via the growth of shear bands.

This situation is illustrated in Fig. 19. This figure presents an optical micrograph taken from a 0.7-mm section of a PET sample stretched at room temperature in an AALM (*n*-hexanol) by 50% at a rate of ~100%/min.
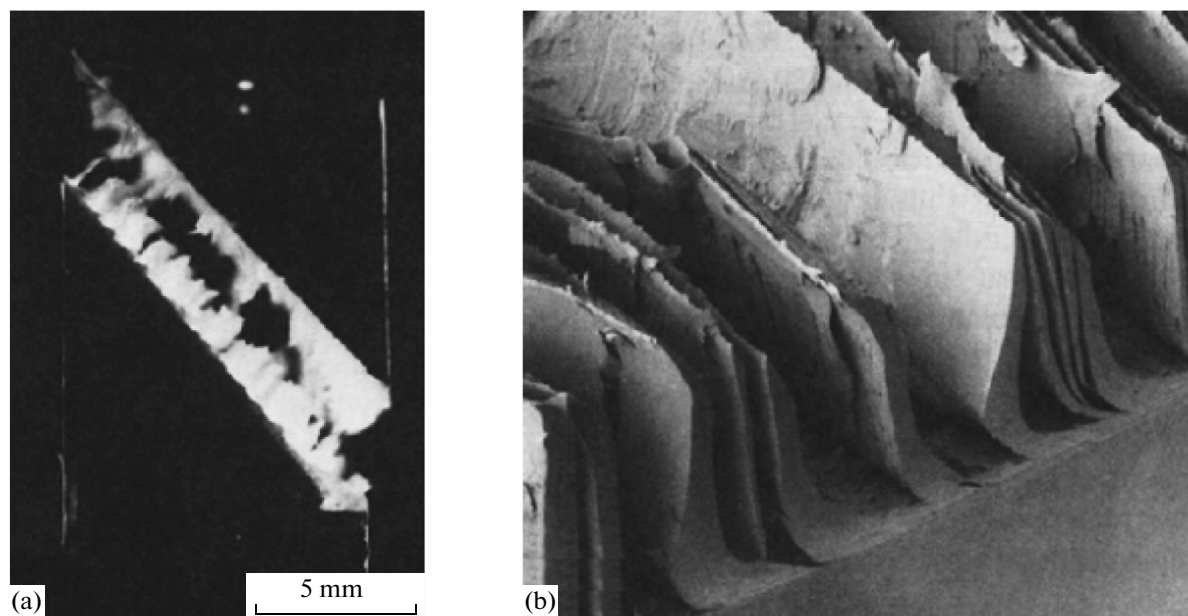
Fig. 17. Panel (a) appearance of a polystyrene sample fractured along a shear band and panel (b) electron micrograph taken from the surface of the fracture along the shear band [56].

It can be clearly seen that, under these conditions, crazes could not grow through the entire polymer cross section and began to widen (Fig. 19a). Nevertheless, the core of the sample continued to be deformed via the development of the shear bands, which did not require the presence of an AALM. At a higher magnification (Fig. 19b), some important features of this type of polymer deformation may be revealed. The shear bands, as well as crazes, are distinctly seen with an optical microscope, thus indicating that they have pronounced boundaries.

The film, the structure of which is presented in Figs. 19a and 19b, was placed as a membrane into a dialysis cell, the chambers of which were filled with aqueous solutions of NaCl on the one side and $AgNO_3$ on the other. It has been shown previously [60] that, when crazes run through a polymer film from one side to another, NaCl and $AgNO_3$ solutions diffuse toward one another through the set of interconnecting pores in the crazes, come together, and form AgCl crystals, which are readily detected with an electron microscope. As can be seen in Figs. 19a and 19b, the massive PET film deformed in the AALM is characterized by an unusual layered structure. Crazes containing real microvoids do not cross the entire film; therefore, its core contains a polymer layer, which is free of crazes but is crossed by shear bands.

Figure 19c depicts the electron micrograph taken from a brittle cleavage of the same PET sample treated with NaCl and $AgNO_3$ solutions. It can be seen that light AgCl crystals have, indeed, been formed in the crazes as a result of the above-described procedure,

thereby indicating the penetration of NaCl and $AgNO_3$ solutions through the entire PET film. Moreover, Fig. 19c shows that that AgCl crystals have been precipitated not only in the microvoids of the crazes, but also in the shear bands (rectilinear channels crossing the polymer at an angle of $\approx 45°$) to distinctly contrast them. The result obtained unambiguously testifies that, although the shear bands contain no real microvoids, they have such a low density that a low-molecular-mass liquid can diffuse through them as through channels.
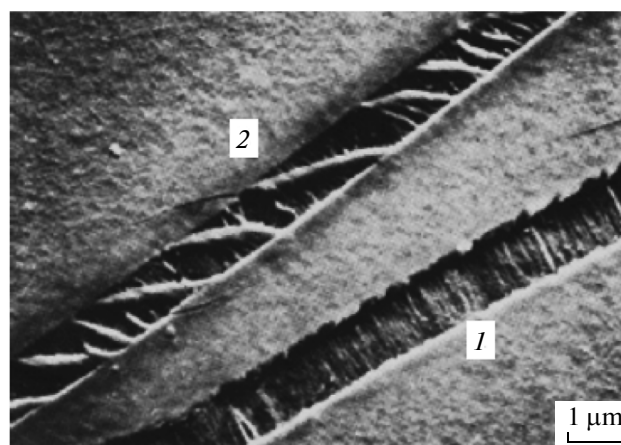

Fig. 18. Electron micrograph of a polystyrene sample containing (*1*) a craze and (*2*) a shear band [56].
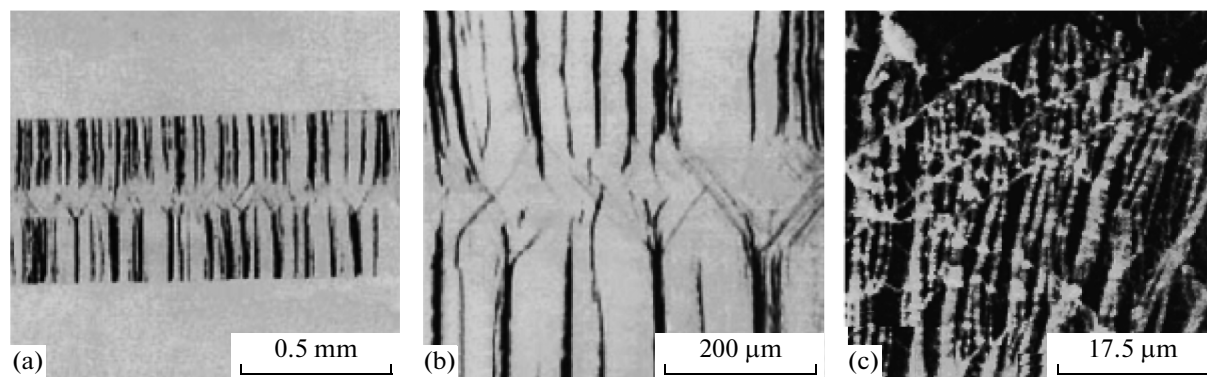
Fig. 19. Optical micrographs taken from a thin section of a PET sample containing (a) crazes and (b) shear bands and (c) an SEM micrograph taken from a low-temperature cleavage of the same sample after it was used as a membrane in a dialysis cell containing aqueous NaCl and $AgNO_3$ solutions [59]. See text for explanations.

Resuming the information presented in this section, an important similarity between the two above-considered structures, crazes and shear bands (Fig. 20), should be noted. It consists in the fact that they both represent through channels in a polymer, with these channels being filled with a finely dispersed fibrillized material. In other words, there is no essential difference between the structures of crazes and shear bands. In both cases, these structural formations have fibrillar morphology and, hence, a large interfacial area. In this connection, it is of no significance whether the deformation is realized via the formation of shear bands or crazes. In both cases, a large interfacial surface typical of the fibrillar structure of shear bands or crazes arises in a polymer. It is of importance that the size (diameter) of fibrillar aggregates in both shear bands and crazes amounts to from a few nanometers to several tens of nanometers [41, 44].

Thus, peculiar zones (shear bands and/or crazes) arise in a glassy polymer under a mechanical load. These zones, first, have a decreased density or even contain real microvoids and, second, are separated from an initial bulk polymer by pronounced boundaries.

EFFECT OF INTERFACES ARISING IN GLASSY POLYMERS ON THEIR MECHANICAL PROPERTIES

The Effect of Interfaces Resulting from Mechanical Loading on Dynamic Mechanical Properties of Glassy Polymers

The study of the dynamic mechanical properties of glassy amorphous polymers subjected to a mechanical action reveals important features of their molecular mobility that result from the appearance of developed interfacial surfaces in the course of their deformation.

In some works devoted to studying the dynamic mechanical properties of polymers preliminarily sub-

jected to mechanical loading, polycarbonate was used as an example to reveal the structural heterogeneity of deformed polymer glasses [61–65].

Let us consider in greater detail a typical example of such a study, in which inelastic deformation of polycarbonate was investigated under conditions of uniaxial stretching and corresponding mechanical losses characterizing internal friction were simultaneously measured. The stress–strain curve of polycarbonate is juxtaposed with corresponding mechanical losses measured in parallel with the mechanical response of the polymer under conditions of stretching at a constant rate [66, 67]. It is clearly seen that, initially (before the mechanical stress is applied), the losses are, as might be expected, low. After the load has been applied, some new "phase" arises in the polymer long before the yield stress is reached (beginning from ≈2% strain). This new phase has a substantially higher compliance, and, accordingly, exhibits higher mechanical losses. The amount of this phase continuously grows due to a continuous increase in the internal friction. This increase rather abruptly stops after the yield stress is reached. The further deformation of the polymer (when a neck is developed) is not accompanied by an increase in the mechanical losses, although they do not markedly decrease as well. If the polymer deformation is stopped in this region of the stress–strain curve, a dramatic decrease is observed in the mechanical losses in parallel with stress relaxation. This result is unambiguously indicative of the relaxation ("healing") of the new "phase" that has been formed as a result of the polymer deformation.

Repeated deformation leads to a dramatic rise in the mechanical losses again, which indicates either the "reanimation" of the relaxed regions with an increased level of mechanical loses or the formation of the same amount of new regions as that in the initial state, which is realized when a polymer reaches the yield stress. This "phase" is formed already in the so-
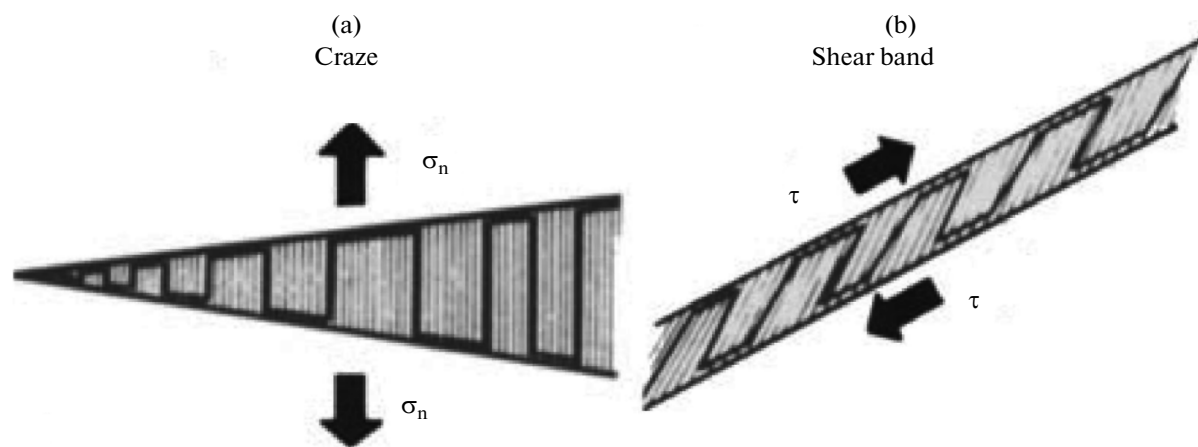
(a)
Craze

(b)
Shear band

Fig. 20. Schematic representation of (a) craze and (b) shear band structures [44, 57].

called Hooke region of the stress–strain curve, and its amount continuously grows until the polymer reaches the yield stress. As soon as the yield stress is reached, i.e., the stress in the polymer ceases to increase, the amount of the new "phase" being formed also reaches a plateau. Hence, the structure of the deformed glass differs from that of the initial glass. Therefore, it may be believed that the initial structure is not responsible for the physicochemical and mechanical abnormalities that a deformed polymer glass exhibits under the conditions of alternating loads (see Fig. 21).

Let us consider this phenomenon in greater detail by the example of the data reported in [68]. In that study, the deformation of amorphous polycarbonate samples to different extents under the conditions of uniaxial compression at room temperature was followed by their cooling with liquid nitrogen. Then, the temperature dependences of their dynamic mechanical characteristics were studied. Figure 22 illustrates the evolution of the phase shift tangent at a loading frequency of 1 Hz and a heating rate of 1 K/min for samples deformed in the plane by 0, 6, 10, 20, 30, and 40%.

For undeformed polycarbonate, β- and α-relaxation processes differ from each other by 200°C: at this frequency, the α-peak corresponds to 420 K, while the β-peak is located at 170 K and strongly extends along the temperature axis due to a large set of relaxation times [69, 70]. It can be clearly seen that, in the case of deformed samples, a very wide relaxation transition ranging from 280 K to T_g arises between the α- and β-transitions. This intermediate peak, which precedes the main α-transition, completely disappears after polymer annealing above T_g, and its position is independent of the strain value. As follows from Fig. 22, the aforementioned transition manifests itself as a wide relaxation peak, which is, subsequently, transformed into a plateau ranging to the main α-transition. The height of this plateau increases with the

strain and reaches a constant value at deformations higher than 30%. The authors supposed that the deformed glassy polymer contains some "zones" with strongly increased molecular mobility as compared with the initial bulk polymer. The appearance of these "zones" with an increased compliance in the glassy polymer imparts unusual mechanical properties to the polymer as a whole. The aforementioned experimental data (Figs. 21, 22) unambiguously indicate that the inelastic deformation of the polymer glass is accompanied by the formation of a second "phase," which has fundamentally different properties. Note that the appearance of a relaxation peak that precedes the main α-transition and results from the deformation of a glassy polymer has previously been observed in [14, 71].

In conclusion of this section, it is necessary to briefly discuss the handful of works devoted to studying the effect of mechanical loading on the molecular mobility in glassy polymers by the method of dielectric spectroscopy. In [72], this method has been employed to show that the α- and β-relaxation transitions in glassy poly(vinyl chloride) (PVC) are spaced along the temperature scale. Mechanical deformation makes these transitions more intense and their temperatures closer to each other. Moreover, it has been shown [73] that mechanical deformation of PMMA has no effect on the position and intensity of the β-transition; however, it strongly increases mechanical α-losses.

Thus, mechanical loading gives rise to the formation of a "phase" the peak of which, which precedes the main α-transition (T_g), is not only shifted toward lower temperatures by several tens of degrees, but also strongly extends ("diffuses") along the temperature scale.
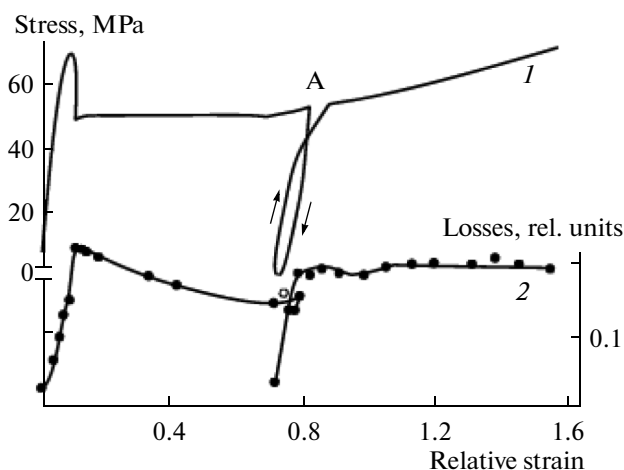
Fig. 21. (*1*) Stress–strain curve and (*2*) corresponding mechanical losses measured for polycarbonate at room temperature. After elongation had reached point A in the stress–strain curve, the stress was eliminated and the sample remained in this state for 1 h. The stretching was then continued [66, 67].

Fig. 22. Temperature dependences of phase shift tangent for polycarbonate samples deformed at room temperature under conditions of uniaxial compression by (*1*) 0, (*2*) 6, (*3*) 10, (*4*) 20, (*5*) 30, and (*6*) 40% [68].

Thermophysical Properties of Polymers Subjected to Mechanical Action

The differences in the molecular mobilities of glassy polymers that contain developed interfaces can be seen from their thermophysical properties.

Figure 23 shows the DSC thermograms of PVC treated in different manners [74]. Curve *1* corresponds to an aged polymer that has been quenched and aged at a temperature below T_g. It can be seen that this polymer exhibits a pronounced endothermal peak in the region of the glass transition. Such thermophysical behavior is inherent in the aging of amorphous polymers and has been considered in detail above (compare Figs. 7 and 23). At the same time, PVC samples subjected to different mechanical actions (stretching, torsion, compression, and rolling) are characterized by a pronounced exothermal peak, which is located below T_g and extends to the region of lower temperatures by many tens of degrees.

The exothermal peak, which is typical of any amorphous polymers subjected to a mechanical action, is located in a temperature range between the α- and β-transitions; therefore, it may be thought that it is related to the large-scale (segmental) molecular motion.

As has been mentioned above, the hydrostatic pressure strongly affects the free volume in a glassy polymer (Fig. 11) and, hence, its basic mechanical characteristics (T_g and stress–strain properties). In connection with this, it is worth noting that this type of deformation has no effect on the character of the molecular motion in a glassy polymer. After the hydrostatic stress is eliminated, a polymer exhibits no abnormalities in the thermophysical behavior. Figure 24
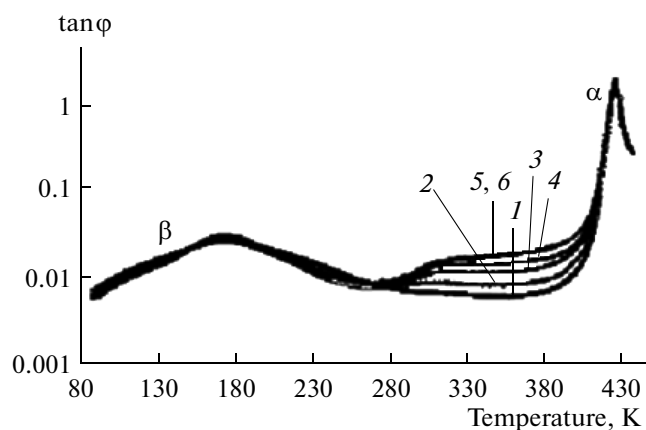
illustrates the DSC curve for polystyrene subjected to a hydrostatic pressure of 10 kbar at 25°C (curve *1*) [75]. It has a well-known pattern with a traditional step in the glass transition region. However, if the same hydrostatic pressure is applied in combination with a shear deformation (Fig. 24, curve *2*), a distinct exothermal effect arises in the DSC thermogram below T_g. This effect extends toward lower temperatures by nearly 50°C. The result obtained unambiguously indicates that it is the shear component of the stress that is responsible for the low-temperature molecular motion in the glassy polymer. We shall consider this effect in greater detail below; here, it should only be noted that the shear deformation gives rise to discrete zones in the glassy polymer; i.e., shear bands the finely dispersed structure of which has been considered above.

Thus, the above-described experimental data suggest that at least two types of large-scale molecular motion may take place in the range of the glassy state of amorphous polymers. First, it is the molecular motion responsible for the physical thermal aging. It transforms a polymer glass into a more equilibrium state. It is of great importance that this kind of molecular motion has an affine character and is realized simultaneously throughout the polymer volume.

Second, there is some type of the large-scale molecular motion that is induced in a glassy bulk polymer by mechanical deformation below its T_g and is realized also in a temperature range lower than T_g. An important feature of this type of the molecular motion is its localization in some peculiar "zones" included into an intact polymer matrix [66, 68]. This means that a deformed glassy polymer has a heterogeneous structure and makes urgent the study of the structural rearrangements that accompany its deformation.
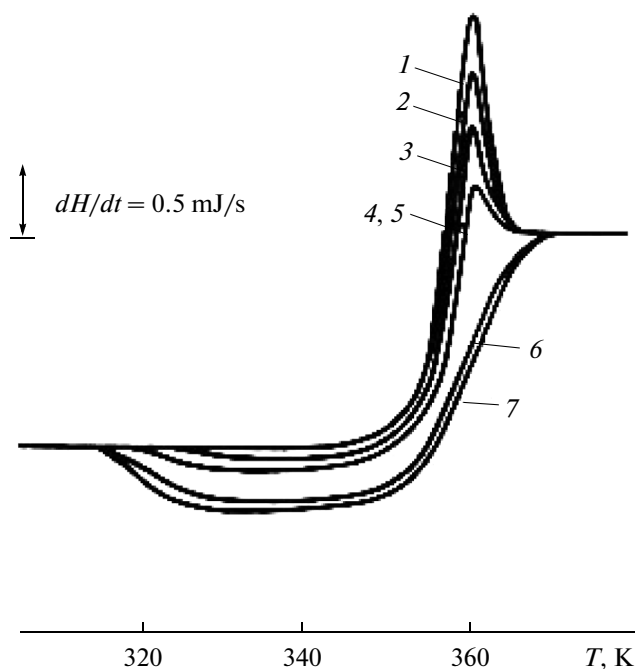
Fig. 23. DSC curves for PVC (*1*) in initial annealed state and after stretching by (*2*) 2, (*3*) 19, and (*4*) 40%; (*5*) torsion deformation by 40%; (*6*) uniaxial compression by 40%; and (*7*) rolling deformation by 40% [74].

Fig. 24. Specific heats of polystyrene samples (heating rate of 20 K/min) subjected to (*1*) uniform compression (hydrostatic pressure of 10 kbar at 25°C) and (*2*) shear deformation on Bridgman anvils (pressure of 10 kbar, temperature of 25°C, and rotation angle of 200°) [75].

Deformation Calorimetry

Thermodynamic studies performed with the use of deformation calorimetry [76−78] have shown that the plastic deformation of polymer glasses fundamentally differs from the plastic deformation of low-molecular-mass solids. It appears that substantial part of the work of deformation (mainly before and in the vicinity of the yield stress) is accumulated by a polymer, rather than being transformed into heat (Fig. 25) [76].

The result obtained indicates that the deformation of a glassy polymer is accompanied by structural rearrangements responsible for the accumulation of the internal energy. In addition, Fig. 25 shows that this process is realized at initial stages of deformation (before and in the vicinity of the polymer yield stress), i.e., in the same region in which abnormalities take place in the thermostimulated restoration of sizes (see below) and in the dynamic mechanical properties.

It has been found by the DSC method [79] that deformed PVC accumulates significant amounts of internal energy. As has been noted in the same work, the accumulated energy begins to be released in the course of annealing at a temperature 30−40°C lower than T_g. Samples of polystyrene and some of its copolymers with poly(methacrylic acid) strained by 40% also accumulate internal energy (1.5 cal g^{-1}) [74]. The authors attributed the generation of this excess internal energy to a decrease in the intensity of the inter-
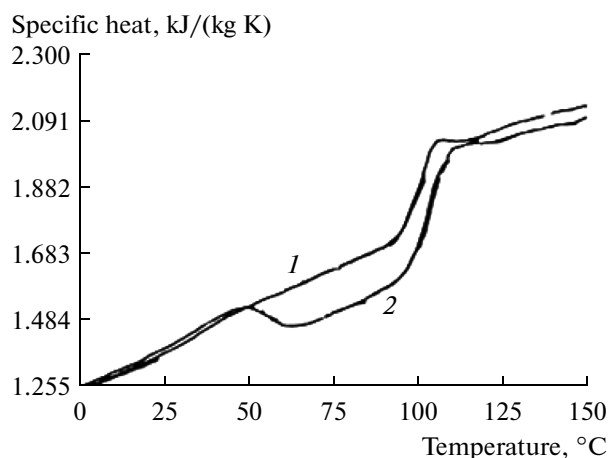
molecular interactions in the polymers due to their inelastic deformation.

Thus, mechanical action on a glassy polymer induces fundamental structural rearrangements in it. The formed regions with a new structure do not eliminate the initial polymer structure completely, but rather coexist with it. This circumstance leads us to think that deformed polymers have a heterogeneous structure and contain, at least, two types of structural elements.

Thermostimulated Restoration of the Sizes of Deformed Glassy Polymers

The possibility of the large-scale molecular motion below T_g can be seen still more evidently when studying the thermostimulated size restoration of deformed glassy polymers. As has been found in a number of works [40, 76−78, 80], a deformed glassy polymer restores its sizes in a peculiar way during annealing.

Figure 26 shows typical temperature dependences for the size restoration of a PMMA sample deformed under the conditions of uniaxial compression [40]. It is clearly seen that this process is strongly affected by the temperature of initial polymer deformation. As follows from Fig. 26, the polymer sample deformed at 120°C (above T_g) restores its sizes in a manner like that described in textbooks. It restores its sizes on reaching T_g. If a sample was deformed below T_g, it almost completely restores its sizes in a temperature range lower than its glass-transition temperature.

Isometric Heating

Subsequently, several more phenomena have been discovered indicating the possibility of large-scale
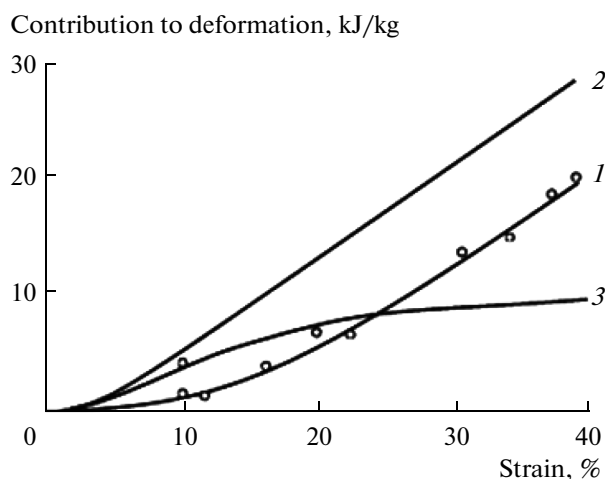
Contribution to deformation, kJ/kg

Fig. 25. Dependences of (*1*) heat, (*2*) mechanical work, and (*3*) accumulated internal energy on strain upon uniaxial compression of polystyrene at 30°C and deformation rate of $5 \times 10^2 \, \text{min}^{-1}$ [76].
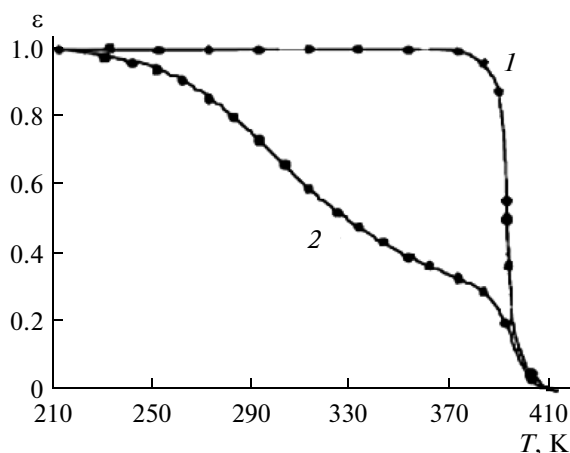

Fig. 26. Temperature dependences of relative restoration of sizes (contraction) for PMMA samples deformed by 20% under the conditions of uniaxial compression at (*1*) 120°C (above T_g) and 20°C (below T_g) [40].

molecular motion in deformed amorphous polymers at temperatures lower than T_g. In particular, the mechanical behavior of deformed glassy polymers upon their isometric heating is among them. It appears that, when a stretched glassy polymer is heated under isometric conditions, the stress increases in it [81, 82]. It is worth noting that this increase begins long before the T_g of the polymer is reached, thus unambiguously confirming the possibility of large-scale molecular motion in glassy amorphous polymers. This mechanical behavior is exemplified in Fig. 27.

It is distinctly seen that deformed glassy polymer (PMMA) exhibits a rise in the stress at temperatures substantially lower than its T_g (115°C). It should be noted that this experimental finding proves the entropic (polymeric) nature of this phenomenon, because a rise in the stress upon heating under isometric conditions may be observed only in an oriented polymer [42].

Resuming the data on the effect of mechanical loading on the molecular mobility in glassy polymers, the following important circumstance must be noted. Mechanical loading induces some structural rearrangements in a glassy polymer that have been revealed above as the formation of the zones of a finely dispersed polymer (shear bands and/or crazes) located inside an undeformed polymer matrix. It is these zones that predetermine the unusual modes of molecular motion in polymers and cause the aforementioned abnormalities in their structure-related mechanical behavior. These abnormalities primarily concern the mechanical (both static and dynamic) and thermophysical properties and have the following feature in common: they manifest themselves in a temperature range below the T_g of an initial bulk poly-

mer. For example, at temperatures below the T_g of an initial polymer, a wide exothermal DSC peak (Figs. 23, 24) and a wide peak of mechanical losses (Fig. 22) are observed. Moreover, a low-temperature thermostimulated restoration of the sizes of deformed glassy polymer samples takes place upon their annealing (Fig. 26) and stresses grow in deformed bulk polymer samples during their isometric annealing below the T_g (Fig. 27).

Peculiarities of Physical Aging of Glassy Polymers Subjected to Mechanical Action

An important property of glassy polymers is their capacity for physical aging. As has been mentioned above, aging represents a directed variation in the properties of a glassy polymer, the driving force of which is the tendency of the polymer toward thermodynamic equilibrium. Heating of an aged polymer above T_g leads to its "rejuvenation," while subsequent cooling of the polymer below its T_g induces the aging process again. Any number of aging–rejuvenation cycles can be implemented in this way. It is worth noting that the thermal (physical) aging/rejuvenation processes proceed uniformly throughout the volume of an amorphous polymer.

Within the framework of this section, it should be noted that an aging process can be induced without resorting to polymer heating above its T_g. This induction may be implemented by a mechanical action onto a polymer within a temperature range of its glassy state (see above). The data characterizing these two types of aging are compared in Fig. 28 [83, 84]. One of them has been realized by heating a polymer above its T_g followed by cooling below the T_g (Fig. 28a), while the second one was implemented by mechanical treat-

ment (rolling) of the polymers at temperatures below their T_g values (Fig. 28b).

As follows from the aforementioned figure, these two types of aging have something in common. In both cases, a noticeable spontaneous increase in the yield stress with time is observed below corresponding T_g values. In both cases, the aging processes gradually lead the "rejuvenated" polymers to a certain quasi-equilibrium state. It must be noted that heating of a polymer, which has been subjected to a mechanical action, above its T_g also completely "rejuvenates" the polymer.

However, data are also available that indicate essential differences between the two aforementioned aging–rejuvenation cycles. DSC enables one to characterize both of these processes and reveal their fundamental differences. Typical data of this kind are presented in Fig. 29. Figure 29a shows the DSC thermograms that characterize the physical aging of amorphous glassy polystyrene. These data are identical to the DSC data on the aging of PET (Fig. 7).

Polystyrene samples were obtained by quenching from the rubberlike state followed by low-temperature annealing for different time periods. It is distinctly seen that, in the course of annealing, the above-described phenomena accompany the physical aging of the amorphous glassy polymer (compare Figs. 29a and 7) [74]. During annealing, the glass-transition "step" is transformed into an endothermal effect (Fig. 29a), with its intensity increasing with annealing time. The effect of physical aging of polymer glasses on the evolution of their DSC thermograms has been thoroughly analyzed in [41, 85]. Here, we would like only to note that the effect of aging on the thermophysical behavior of a polymer does not prevent us from the independent investigations of the processes that accompany the deformation of the same samples.

Indeed, the deformation of a polymer within the range of its grassy state (below T_g) also strongly affects its thermophysical properties (Fig. 29b); however, this effect is revealed in an essentially different way. Figure 29b shows that the deformed polymer is characterized by a wide exothermal DSC peak located below T_g, while the undeformed polymer exhibits only an endothermal peak in the region of its T_g (compare Figs. 29a and 29b). The evolution of the aforementioned peaks during low-temperature annealing is worth noting. It appears that the exothermal peak (curves 1–3) gradually decreases in the course of the low-temperature annealing and disappears completely (curves 4–7) after long-term annealing. At the same time, the endothermal peak relevant to the physical aging of the quenched glassy polymer, on the contrary, increases during the annealing. In other words, the processes of the physical aging upon the low-temperature annealing of the quenched polymer and the polymer subjected to the mechanical action are accompanied by
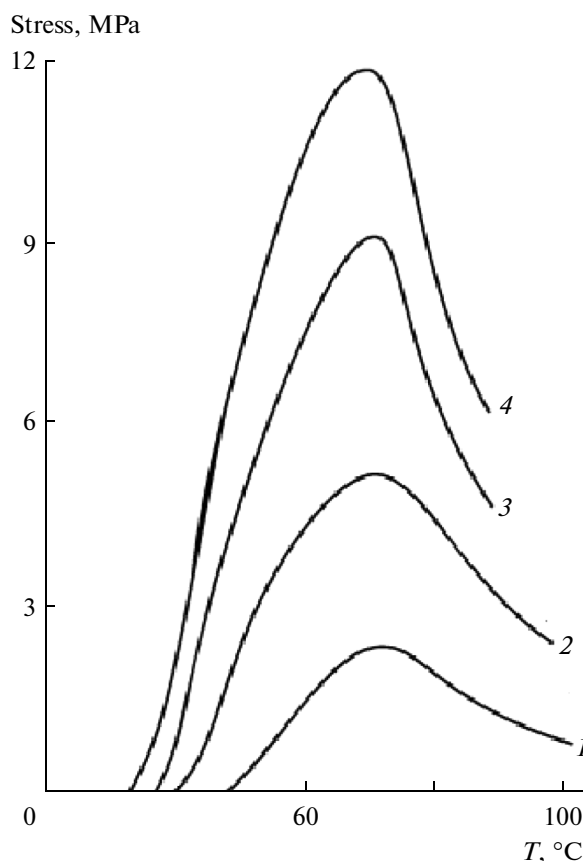

Fig. 27. Isometric heating curves for PMMA samples stretched to relative strains of (1) 1.5, (2) 2.5, (3) 3.25, and (4) 3.9 at 105°C [81].

thermal effects with opposite signs. Moreover, the comparison of Figs. 29a and 29b suggests that it is as if the two aforementioned thermophysical processes do not notice one another and develop independently during the annealing.

The structural studies reveal another important difference between the two above-considered aging processes. It turns out that the aging of a glassy polymer subjected to a mechanical action not only changes its physicomechanical properties, but also eliminates (heals) all interfaces generated by the mechanical stress. In other words, while the aging of a polymer subjected to a thermal treatment above its T_g is a certain bulk process, the aging of a mechanically rejuvenated glassy polymer is accompanied by healing of developed interfaces that are typical of shear bands and crazes; i.e., it is, in reality, some surface phenomenon.

The healing of interfaces in polymers has been intensely studied for a long time [86]. When two planar surfaces of the same polymer are brought into contact, the interface is, as a rule, gradually disappeared ("healed"), and the material becomes monolithic. It is of importance that the monolith is formed only when
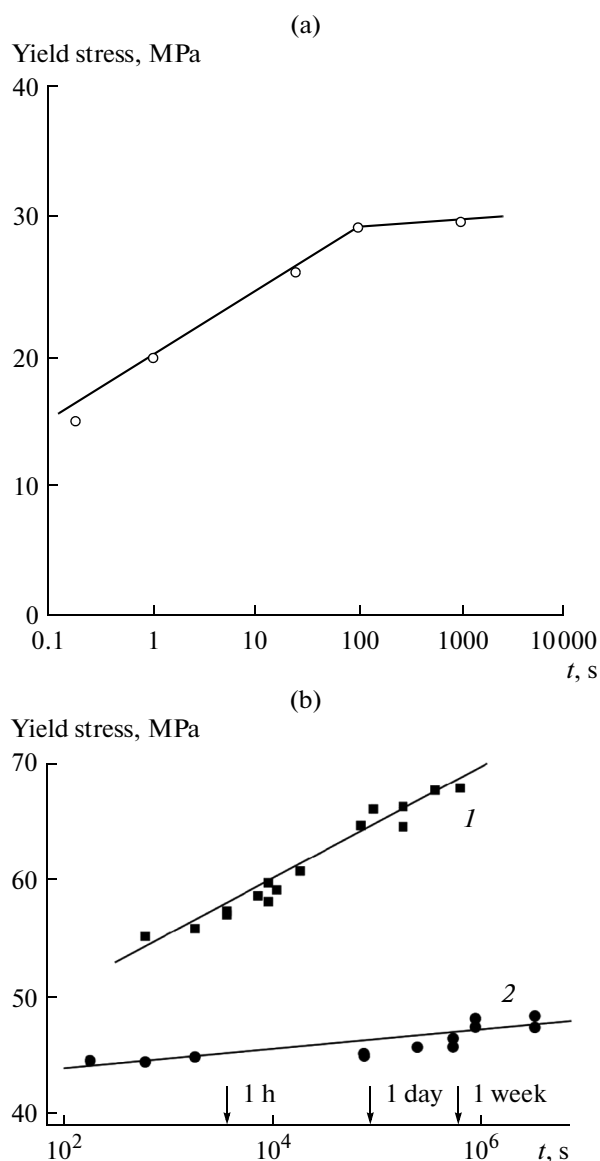
(a)

Yield stress, MPa

(b)

Yield stress, MPa

Fig. 28. Panel (a) dependence of yield stress on aging time for an epoxy resin sample thermally treated at a temperature higher than T_g [83] and panel (b) analogous dependences for (1) polystyrene and (2) polycarbonate samples preliminarily subjected to rolling [84].

the polymer, whose surfaces are brought in contact, has a temperature higher than its T_g. As has been mentioned above, at a temperature higher than T_g, a polymer occurs in a rubberlike state, in which its large-scale (segmental) molecular mobility is substantially facilitated. Therefore, polymer segments diffuse through the interface, form a so-called network of entanglements, and completely heal the interface in the long run. It is well known that industrial rubber articles to be stored are talced in order to prevent this process. Talc particles create obstacles in the way of establishment of tight contact between polymer surfaces, thereby suppressing the healing process.

Nevertheless, when a polymer subjected to a mechanical action is aged, the "interfaces" of crazes and shear bands are healed spontaneously at a temperature several tens of degrees lower than the T_g of the initial undeformed polymer, at which the segmental mobility cannot, seemingly, be realized [2].

Let us illustrate this effect by the example of the thermostimulated healing of shear bands in amorphous PET. The influence of annealing temperature on the state of shear bands formed in the polymer under conditions similar to uniaxial compression was studied in [87]. A spherical indenter was impressed into an amorphous PET film at room temperature, and the deformation pattern was inspected with an optical microscope. Figure 30a depicts the micrograph taken from a deformed polymer after it was annealed at 40°C, i.e., at a temperature substantially lower than its T_g. It is clearly seen that, under these conditions, polymer deformation is accompanied by the formation and development of a set of shear bands. When the annealing temperature is increased to 70°C (Fig. 30b), the shear bands appear to be merged and less pronounced; at a temperature of 75°C, which is close to the T_g, the shear bands are, at last, completely healed and cannot be observed with the help of an optical microscope (Fig. 30c).

Thus, the low-temperature annealing (physical aging) of a polymer containing shear bands leads to the complete healing of interfaces, and this process mainly occurs in a temperature range below the T_g of the polymer. The low-temperature (below the T_g of a bulk polymer) relaxation is inherent in crazes as well [41].

EFFECT OF POLYMER PHASE SIZES ON THE POLYMER MOLECULAR MOBILITY

Thus, on the one hand, the aging of a mechanically rejuvenated polymer is accompanied by the efficient healing of interfaces that have been formed in a glassy polymer as a result of a mechanical action. On the other hand, this process frequently occurs at temperatures several tens of degrees lower than polymer T_g, when the large-scale (segmental) motion seems to be "frozen," i.e., actually forbidden [1−3].

This contradiction may be eliminated using the results of numerous studies that were initiated by groundbreaking work [88] performed in 1994. In that work, ellipsometry was employed to measure the T_g of thin polystyrene films applied onto a hydrogen-passivated silicon substrate. The film thickness was decreased from 3000 to 100 Å. The authors seem to be the first to show that, beginning from a thickness of 400 Å, polystyrene T_g starts to drastically decrease relative to the T_g value of the bulk polymer. At a film thickness of 100 Å, this decrease was as large as 25 K, which was far beyond the error in the determination of T_g by ellipsometry. The weight-average molecular
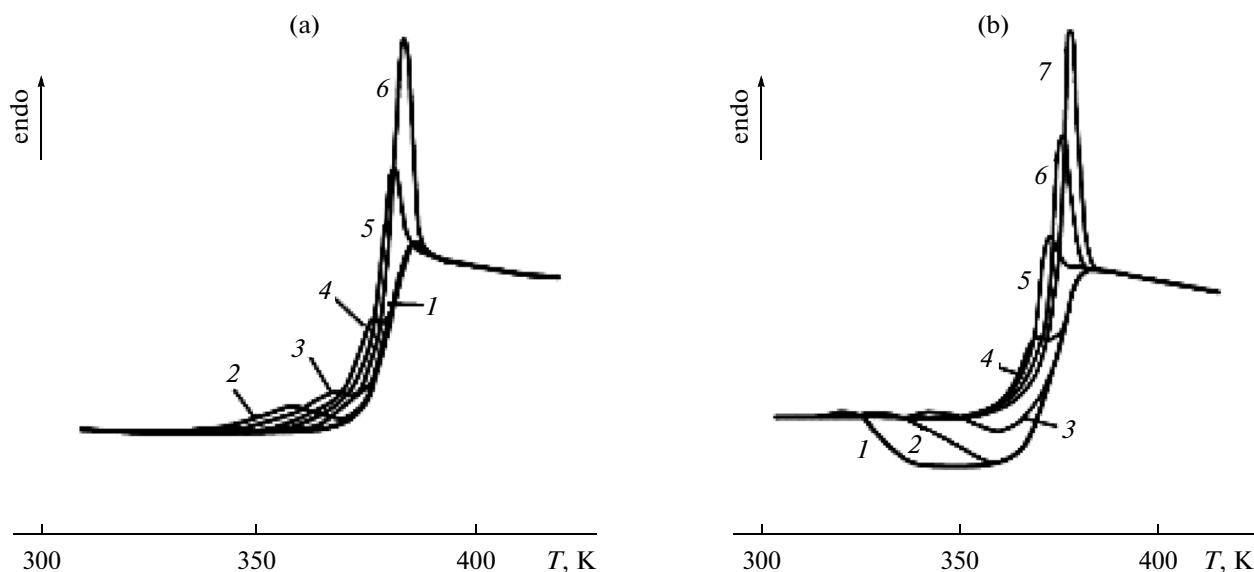
Fig. 29. DSC curves for samples of (a) quenched and (b) preliminarily compressed polystyrene after annealing. Panel (a) annealing at 60°C for (*1*) 0, (*2*) 0.2, (*3*) 1, (*4*) 10, (*5*) 90, and (*6*) 170 h and panel (b) annealing at 70°C for (*1*) 0, (*2*) 0.003, (*3*) 0.08, (*4*) 1.5, (*5*) 6, (*6*) 11, and (*7*) 50 h [74].

mass (M_w) of polystyrene ranged from 120×10^3 to 2900×10^3 Da; i.e., the sizes of macromolecular coils varied from 200 to 1000 Å. In all cases, the dependence of T_g on M_w was not observed, and the data obtained were adequately described by relation $T_g = T_g^{bulk}\left[1 - \left(\dfrac{a}{h}\right)^{\delta}\right]$, where T_g^{bulk} is the glass-transition temperature of bulk polystyrene, h is the film thickness, $a = 32$ Å, and $\delta = 1.8$.

Then, many works devoted to this scope have been published, and, at present, many reviews generalizing the results of these studies are available. Today, it is believed to be reliably established that T_g dramatically decreases in surface layers, thin (nanosized) films, or nanoparticles of amorphous polymers [41, 44, 89–100]. This phenomenon has a general character and is observed for all amorphous polymers. Let us illustrate this effect by the example of an amorphous polymer, which has been most profoundly studied in this respect, i.e., polystyrene.

The data in Fig. 31a show that T_g, which is an important characteristic of a polymer, begins to rapidly decrease, when the polymer film thickness becomes smaller than 70–80 nm. The magnitude of the decrease in the T_g may reach several tens or even hundreds of degrees. It is worth noting that the drastic decrease in T_g of surface layers and thin films of glassy polymers is directly confirmed by the measurements of their elasticity moduli. In particular, such an assessment was carried out in work [101], results of which are presented in Fig. 31b, which shows the elasticity moduli of glassy polystyrene films as functions of their

thicknesses. It follows from Fig. 31b that, when the film thickness becomes smaller than 50–70 nm, the elasticity modulus begins to dramatically decrease irrespective of the polymer molecular mass. This decrease is rather high (at least four to five times). The data obtained are in absolute agreement with the aforementioned results of measuring the T_g values for thin films of glassy polymers (compare Figs. 31a and 31b).

The T_g of the finely dispersed material of crazes is also decreased relative to the ambient bulk polymer, as was mentioned in many studies. In [102], the elasticity modulus of a material in crazes of a glassy polymer was directly measured by atomic force microscopy. The modulus of the craze material has appeared to be as low as 3–10% of the elasticity modulus of the bulk glassy polymer. The result obtained suggests that the finely dispersed material of crazes, as well as the material of shear bands, has T_g substantially lower than that of the ambient bulk polymer.

The first matter that should be mentioned is the very strong decrease in the T_g of polymers in nanosized layers. Second, simple calculations show that the dispersion of a polymer into very small (nanosized) aggregates of oriented macromolecules in shear bands and crazes gives rise to the formation of highly developed interfacial surface (several hundreds of square meters per gram). This obviously causes thermodynamic destabilization of such systems, and processes aimed at a reduction in the interfacial surface area spontaneously occur in them under the action of various factors. These two circumstances enable us to consistently explain the effect of mechanical stresses on
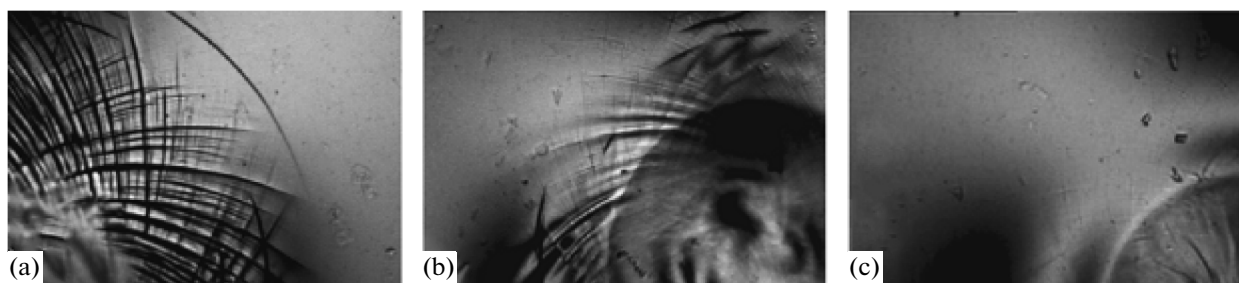
Fig. 30. Optical micrographs of a PET sample, which, after the formation of shear bands, was annealed at (a) 40, (b) 70, and (c) 75°C [87].

the peculiarities of the molecular motion in glassy polymers and, in particular, to make grounded hypotheses regarding the aging mechanism of mechanically "rejuvenated" glassy polymers.

ON THE PHYSICAL REASONS FOR THE EFFECT OF MECHANICAL STRESS ON MOLECULAR MOBILITY IN GLASSY POLYMERS

Thus, analysis of the structural data allows us to formulate general notions regarding the molecular mobility in glassy polymers and the effect of an external mechanical stress on it. As has been mentioned above, polymer glasses obtained from melts have a thermodynamically nonequilibrium structure. It is natural that such a system is unstable and gradually passes into a more equilibrium state under the action of thermal motion. This process is referred to as the physical or thermal aging of polymer glasses. Because of the low rates of molecular rearrangements in glassy polymers, the aging process may last several days or even months. The mechanism of molecular rearrangements that underlie the aging process remains to be studied; however, it may be stated with a high probability that these rearrangements are impossible without the large-scale (segmental) molecular motion. It should be especially noted that the aging of glassy polymers has an affine character; i.e., it develops uniformly and simultaneously in the entire polymer volume.

Now, let us consider the literature data that concern the effect of a mechanical stress on the features of the molecular motion in glassy polymers. Remember that these features are observed, first, in experiments on deformation calorimetry, which show that high energy is accumulated in a glassy polymer at initial stages of its deformation (Fig. 25) [76–78]. Second, the deformation of a glassy polymer gives rise to the appearance of a wide exothermal peak in its DSC thermograms at temperatures below T_g (Fig. 23).

The energy balance of glassy polymer deformation essentially differs from corresponding characteristics of low-molecular-mass plastic bodies. While, during the deformation of a low-molecular-mass plastic body (e.g., copper metal), all supplied energy is transformed into heat [103], in the course of the deformation of a glassy polymer, it accumulates part of the mechanical energy in the form of its internal energy (Fig. 25). This effect is obviously associated with some irreversible rearrangements in the structure of a polymer being deformed. As has been shown above, the structure of a glassy polymer is indeed subjected to essential changes during its deformation. These changes are associated with the formation of discrete zones (shear bands and crazes) in the polymer, with these zones containing a finely dispersed fibrillized material. According to some assessments [48], this material has a specific surface area on the order of several hundreds of square meters per gram. It is obvious that the presence of the interfacial surface as large as this must affect the internal energy of the polymer. In this connection, it is of importance to estimate the possibility of internal energy accumulation by a polymer via an increase in the interfacial energy.

A question arises of whether the experimentally determined accumulation of the internal energy as high as this upon polymer deformation may be attributed to the development of interfaces in shear bands and/or crazes. In order to answer this question, the internal energy that a polymer can accumulate exclusively due to the formation of an interfacial surface upon its deformation via the development of shear bands and/or crazes has been determined quantitatively [104]. This estimation is based on the assumption that, during the stretching of a glassy polymer to nearly its yield stress, the whole deformation occurs via the formation and development of the discrete zones (shear bands and/or crazes), which contain plastically deformed fibrillized polymer. In accordance with the estimation performed [104], the internal energy accumulated by a polymer upon its deformation to the yield stress is 1.6–2.0 J cm^{-3}, which absolutely agrees with the internal energy of 2–3 J cm^{-3} determined for polystyrene, polycarbonate, and PMMA by deformation calorimetry [76–78].

Thus, polymer glass deformation, which is responsible for the so-called rejuvenation of the polymer, is

accompanied by a rearrangement of its structure. This rearrangement occurs due to the formation of particular zones (shear bands and/or crazes) in a plastically deformed polymer. As a result, the deformed polymer has a "two-phase" structure, which is schematically presented in Fig. 32. It is the formation of this structure that is, as a matter of fact, referred to as the rejuvenation of a glassy polymer with the help of the mechanical action. It is of great importance for understanding the phenomena under consideration that the shear bands and crazes are filled with a finely dispersed oriented polymer.

Now, let us see what takes place during an inverse process, i.e., the aging of a mechanically rejuvenated glassy polymer, the structure of which is schematically represented in Fig. 32 [105]. As has been repeatedly noted above, a deformed glassy polymer has a heterogeneous structure and contains discrete zones (shear bands and/or crazes), which are characterized by a highly developed interfacial surface. Therefore, such a polymer is thermodynamically unstable, and processes leading to diminishing (healing) of the interfaces begin to proceed spontaneously in it. It is natural that heating (annealing) drastically accelerates these processes. The annealing of a deformed polymer not only leads to the restoration of its sizes, but is also accompanied by the disappearance (healing) of the aforementioned interfaces (Fig. 32). In fact, DSC experiments are accompanied by such annealing. The data presented in Fig. 29 show that the healing of the interfaces upon the low-temperature annealing (below the T_g) of deformed glassy polymers is accompanied by the appearance of a wide exothermal peak extended actually from the β-transition to the T_g in the DSC thermograms. Note that the width of this DSC peak almost coincides with the temperature range corresponding to the abnormalities in the mechanical behavior of deformed polymers.

The existence of the aforementioned low-temperature exothermal DSC peak (Fig. 29) becomes understandable in the context of the above-developed ideas of the role of interfacial surface of the discrete zones (shear bands and crazes) that result from the inelastic deformation of polymer glasses. When a deformed glassy polymer is heated at temperatures lower than its T_g, the local T_g of the finely dispersed oriented material in the shear bands and crazes is reached.

This circumstance brings about two consequences. First, the oriented material of the shear bands and crazes undergoes a contraction, which is accompanied by the restoration of polymer sizes via the ordinary entropy-related mechanism, as it has been considered in the previous section. Second, since the contracted rubberlike material of shear bands and crazes has a temperature higher than its local T_g (but lower than the T_g of the bulk polymer), the process of healing the "excess" interfacial surface area begins. The issue is
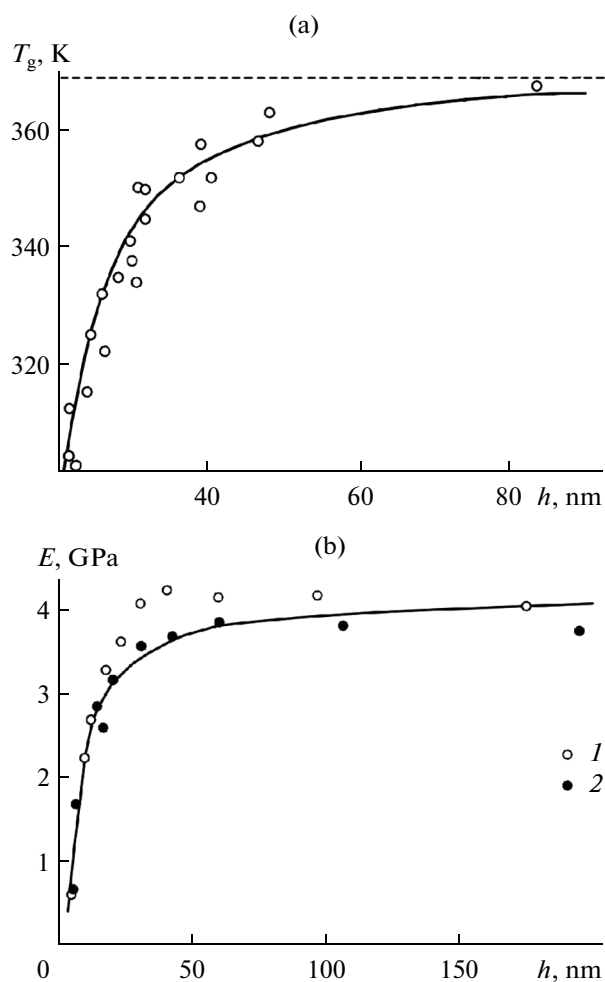

Fig. 31. Panel (a) dependence of T_g on thickness for free polystyrene films ($M_w = (116-347) \times 10^3$) [89] (dashed line shows T_g of bulk polystyrene) and panel (b) dependences of elasticity modulus on thickness for polystyrene films with $M_w = (1)$ 1800×10^3 and (2) 114×10^3 [101].

that healing of the interfaces (autoadhesion) is possible only if a polymer is in the highly elastic state state [41, 106]. The mechanism of the healing consists in the interdiffusion of chain segments through interfaces, and this process may take place provided that the segmental mobility of this kind is realized in the polymer. The processes relevant to the reduction in the interfacial surface area (healing) are thermodynamically advantageous; therefore, they proceed spontaneously under the conditions that provide the necessary molecular mobility. It is clear that the healing of an interface is always an exothermal process, because it is accompanied by a decrease in the system free energy. It is this effect that is observed in the DSC thermograms (Fig. 29) as the exothermal peak located between the β- and α-transitions in a bulk polymer.

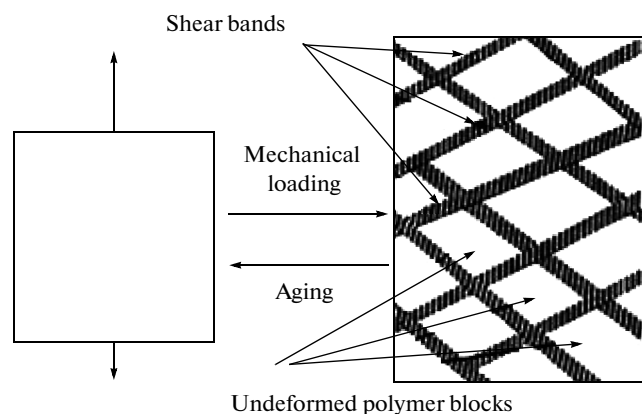The internal energy that a polymer accumulates at initial stages of deformation is released in the form of

Shear bands

Mechanical
loading

Aging

Undeformed polymer blocks

Fig. 32. Schematic representation of structural rearrangements accompanying deformation of a glassy polymer in air [105]. See text for explanations.

heat due to the healing of the interfaces upon the subsequent annealing of the polymer. It is not surprising that the thermal energy determined by DSC is 2–3 J cm^{-3}; i.e., it exactly corresponds to the amount of the internal energy accumulated as a result of the deformation of the glassy polymer.

Thus, all known features of the molecular motion in glassy polymers and the influence of external mechanical stresses on them may be explained taking into account two factors. First, the loading of glassy polymers gives rise to the formation and development of the zones of plastically oriented polymer (shear bands and/or crazes) with pronounced boundaries. Second, the finely dispersed material that fills these formations has a decreased T_g, which, in particular, explains the abnormalities in the mechanical, thermophysical, thermodynamic, sorption, and other properties of deformed polymers at temperatures lower than the T_g of the initial bulk polymers.

CONCLUSIONS

The above-considered information leads us to propose some generalizations concerning the features of the molecular motion in glassy polymers. These features may be conventionally divided into two parts.

First, this is the molecular motion responsible for the aging of freshly formed quenched polymer glasses. The quenching of an amorphous polymer occurring at a temperature higher than its T_g transfers it into a thermodynamically nonequilibrium state that is characterized by an increased content of free volume and conformation of macromolecules that is nonequilibrium under these conditions. As a result, the physical or thermal aging begins, which brings the polymer closer to the equilibrium state. In spite of the fact that the physical aging of a polymer occurs in the tempera-

ture range corresponding to its glassy state, it may be believed that this process is, in particular, associated with the large-scale (segmental) molecular motion, which is evident from, e.g., an increase in the T_g of the polymer. Even a short-term heating of an aged polymer above the T_g transfers it into the initial (postquenching) state, while the aging process begins again (the "rejuvenation" effect). The uniformity of the physical aging process over polymer volume (affinity) is also an important circumstance.

Second, the aging process may be initiated in an essentially different way. Being subjected to a mechanical action (uniaxial compression, torsion, and rolling), a polymer passes to a state, in which its properties are similar to those of a polymer subjected to heating above its T_g. A mechanically rejuvenated polymer exhibits actually no yield stress under the conditions of uniaxial stretching and a subsequent decrease in the stress; moreover, its thermophysical, thermodynamic and other properties are changed. At the same time, such mechanically rejuvenated polymer undergoes a spontaneous aging process in the temperature range corresponding to the glassy state, with all properties of the polymer varying toward the initial "nonrejuvenated" state during this process.

Analysis of the published data has shown that these two aging processes, which have some features in common, are realized via different molecular mechanisms. The mechanical rejuvenation of a polymer occurs upon its slight deformation at a temperature lower than its T_g. It is of importance to note that the deformation of a glassy polymer is always nonuniform over its volume. At the initial stages of loading (uniaxial compression or stretching, shear, or torsion), zones of inelastic deformation (shear bands and/or crazes) arise and develop in a glassy polymer. The key circumstance for understanding the molecular processes occurring in a deformed glassy polymer is that the aforementioned zones are filled with an oriented fibrillized material, which has pronounced bounders and fibril sizes (diameters) of a few to several tens of nanometers. At such small sizes of fibrillar aggregates of macromolecules, the "phase" of the material filling the shear bands and crazes has a very large specific surface area (hundreds of square meters per gram). This circumstance transforms the deformed glassy polymer into a thermodynamically unstable system and generates the driving force of the inverse process, i.e., the coalescence of interfacial surfaces, which is, actually, the aging process in this case. However, such coalescence requires a high molecular mobility of macromolecular chains or their fragments, which would ensure their diffusion through an interface. This mobility of polymer chains seems to be impossible in the temperature range of the glassy state, in which the large-scale (segmental) molecular mobility is believed to be "frozen." This contradiction is easily eliminated taking

into account the phenomenon (discovered in the mid-1990s) of a very strong decrease (by many tens of degrees) in the T_g of amorphous polymers in nano-sized volumes. These sizes are inherent in the fibrillar macromolecular aggregates that fill the shear bands and crazes in deformed glassy polymers.

Thus, mechanical stress strongly affects molecular mobility in glassy polymers. This effect manifests itself as follows. Mechanical stress gives rise to the formation of peculiar zones (shear bands and/or crazes) in a polymer matrix, with these zones being filled with a finely dispersed oriented material, which has a highly developed surface and nanoscopic sizes of structural elements. As a result, a "two-phase" system is formed consisting of structural elements of two types, with one of them having a strongly decreased T_g. This circumstance represents the physical reason for all abnormalities observed in the structure-related mechanical behavior of deformed glassy polymers.

ACKNOWLEDGMENTS

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