On the Nature of Abnormalities in the Structural Mechanical Behavior of Glassy Polymers

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Abstract—Literature data on abnormalities in the mechanical behavior (stress relaxation in the initial section of the stress–strain (compression) diagram, stress growth under isothermal heating, a low-temperature contribution to the temperature-induced strain recovery of deformed polymer glasses, a soft compliant phase upon the tensile drawing of a glassy polymer revealed by dynamic mechanical tests) and in the thermophysical behavior (accumulation of internal energy at early stages of deformation and an exothermic DSC peak below the glass transition temperature) of the deformed glassy polymers are considered. The above abnormalities can be explained taking into account two fundamental features of amorphous polymers, first, the inhomogeneous character of inelastic deformation in glassy polymers, which leads to the development of discrete regions of plastically deformed material in the initial polymer (shear bands and/or crazes), and, second, a marked decrease in T_g of highly dispersed oriented material filling both shear bands and crazes.

Keywords: deformation mechanism for glassy polymers, abnormalities of structural mechanical behavior, low-temperature relaxation of deformed glassy polymers, accumulation of internal energy upon deformation, crazing and shearing, reduced glass transition temperature in thin films and surface layers of amorphous polymers.

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CONTENTS

1. INTRODUCTION

The structure, properties, and deformation mechanism of glassy polymers have been the subject of extensive research over the years. Research materials relating to the characteristics of the glassy state of
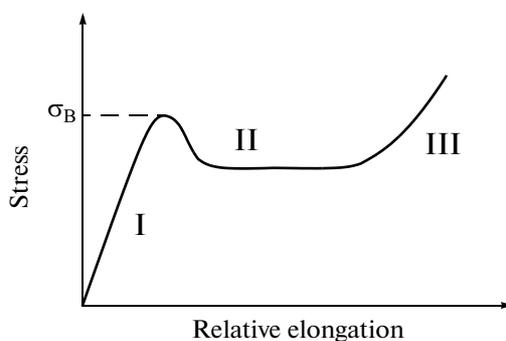
Fig. 1. Typical plot of the stress—strain curve of glassy polymer. See explanations in the text.

amorphous polymers are so voluminous that the authors in no way claim that the topic is completely covered in a single review. The purpose of this publication was to examine and analyze experimental data on the anomalous physicochemical and physicomechanical behavior of glassy polymers, accumulated to date.

Before turning to the abnormalities in the structural and mechanical behavior of amorphous polymers, it is necessary to briefly recall some basic modern concepts of the mechanism of their deformation. All of the characteristic properties of polymers are due to a chain structure of their molecules and the fundamental property associated with this structure, namely, flexibility. The flexibility of macromolecules, that is, the ability to change shape (conformation) under the action of external stresses and thermal motion, determines one of the unique mechanical properties of amorphous polymers, i.e., large reversible deformation. This property is that a polymer stretched many times almost instantly restores to its original size as soon as it is released from the stretching device. Note that significant reversible deformation is homogeneous (affine); that is, it is developed simultaneously throughout the volume of the deformed polymer.

In its classical form, a large reversible deformation occurs only in polymers, which are in a highly elastic state. Large inelastic deformations can also be achieved below the glass transition temperature (T_g), but their reversibility can only be achieved by heating the deformed polymer above T_g.

The mechanical behavior of glassy polymers is usually illustrated by means of the stress—strain curve (Fig. 1). This curve consists of three main plots, i.e., (*1*) the so-called elastic section, (*2*) the plateau region where the development of the neck begins, (*3*) and the section where the polymer passed into the neck is homogeneously deformed. In this review, the phenomena and processes that take place mainly in the first two sections of the stress—strain curve of polymer will be considered and analyzed. Polymers subjected to deformation up to these values are briefly described in textbooks as follows: @In the first part (of the stress—strain curve), the polymer is deformed elastically. Deformation is achieved because of increasing intermolecular distances. Stretched (up to strain values corresponding to the second part of the stress—strain curve) glassy polymer cannot shrink spontaneously. However, when heated above T_g, as soon as the segments acquire the capacity for thermal displacement, the sample will shrink to a length close to the initial one [1].

The aforementioned provisions about the glassy state of polymers as a condition in which large-scale molecular motion is frozen are not fully correct. For more than half a century, experimental data that do not fit into the above profile have been accumulating in the scientific literature. Let us consider the main findings of the abnormal structural and mechanical behavior of amorphous glassy polymers. In this regard, it is first necessary to examine the feasibility of implementing certain types of large-scale molecular motion in the temperatures within the glassy state of amorphous polymers.

2. PHYSICAL AGING OF POLYMER GLASSES

For many decades, the authors of numerous studies have noted that the mechanical, thermophysical, physicochemical, and other properties of polymer glasses are not stable. In other words, in glassy polymers, some processes that lead to a change in the whole complex of physicomechanical, thermophysical, diffusion, and other properties occurs spontaneously in time [2]. It is obvious that these processes, known as physical aging, are caused by specific types of molecular motion and are achieved in amorphous polymers below their T_g.
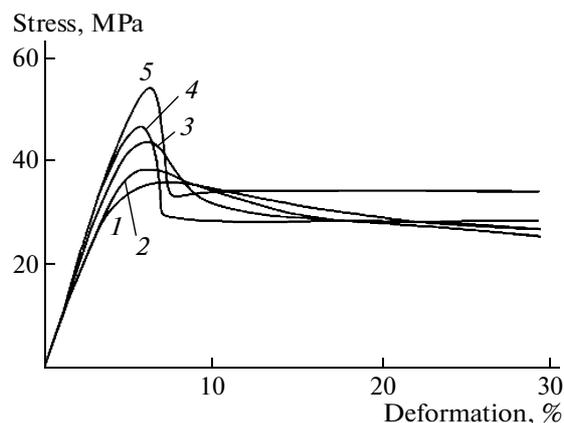
Fig. 2. Stress—strain curves of glassy PET at room temperature: low-temperature annealing time (*1*) 0.16, (*2*) 1.5, (*3*) 16.6, (*4*) 166.6, and (*5*) 1166.6 h; the annealing temperature, 60°C [3].
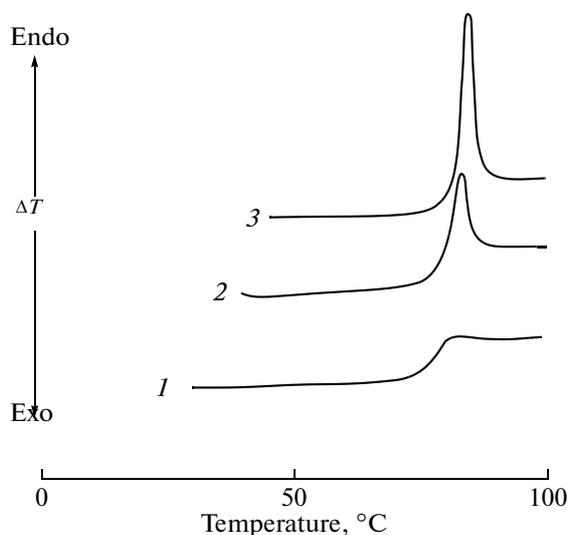

Fig. 3. DSC thermogram of amorphous PET annealed at 65°C for (*1*) 0, (*2*) 1, and (*3*) 45 h [4].

Consider the most typical examples of the phenomenon of physical aging of polymer glasses. The tensile curves of amorphous PET subjected to low-temperature annealing at a temperature of 60°C for various periods of time [3] are shown in Fig. 2. Note that this annealing temperature is well below the glass transition temperature of PET (75−78°C). It follows from Fig. 2 that the low-temperature annealing leads to a significant increase in the modulus and yield stress of the glassy polymer.

These changes in mechanical properties during the physical aging of a glassy polymer are also accompanied by a significant change in its thermophysical properties. This is unambiguously seen from the DSC data. Typical data of this kind are shown in Fig. 3. It is clearly seen that a step in the region of polymer vitrification, which is usually observed in the thermograms, is transformed into a kind of endothermic peak while the sample is annealed; the peak becomes more intense during the low-temperature annealing [4]. Figure 4 presents the dependence of (*1*) dynamic modulus, (*2*) logarithmic decrement, and (*3*) enthalpy on the time of low-temperature annealing of amorphous PET. It can be seen that all of these characteristics are clearly correlated with each other, as well as with the data of mechanical tests presented in Fig. 2.

It is important to note that aging during low-temperature annealing (below T_g of amorphous polymer) is a thermally reversible process. It is sufficient to heat the aged polymer above its glass transition temperature to have it be rejuvenated (transferred to the state that it was in prior to annealing); as a result, a new cycle of aging can be completely reproduced.
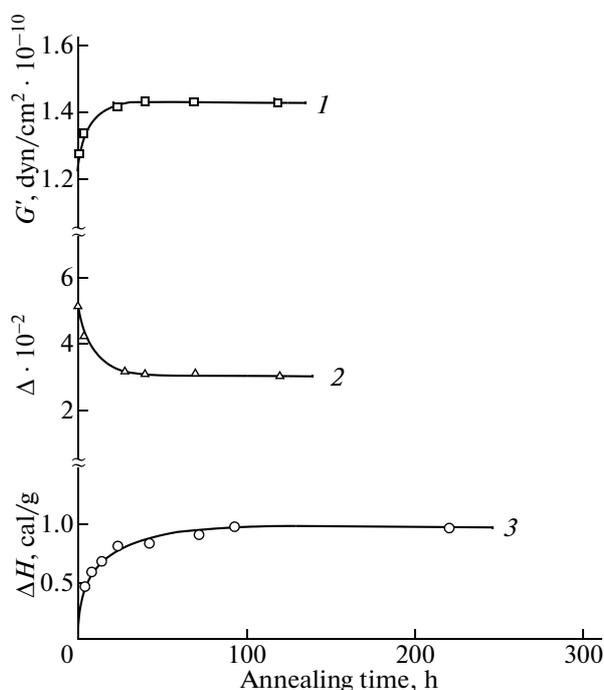
Fig. 4. Dependence of (*1*) dynamic modulus, (*2*) logarithmic decrement, and (*3*) enthalpy on the time of low-temperature (below T_g) annealing of amorphous PET [4].

One of the key issues of aging in polymer glasses is the question of the molecular mechanism of this phenomenon. In this context, information about the structural changes that accompany aging becomes important. Amorphous polymers are structurally inhomogeneous solids with dimensions of inhomogeneities of units or tens of angstroms [5–7]. In numerous studies, an inhomogeneous structure of polymer glasses and, in particular, the existence of some ordered domains in them are assumed to explain the features of aging processes [8–10]. The heterogeneity of the structure of amorphous polymers has a fluctuation, nonequilibrium nature rather than a phase nature, which poses significant experimental difficulties in its study. The reasons for these difficulties lie in the inability to use direct structural methods based on the phase contrast of samples under study (X-ray analysis, electron diffraction). Repeated attempts were made to detect heterogeneities of the structure (domains) in amorphous polymers by the direct microscopic method. For example, the structure of amorphous PS was investigated using electron microscopy (replica method) depending on the time of its low-temperature annealing [11]. The authors were able to detect and describe some kind of grit in the structure of the polymer, which increased with temperature and annealing time (grain size changed during annealing from 300 to 700 Å). The growth in the inhomogeneity of the polymer was confirmed by the electron diffraction data. The authors concluded that during physical aging, there are certain molecular structural changes, but their relationship with the properties had not been established. Unfortunately, the heterogeneity of the polymer on the submolecular level found in the paper cited above did not give an adequate picture of the structure of amorphous polymers.

In connection with this, the understanding of the structure of polymer glasses and its evolution during thermal physical aging is based on data obtained by indirect methods. One of these methods is the study of the behavior of low-molecular-weight substances introduced into glassy polymers. This is due to the fact that the characteristics such as the diffusion, permeability, and mobility of low-molecular-weight compounds in polymers are related to the free volume of the polymer that largely also determines the realization of the processes of physical aging.

For example, the rotation time of low-molecular probes (tetracene and rubrene) in PS during its aging were studied in [12]. It was found that the rotation times varied by more than an order of magnitude during isothermal aging of PS, which was in full agreement with the corresponding time dependence of the relaxation of volume and enthalpy. The difference in the evolution of the rotation times of two probes in the PS matrix was explained by its spatial heterogeneity, due to which the aging process took place in some small regions of the polymer faster and more densely than in others.

The authors of [13] come to similar conclusions; they investigated the aging process in polyetherether-ketone (PEEK) at temperatures 80−120°C by the methods of density measurement, DSC, gas transport, dynamic mechanical properties, and creep flow. It was shown that, with aging near T_g, in addition to the decrease in the free volume, the adsorption of dichloromethane at low concentrations decreased, leading to speculation about the origin of ordered domains impermeable to vapors at low concentrations, made earlier in [14−16].

Thus, numerous investigations of the processes of physical aging of amorphous polymers lead to the conclusion that their spatial structure is heterogeneous.

3. ON THE MOLECULAR MECHANISM OF THERMAL AGING OF GLASSY POLYMERS

The appearance of a nonequilibrium structure in glassy polymer and its relaxation in low-temperature annealing is often associated with the transition of the polymer from a highly elastic to a glassy state. It is obvious that, in the cooling of the polymer melt, the fraction of free volume in it naturally declines. This fraction is only close to its equilibrium value when far from T_g. When approaching the glass transition temperature, the viscosity of the polymer begins to increase rapidly, causing the structure of the polymer characteristic for the rubbery state to be frozen in the transition of the polymer in the glassy state. Thermal physical aging is in fact the spontaneous transition of polymer glass to the state of thermodynamic equilibrium.

The evolution of free volume plays an important role in the process of physical aging. Based on this pattern, several models have been proposed to describe the mechanism of physical aging [2, 17, 18]. These models are all based on experimental fact, which divides the aging process into two components, i.e., a thermally activated process described by the Arrhenius equation and the process driven by an excess of free volume in the system, which determines how far the system is from thermodynamic equilibrium. In other words, the process of physical aging of the polymer depends, first, on some kind of molecular motion in the temperatures within the glassy state and, second, on the migration of the free volume. Despite the large number of studies on the elucidation of the mechanism of physical aging, clarity on this issue has not been achieved to date.

In this review, we should at least briefly consider the question of the nature of the molecular motion responsible for the aging of polymer glasses. As noted above, the cooling of the polymer from temperature higher than T_g leads to the freezing of nonequilibrium conformations of macromolecules. The transformation into equilibrium conformations is attributed to the process of physical aging. As the aging process stops at temperatures below the temperature of β-transition, it is reasonable to assume that β-relaxation is responsible for this process. The activation energy of β-transition is typically ~30−50 kJ/mol and increases to 200−300 kJ/mol at T_g [19]. This is explained by the fact that the β-transition is accompanied by the movement of only one to two bonds, whereas the α-transition is more cooperative and requires 8−20 bonds for its implementation. The authors of [20] suggest that the process of physical aging is associated with the redistribution of free volume rather than with simply a shift in the relaxation processes along the temperature scale.

The most detailed analysis of this issue is given in [21]. The authors conclude that β-molecular motion is responsible for the observed effects of physical aging of polymer glasses. Note that, like the α-relaxation, β-relaxation has a large-scale segmental nature, but this is the noncooperative movement of the segment, which, in the case of vitreous body, can only occur in places with loose molecular packing (high concentration of free volume). The violation of the cooperativity of molecular motion assumes a kind of structural heterogeneity of the glassy polymer. It follows that, for β-molecular motion, the polymer glass should have a heterogeneous structure. That is why the molecular motion is detected in the temperature range below the glass transition temperature. Therefore, the point of view of the authors [21] fully corresponds to the results of numerous studies in which the authors believe that the structure of glassy amorphous polymer is inhomogeneous.

Given the affinity of the process of physical aging, one can try to estimate the size of volumes in which they occur. Obviously, these volumes are commensurate with the size of the free-volume holes determined by the method of positron annihilation. The number of these holes is on the order of $1-2 \times 10^{19}$ cm^{-3} and their size is ~2 Å [22]. Since these processes occur in the entire volume of the polymer at the same time, it is clear that the number of these zones is very large and comparable with the number of macromolecules per unit volume of the polymer.

Thus, the phenomenon of physical thermal aging of polymeric glasses clearly indicates that, at the temperature within the glassy state of amorphous polymers, spontaneous structural adjustments occur. Although the full mechanism of this phenomenon is not yet clear, there is no doubt about the possibility
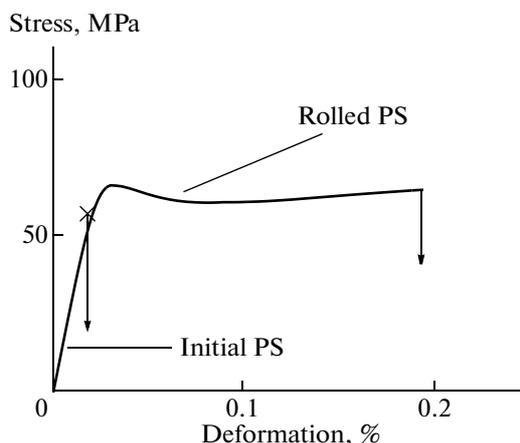
Fig. 5. Effect of rolling on stress–strain curve of PS at room temperature. Arrows indicate discontinuous elongations of PS [23].

of large-scale molecular motion in polymers below their T_g. It is important to note that the process of physical aging occurs simultaneously throughout the entire volume of glassy polymer, that is, is affine in character.

4. EFFECT OF MECHANICAL STRESS ON THE PROCESS OF PHYSICAL AGING OF POLYMER GLASSES

We noted above that the process of physical aging can easily be reset. To do this, it is sufficient to heat the aged polymeric glass to a temperature above its T_g; as a result, it acquires all the properties that it had prior to the process of thermal aging. Thus, subsequent low-temperature annealing will again be accompanied by all of the features of thermal aging as described above.

However, it appears that there is another factor that is also able to run the mechanism of physical aging, i.e., the mechanical effect on the glassy polymer. The above effect can easily be accomplished by, e.g., uniaxial compression or rolling in the temperature range below T_g of the polymer film. A typical example of this kind is shown in Fig. 5 [23]. The figure shows that the preliminary mechanical treatment (in this case, rolling) leads to an effect similar to the rejuvenation of the polymer aged by heating above the glass transition temperature followed by rapid cooling (quenching). Indeed, the mechanically rejuvenated polymer has almost no yield stress and the subsequent drop in strain.

It is well known that, under uniaxial tension at room temperature, PS is a brittle material and its failure occurs in the strains on the order of 1–2% (on a so-called Hooke section of the stress–strain curve). However, after the mechanical impact, PS shows a ductile behavior and its elongation at break is 30% at room temperature. The effect of mechanical stress on the glassy polymer can even be detected visually. Figure 6 shows the photographs of two samples of PS, the mechanical behavior of which is characterized in Fig. 5. It is clear that original PS is a brittle material, that collapses under tension by 1–2%. The destruction is preceded by the intensive development of crazes, which serve as nuclei for the main crack [24]. If PS is subjected to predeformation on rollers (rolling), it becomes cloudy, opaque, and can be deformed in any conditions, even rolled up in a tube (Fig. 6b).

Annealing of the deformed polymer above its glass transition temperature fully restores the original properties of the polymer and eliminates the effect of mechanical rejuvenation [25, 26]. Moreover, the mechanically rejuvenated polymer spontaneously recovers in time their original mechanical properties without annealing. This effect is demonstrated in Fig. 7 [27]. It is clear that, over time, the yield strength appears and begins to increase, and PS recovers all of its original properties at room temperature within 48 hours after rolling (Fig. 7), including the ability to be decomposed at small strains. As follows from the data presented in Figs. 5–7, the rejuvenation of the polymer with mechanical action triggers of a kind of physical aging that occurs spontaneously over time.
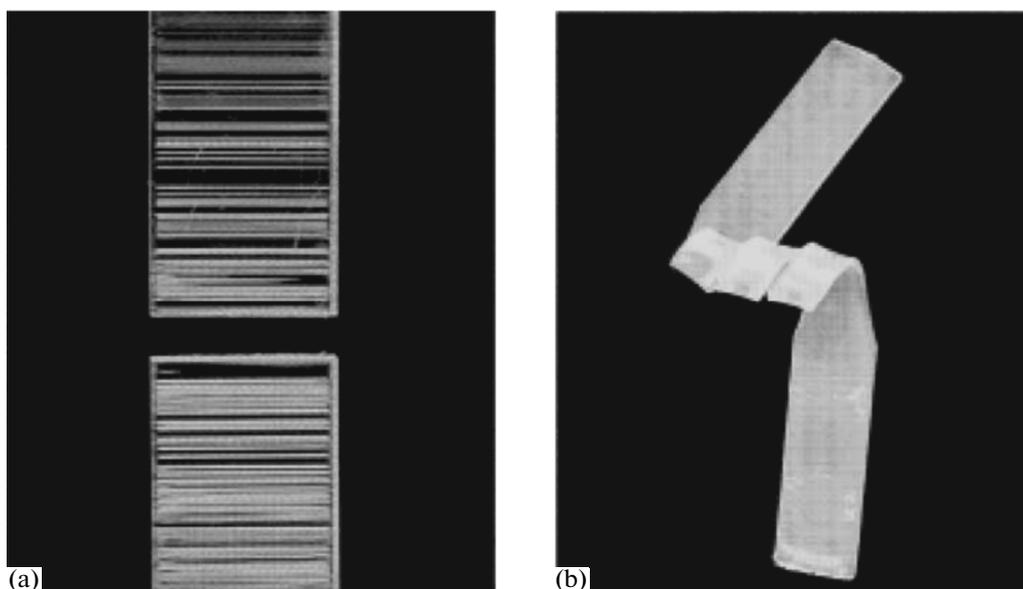
Fig. 6. Appearance of PS films after their deformation in air at room temperature: (a) original PS and (b) sample of the PS previously subjected to rolling [23].
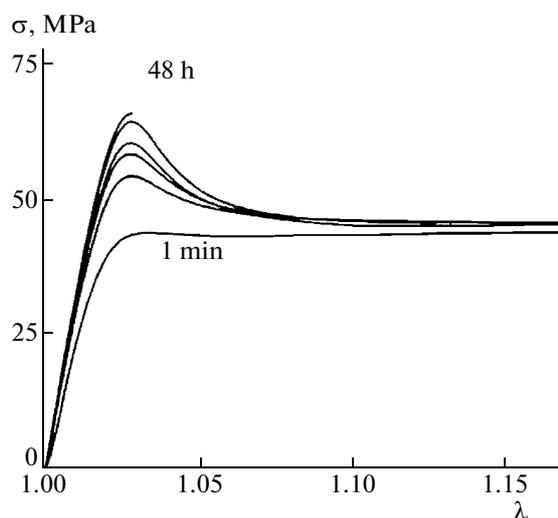

Fig. 7. Stress–strain curves of PS samples obtained at room temperature at different time intervals after rolling treatment [27].

5. PROPERTIES OF GLASSY POLYMERS SUBJECTED TO MECHANICAL STRESS

Thus, the mechanical effect on the glassy polymer, even at small strains, most strongly affects its properties. Let us consider how the mechanical loading of glassy polymer under various conditions affects its fundamental properties.

5.1. Stress Relaxation

We noted above that it has been suggested in textbooks that the deformation of a glassy polymer in the first stage of its deformation (a so-called elastic Hooke section of the stress–strain curve) is elastic and occurs due to the increase in intermolecular distances [1]. However, Yu. S. Lazurkin [28] was probably the first to observe the inelastic deformation of glassy polymer in the first, so-called elastic, Hooke section of its stretching curve. He found that, in the temperature range of the glassy state and at the deformation
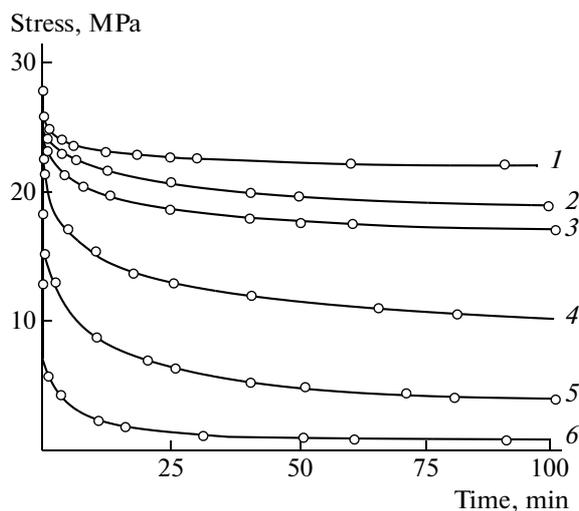
Stress, MPa

Fig. 8. Stress relaxation curves of PMMA in the glassy state: test temperature (*1*) 18, (*2*) 25, (*3*) 40, (*4*) 54, (*5*) 71, and (*6*) 83°C; initial stress was approximately 0.5 of the yield stress [28].

below the yield stress, there were relatively fast relaxation processes in amorphous polymer. After unloading, these deformations continuously decrease and eventually vanish in a relatively short time without heating above T_g. Lazurkin calls these processes "elastic aftereffect deformation" (EAD). The consequence of inelastic processes is, e.g., a significant stress relaxation in the glassy polymer in the so-called Hooke part of its stress–strain curve (compression). A series of these stress relaxation curves for a glassy PMMA is shown in Fig. 8 [28]. It is clearly seen that, under these conditions, the glassy polymer demonstrates the mechanical behavior that is not characteristic of an elastic Hooke solid. Note that the stress relaxation is also manifested in the force and temperature ranges below T_g and below the yield stress.

Lazurkin also found that, in the glassy polymer stressed in the so-called Hooke section, a strong birefringence occurred that relaxed with time. The signs of birefringence are always the same for EAD and forced elastic deformation, that is, in a polymer oriented in the neck. At the same time, the sign of birefringence for elastic deformation does not coincide with the sign of birefringence that the polymer acquires as a result of its molecular orientation. Based on this, Lazurkin concludes that there is no fundamental difference between the EAD and forced elastic deformation. Both of these deformations are associated with large-scale structural rearrangements caused by conformational transformations in the polymer chains. Lazurkin comes to the conclusion that, first, the deformed amorphous polymer has a kind of molecular mobility within the glassy state and, second, that both types of deformation, i.e., forced-elastic and elastic aftereffect, are orientational in character. They are associated with rearrangements of molecular chains, which leads to the emergence of a preferred orientation. The results have not been fully explained because it is believed that, in the glassy state, a large-scale molecular motion is frozen and, at this level, no spontaneous molecular processes are impossible.

5.2. Isometric Heating

4   Further experiments revealed a whole series of phenomena that inducate possible large-scale molecular motion in amorphous polymers in the temperature range below their glass transition temperature.

5   In particulr, one of these experimental observations is the mechanical behavior of deformed glassy polymers upon their isometric heating. It turns out that, during heating, growing tension is observed in the stretched glassy polymer under isometric conditions [29, 30]. Importantly, this growth begins long before the glass transition temperature of the polymer. This result also clearly indicates the possibility of large-scale molecular motions within the glassy state of amorphous polymers. An example of this mechanical behavior is presented in Fig. 9. It is clear that the deformed polymer (PMMA) exhibits a significant increase in tension at temperatures much lower than its glass transition temperature (115°C). It is important to note that this experimental fact proves the entropy (polymeric) nature of the phenomenon because the increase in tension in the heating under isometric conditions can only be observed in the oriented polymer [31].
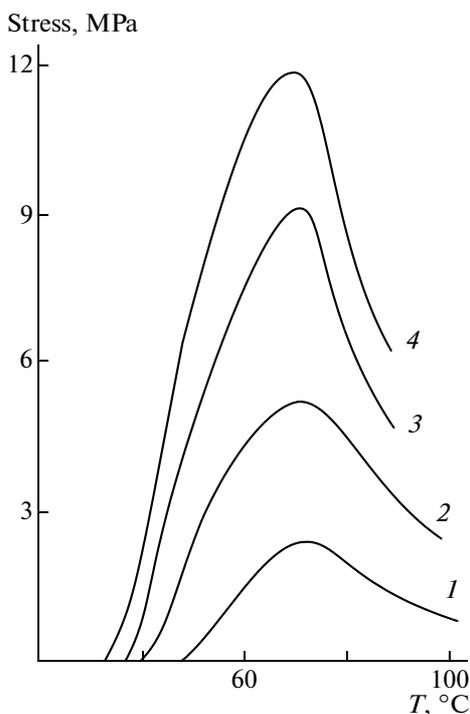
Fig. 9. Isometric heating curves of PMMA samples deformed up to $\lambda =$ (*1*) 1.5, (*2*) 2.5, (*3*) 3.25, and (*4*) 3.9 at 105°C [29].

5.3. Thermally Stimulated Size Recovery of Deformed Glassy Polymers

The fact that large-scale molecular motion can occur is detected even more clearly in the study of the thermally stimulated size recovery of deformed glassy polymers. It has been established in numerous studies [32−36] that the deformed glassy polymer recovers its size during the annealing in a very peculiar way. Typical temperature dependences of the size restoration of PMMA deformed in uniaxial compression are presented in Figs. 10a and 10b [33]. It is clear that this process is most strongly affected by two factors, i.e., the temperature and the magnitude of deformation of the original polymer. As can be seen from Fig. 10a, the restoration of the size of the polymer deformed at 120°C (above T_g) occurs according to conventional views about the process. The polymer recovers its size when it reaches T_g. If the sample was deformed to small magnitudes below T_g, it is fully restored to its size in the temperature range below the corresponding T_g.

The magnitude of deformation also has the strongest effect on the relaxation of the deformed polymer (Fig. 10b). If the polymer is deformed below T_g by the magnitude before and about the yield stress of the polymer, it fully restores its size in the temperature range below T_g. In the deformation of the polymer to
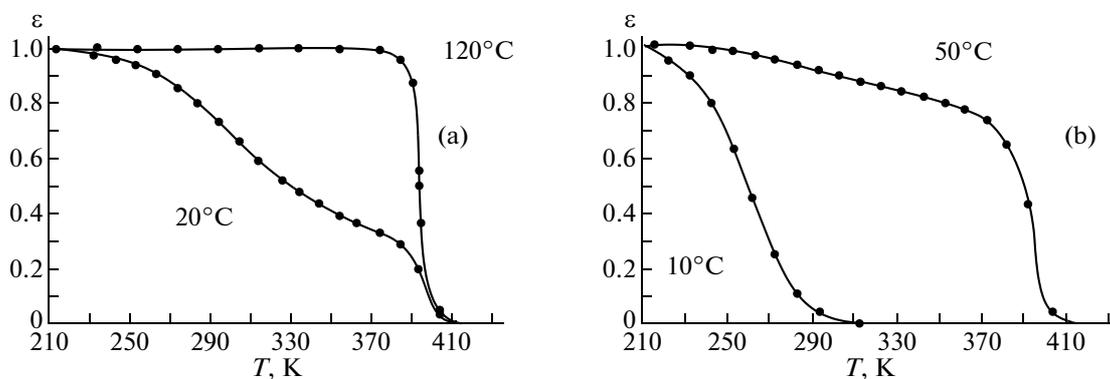

Fig. 10. Effect of (a) temperature and (b) magnitude of deformation of PMMA on thermally stimulated recovery of its size [33].
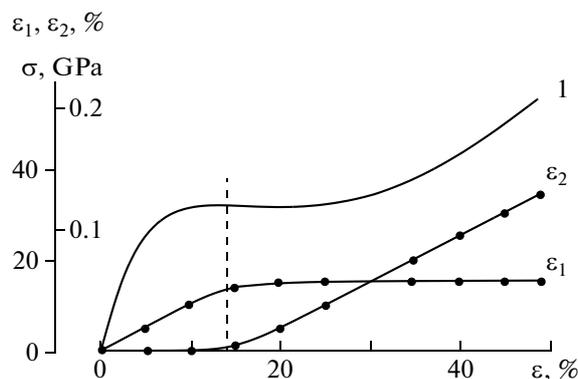
Fig. 11. Curve of uniaxial compression of PMMA (*1*) at room temperature and (ε) low-temperature and (ε_1) high-temperature contributions to the thermally stimulated shrinkage during annealing [33].

the values larger than the yield stress, a high-temperature component of the thermally stimulated recovery of the size of the polymer appears.

The effect of the deformation magnitude of the glassy polymer on the nature of its thermally stimulated recovery is shown in Fig. 11. In this figure, the curve of uniaxial compression of the polymer is compared with the high-temperature (ε_1) and low-temperature (ε_2) contributions to the thermally stimulated restoration of its size. It follows from the figure that, if the glassy polymer is deformed below its yield point, it fully recovers its size in the temperature range below the glass transition temperature. With increasing deformation up to values exceeding the yield point, the polymer begins to accumulate a high-temperature component of its thermally stimulated size recovery, that is, the part that relaxes in the glass transition temperature of the polymer. In this process, the low-temperature contribution to the recovery of the sample size does not disappear, but simply stops changing in magnitude.

It is important to note another feature of the thermomechanical behavior of deformed glassy polymers. After the deformation of the polymer, there is a part of deformation that relaxes at a temperature of the experiment immediately after unloading. It turned out that this contribution to the thermally stimulated restoration of the sample sizes is not elastic in the true sense of the word and can be fixed by deep cooling of the polymer in the deformed state [37]. After unloading and annealing, this part of the residual strain relaxes in the temperature range below the temperature of deformation. This last result emphasizes once again the suggestion expressed for the first time in [28] that the deformation of the glassy polymer in the so-called Hooke section is not truly elastic (reversible).

5.4. Dynamic Mechanical Properties

The study of the dynamic mechanical properties of amorphous polymers also shows a number of abnormalities, which indicates that large-scale (segmental) molecular motion in amorphous polymers can occur below their T_g. This kind of molecular motion was discovered experimentally in several studies [38–42].

Let us consider this phenomenon based on the example of the data obtained in [43]. In this work, amorphous polycarbonate (PC) was deformed to different values under uniaxial compression at room temperature, after which the samples were cooled with liquid nitrogen; then, the temperature dependence of the dynamic mechanical properties of the samples was studied. The evolution of $\tan \varphi$ at a load frequency of 1 Hz and a heating rate of 1 K min^{-1} for the samples deformed in the plane at 0, 6, 10, 20, 30 and 40% is demonstrated in Fig. 12.

For undeformed PC, the β- and α-relaxations are separated by more than 200°C. The α-peak at this frequency corresponds to 420 K, while the β-peak is located at 170 K and strongly stretched along the temperature axis because it is related to a wide distribution of the relaxation times [44, 45]. It is clear that in the case of deformed PC samples, a very broad relaxation transition appears between α- and β-transitions, extending from 280 K to T_g. This peak is completely eliminated by annealing the polymer above T_g. The position of this peak is independent of the deformation magnitude. As can be seen from Fig. 12, this transition is realized in the form of a broad relaxation peak, which is then converted to a plateau that extends to the main α-transition. The height of this plateau increases with increasing strain and reaches saturation at deformations of more than 30%. The authors suggest that, in the deformed glassy polymer,
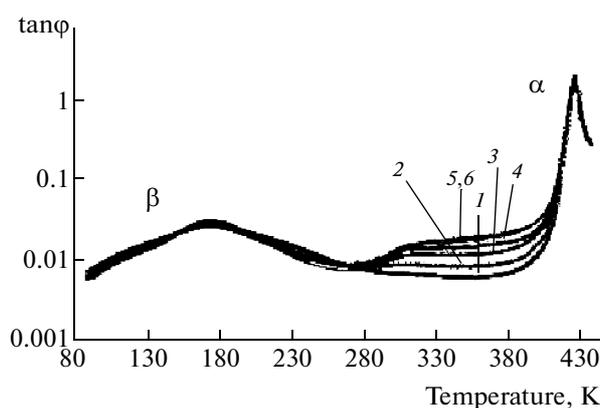
Fig. 12. Temperature dependence of tangent of phase shift of PC samples deformed at room temperature under uniaxial compression at (*1*) 0, (*2*) 6, (*3*) 10, (*4*) 20, (*5*) 30, and (*6*) 40% [43].

there are certain zones in which molecular mobility is greatly increased in comparison with the original block polymer. The emergence of zones with high ductility in a glassy polymer imparts the whole polymer very unusual mechanical properties. The presented experimental results (Fig. 12) clearly indicate that the inelastic deformation of polymer glasses leads to the formation of a sort of second phase that has significantly different properties. Note that the appearance of the relaxation peak caused by the deformation of the glassy polymer was observed previously [46, 47].

The structural heterogeneity of the deformed polymer glass was found in the study of the dynamic mechanical properties of PC under its tension at a constant rate. The inelastic deformation of glassy polymers (PC) under uniaxial tension was investigated in [48]; simultaneously, the internal friction processes were measured.

The strain–strength curve of PC and the appropriate mechanical loss, measured in parallel with the mechanical response of the polymer under tension at a constant rate, are matched in Fig. 13. It is clearly seen that, initially (before the application of mechanical stress), as expected for a polymer glass, the losses are small. After applying tensile load, long before the yield point of the polymer (from ~2% elongation), some new phase occurs in the polymer, which has a much greater ductility and, consequently, significantly higher mechanical losses. The amount of this phase is continuously growing, as there is a continuous increase in internal friction. This increase is quite sharply terminated after reaching the yield point. Further deformation of the polymer (in the section where there the neck is developed) is not accompanied by an increase in mechanical loss, but no significant decline occurs either. If the deformation of the polymer is stopped at this section of the tension curve, then along with the relaxation of tension, a fairly sharp drop in the mechanical loss is observed. This result clearly indicates the relaxation (healing) of the new phase that emerged during the deformation of the polymer. The resumption of strain again sharply increases the level of mechanical losses, indicating the resuscitation of relaxed areas with a high level of mechanical loss and the emergence of new areas, but in the same amount as in the initial state achieved when the polymer yield stress is reached. This phase occurs even in the so-called Hooke section of the stress–strain curve, and its amount increases continuously until the polymer yield stress. Once the yield point is reached, that is, the tension in the polymer ceases to increase, the mount of the appearing new phase also reaches the limit values. Consequently, the deformed glass has a different structure than the original, and we can assume that the initial nonequilibrium structure of polymer glasses is not responsible for the physicochemical and physicomechanical anomalies that the deformed polymer glass demonstrates.

It is important to note that the processes that occur in a deformed glassy polymer are not identical to the physical aging processes described above. Indeed, we noted that physical aging has an affine character; that is, it is uniformly and simultaneously developed throughout the volume of the glassy polymer. At the same time, the data of [43, 48] suggest that, in the deformed polymer glass, there are discrete zones where large-scale molecular motion is dramatically facilitated.

5.5. Thermophysical Properties

Numerous thermodynamic studies using deformation calorimetry demonstrated that plastic deformation of polymer glasses is fundamentally different from the corresponding process taking place in the low-molecular solids [34–36]. It turns out that much of the work of deformation (mainly in the field before
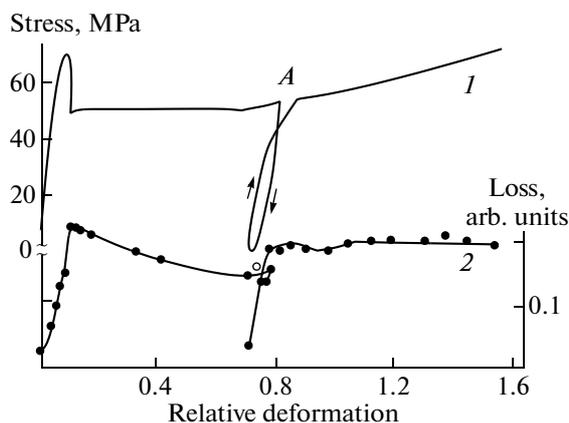
Fig. 13. (*1*) Strain curve and (*2*) the corresponding mechanical losses in PC at room temperature. After reaching elongation corresponding to point *A* on the curve, stress was reduced to zero and sample was stored for 1 h; after the break, stretching was continued [48].
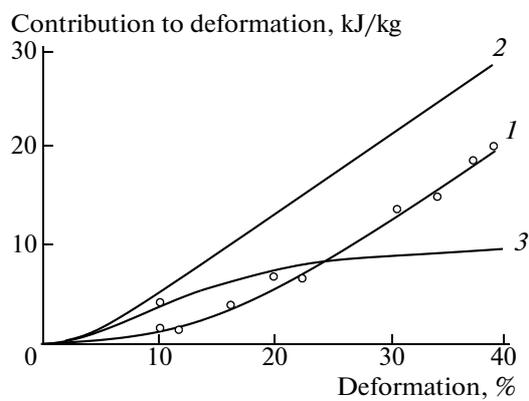

Fig. 14. Dependence of (*1*) heat, (*2*) mechanical work, and (*3*) accumulated internal energy on the magnitude of uniaxial compression of PS at 30°C and a strain rate of $5 \times 10^2 \, \mathrm{min}^{-1}$ [35].

and at the yield stress) is accumulated by a polymer rather than converted into heat (Fig. 14) [35]. This result suggests that, during the process of deformation of the glassy polymer, there are some structural changes responsible for the accumulation of internal energy. It also follows from Fig. 14 that the occurrence of these structures is observed during the initial stages of deformation (before and at the yield point of the polymer), that is, in the same place where there are abnormalities in the thermally stimulated size recovery and dynamic mechanical properties (for comparison see Figs. 11 and 14).

It was found by DSC that deformed PVC contained measurable amounts of internal energy [49]. It is also noted that the stored energy begins to be released during annealing at 30–40°C below T_g. It was found for PS and some of its copolymers with polymethacrylic acid (PMA) that samples deformed by 40% also accumulated the internal energy (1.5 kcal/g) [21]. The authors attributed the origin of the excess internal energy to a decrease in the intensity of intermolecular interactions in the polymer, which is associated with its inelastic deformation.

In the analysis of the DSC data, it should be noted that this method detects not only the effect of deformation on the thermophysical properties of the glassy polymers, but also specific types of molecular motion caused by the processes of its physical aging (see Fig. 3). These changes in mechanical properties during the physical aging of glassy polymer are also accompanied by a significant change in its thermophysical properties. Typical data of this kind are shown in Fig. 15. The DSC thermograms that characterize the process of physical aging of amorphous glassy PS are presented in Fig. 15a. PS was obtained by quenching from the highly elastic state, after which it was subjected to low-temperature annealing for various periods of time. It is clear that during the annealing, the aforementioned phenomena occur that accompany the process of physical aging of amorphous glassy polymer (for comparison see Figs. 15a and 3) [21]. During annealing, the step of glass formation is transformed into a kind of endothermic effect
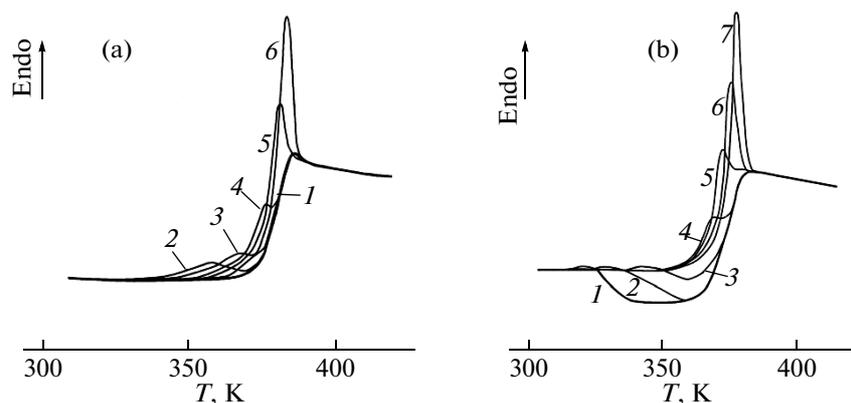
Fig. 15. DSC curves of PS (a) quenched and (b) and predeformed by compression after annealing at 60 and 70°C, respectively: (a) annealing for (*1*) 0, (*2*) 0.2, (*3*) 1, (*4*) 10, (*5*) 90, and (*6*) 170 h and (b) annealing for (*1*) 0, (*2*) 0.003, (*3*) 0.08, (*4*) 1.5, (*5*) 6, (*6*) 11, and (*7*) 50 h [21].

(Fig. 15a), the intensity of which increases with increasing annealing time. A detailed analysis of the effect of physical aging of polymer glasses on the evolution of the DSC thermograms is given in [2, 21, 50]. Here, we would like to note that the effect of aging on the thermophysical behavior of the polymer does not interfere with a separate study of the processes taking place during their deformation.

Indeed, the deformation of the polymer within its glassy state (below T_g) also has the strongest effect on its thermophysical properties (Fig. 15 b); however, this effect is revealed in a fundamentally different way. It follows from Fig. 15b that the deformed polymer contains a broad exothermic DSC peak located below the glass transition temperature, while the undeformed polymer contains only an endothermic peak approximately at its glass transition temperature (for comparison see Figs. 15a and 15b). It is important to note the evolution of these peaks in the low-temperature annealing. It turns out that the exothermic peak (curves *1–3*) is gradually decreased during the low-temperature annealing and disappears completely (curves *4–7*) at large annealing times. At the same time, by contrast, the endothermic peak, which is responsible for the physical aging of glassy polymers increases in the annealing process. In other words, the process of physical aging and the relaxation of the structure of the deformed glassy polymer under low-temperature annealing are accompanied by thermal effects of opposite signs. Moreover, it can be seen from a comparison of Figs. 15a and 15b that two of the above-mentioned thermophysical process occur without recognizing each other and evolve independently of the annealing process.

Thus, the above experimental data indicate that, within the glassy state of amorphous polymers, at least two types of large-scale molecular motion can occur. First is the molecular motion responsible for the process of physical thermal aging. This type of molecular motion leads to a more equilibrium state of the polymer glass. It is important to note that this kind of molecular motion is affine in nature and simultaneously implemented in the entire volume of the polymer.

Second, there is some kind of large-scale molecular motion that is introduced into the glassy polymer by the mechanical deformation of the block polymer below T_g and is also implemented below its glass transition temperature. An important feature of this type of molecular motion is its localization in certain special zones that are included in the unmodified polymer matrix [43, 48]. This means that the deformed glassy polymer is heterogeneous in its structure, which makes the problem of establishing the structural rearrangements accompanying strain actual.

6. SPATIAL HETEROGENEITY OF THE DEFORMATION OF POLYMER GLASSES

Studies of the structure of deformed glassy polymers are numerous and have a long history. In these studies, a very important experimental fact has been established. It turns out that the affinity (uniformity) of the deformation is only characteristic of amorphous polymers that are in a highly elastic state (in the temperature region above the corresponding glass transition temperature) [31]. At the same time, numerous direct microscopic observations revealed that the inelastic deformation of glassy polymers is always nonuniform over its volume. In particular, the heterogeneity of strain over the volume is clearly manifested at least in the fact that, under uniaxial tension, a neck occurs and develops in the glassy polymer. However, the structural heterogeneity of deformation is also observed before its appearance with strains that do not
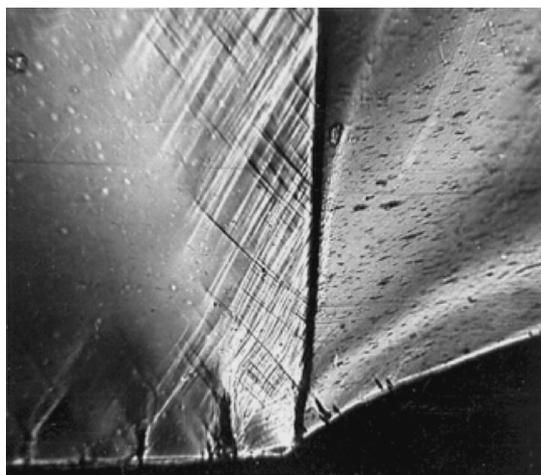
Fig. 16. Light micrograph of PET sample deformed at room temperature with the formation of a neck: (right) section of sample transformed into the neck and (left) undeformed section of sample. Photo was taken in crossed polaroids [51].

exceed the yield strength of the polymer, that is, where there are all of the above-mentioned anomalies in their properties.

For example, in his classic paper [28], Lazurkin was apparently the first who noted that, at the yield stress, the deformation of the polymer became nonuniform. In the polymer, there is a system of inhomogeneities that is easily detected with a light microscope and even the naked eye. These inhomogeneities are straight lines that intersect the polymer at an angle of 45–55° to the axis of elongation. Similar to low-molecular-weight solids, Lazurkin calls them "shear bands" and notes that, for their appearance, microscopic irregularities, i.e., stress raisers, should occur.

These shear bands are easily detected by direct microscopic examination. A light micrograph of a PET sample deformed at room temperature with the formation of a neck is shown in Fig. 16. It is clear that the portion of the sample that has not yet passed into the oriented state (in the neck) is penetrated by the shear bands. At first glance, the material of the neck does not contain these bands [51].

The procedure of decorating samples for electron-microscopic examination was used in [52], which enables the observation, in particular of the evolution of the shear bands, including the structure of the propagating neck. The point of this technique is to apply a thin (nanometer) layer of a metal to the polymer surface before the deformation. The subsequent deformation of the polymer allows one to visualize the structural changes that occur in the polymer using the coating. A micrograph of a section of the polymer localized at the boundary between his neck and unoriented part is given in Fig. 17a. At this point, the sample thickness is decreased, which results in a fairly sharp bending of its initially smooth surface. This deformation is naturally accompanied by cracking of the coating. Furthermore, the used procedure helps to visualize the emergence of the shear bands in this area. It is clear that these bands are distributed through a specified transition zone as straight lines at an angle of ~45° to the axis of tensile stress.

The transition layer between the unoriented part of the polymer and the propagating neck moves over the sample to its complete transition to the neck. Figure 17b demonstrates the section of the sample with a fragment of the transition layer; the part of the sample passed into the neck is also shown. It is clearly seen that the shear bands that emerged in the transition layer reach the area of the neck. It turns out that these shear bands at the exit in the neck lose their orientation in the 45° direction to the axis of elongation; they are turned almost along the stretch axis and are included in the structure of the neck. These shear bands included the structure of the neck are clearly visible in areas remote to any distance from the transition zone of the polymer in the neck (Fig. 17c). Surely, after shear bands are incorporated in the structure of the neck, they cannot be called shear bands. As follows from the data, the appearing neck is not homogeneous in structure. Although the shear bands are included in the material of the neck, the material remembers that the transition to the neck proceeds via the polymer containing shear zones. If the neck of the PET is subjected to shrinkage, for example, by a swelling solvent, a system of shifts recorded using a light microscope emerges in the resulting material [53].

The inhomogeneity of the plastic deformation of a glassy polymer can easily be identified, even in the strain areas that do not exceed the yield strength. Figure 18 shows a light micrograph of a sample of glassy PET subjected to the action of a constant load at a tension of ~0.7 of the yield stress. However, clearly vis-
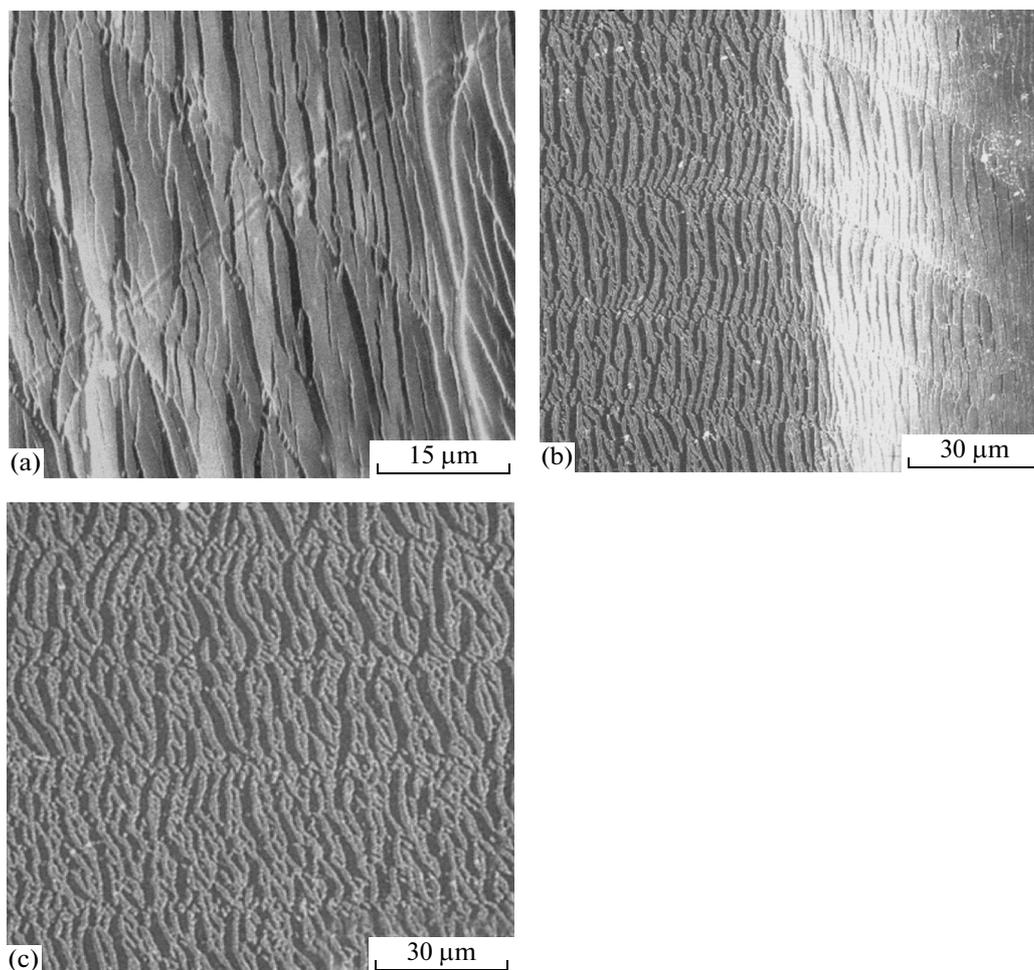
Fig. 17. Electron micrographs of PET sample with thin (10-nm) platinum coating, stretched at room temperature with formation of a neck (tensile axis is horizontal): (a) area of transition of the polymer into the neck, (b) section of the sample in which transition layer (right) and part of the formed neck (left) coexist, and (c) formed neck removed from transition layer [52].

ible heterogeneity occurs in the polymer. Along with a system of shear bands oriented at an angle of ~45° with respect to the tensile stress, other areas of plastic-oriented polymer can be seen in the polymer that propagate perpendicular to the tensile stress. These are so-called crazes, that is, zones of deformed polymer, which contain a significant amount of microscopic voids [54–56].

The structural heterogeneity of the deformed glassy polymer is uniquely identified by small-angle X-ray scattering. For example, it was found that, at 3–5% strain (known to be lower than the corresponding yield stress), intense diffuse X-ray scattering occurs in PS and PVAc in the temperature range of 10–20°C below their glass transition temperatures [57]. This result clearly indicates that, under these conditions, in the so-called Hooke section of the stress–strain curve, a kind of discontinuity of the glassy polymer occurs and interfaces emerge, which are the source of small-angle X-ray scattering.

The emergence and development of structural inhomogeneities takes place not only during the deformation of polymer films as discussed above. Under uniaxial compression of block polymers, when many anomalies in the mechanical behavior of glassy polymers were found [32–36], the development of zones of inelastic deformation is much more difficult to observe. In this case, as a rule, a solid cylindrical specimen subjected to uniaxial compression becomes barrel-like in shape. It is very difficult to record any irregularities in these samples.

Nevertheless, the use of well-known methods to prepare samples for direct microscopic examination allows us to solve this problem. For example, microsections were cut from the blocks of a number of glassy polymers deformed under uniaxial compression [58]. The resulting sections were examined using a polarizing light microscope. It was found that the deformed glassy polymer (PS, PC, PET, PMMA at −130°C
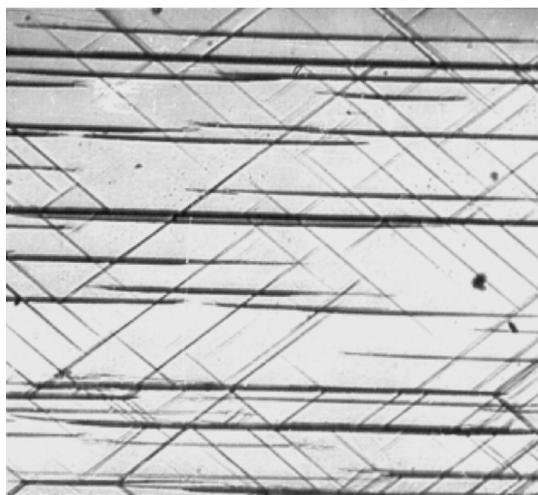
Fig. 18. Light micrograph of PET sample deformed at room temperature under a constant tensile load (the tension axis is vertical) of ~0.7 from yield stress for 2 h [51].
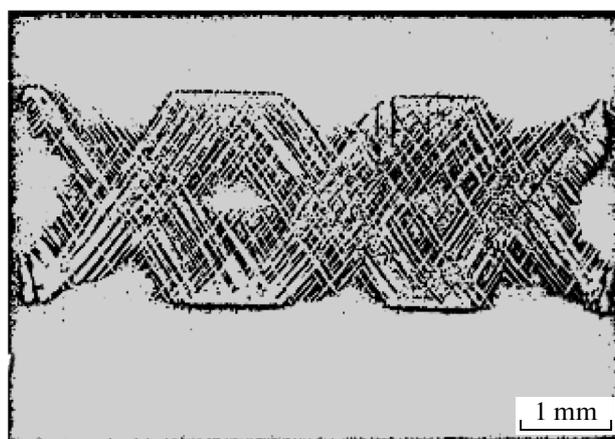

1 mm

Fig. 19. Light micrograph of a thin cross cut of PS sample subjected to uniaxial compression; compression axis is vertical [58].

and higher) contains a straight strip ~1 μm in width, which have strong birefringence and are separated by the blocks of original undeformed material. A micrograph of a thin slice from the block PS sample deformed under uniaxial compression is shown in Fig. 19. It is clear that this sample is literally saturated with shear bands. In other words, under these conditions, the polymer is deformed by the development of shear bands. Note that strong birefringence is observed, not only in the shear bands, but also in crazes [55], which indicates the molecular orientation of the material filling these formations.

It is important to note that the above anomalies in the thermophysical properties of deformed glassy polymers are only detected in the case when, during deformation, discrete zones of deformed material (shear bands and/or crazes) appear in them. Thus, in the polymer deformed under hydrostatic compression, when a true elastic deformation occurs, no significant abnormalities in the DSC thermograms are observed. At the same time, the deformation of hydrostatic compression in combination with the shear, that is, under conditions where shear bands are realized, leads to an exothermal effect in the DSC curves in the temperature region below T_g of amorphous polymer [59].

It is important to note that both crazes [55] and shear bands are completely healed during annealing of the polymer. In [60], the effect of annealing temperature on the condition of shear bands obtained in the polymer under conditions close to uniaxial compression was investigated. A spherical indenter was pressed in a film of amorphous PET at room temperature and a picture of the deformation was investigated in the light microscope. A picture of the deformed polymer after annealing at 40°C, that is, well below its T_g, is given in Fig. 20. It is clear that under these conditions, the deformation of the polymer is accompanied by
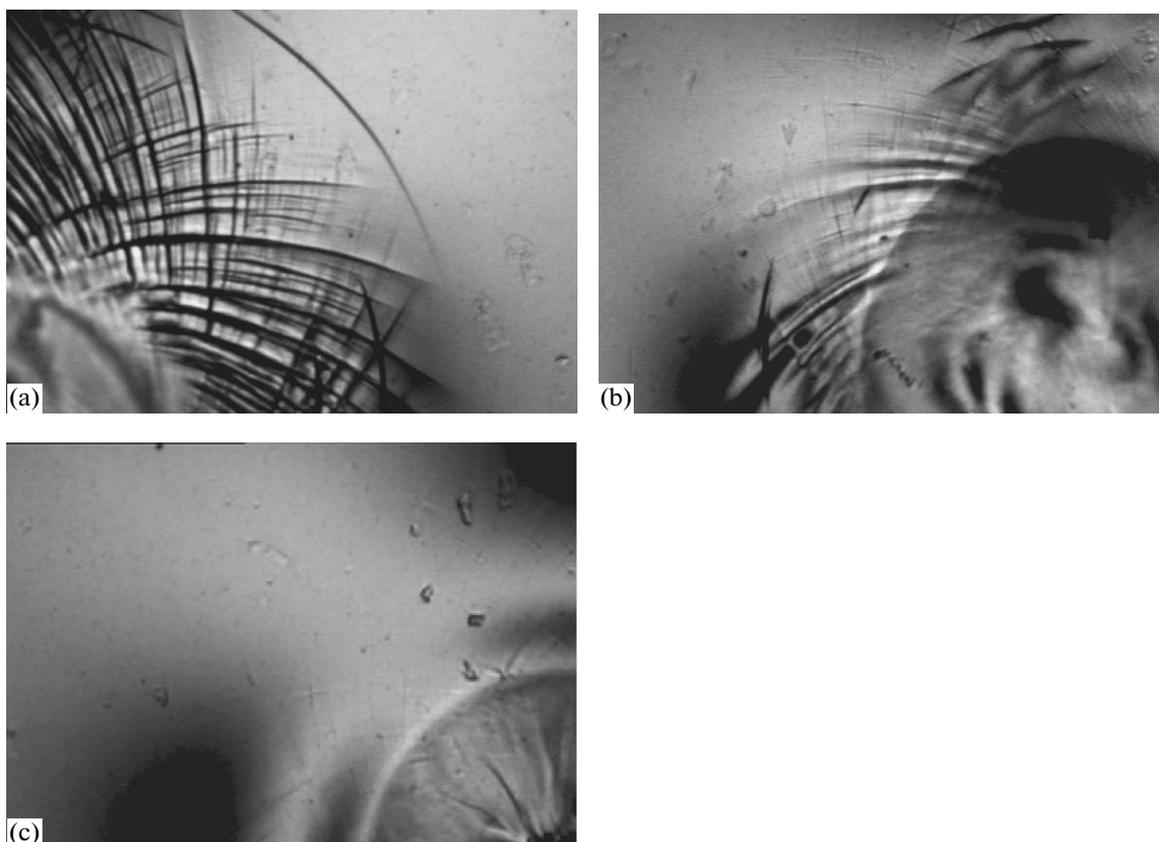
Fig. 20. Light micrograph of the PET sample in which shear bands were implemented, and which was further subjected to annealing at (a) 40, (b) 70, and (c) 75°C [60].

the emergence and development of a shear system. With increasing annealing temperature to 70°C (Fig. 20b), the shear bands are diffused and less pronounced. Finally, at the glass transition temperature (75°C), the shear bands are complete healed; as a result, they cannot be recorded with the light microscope (Fig. 20c). As can be seen, the annealing of the polymer containing shear bands leads to the complete healing of the interfaces; this process occurs at temperatures below its T_g. Low-temperature (below T_g of a block polymer) relaxation is also characteristic for crazes [55].

This result suggests that the above mentioned anomalies in the mechanical and thermophysical behavior of deformed glassy polymers are in some way connected with the processes occurring in the zones of plastically deformed polymer (crazes and shear bands). This is fairly obvious, since the blocks of undeformed polymer are separated by shear bands and/or crazes do not differ from the original polymer, that is, they do not contain an excess of internal energy and do not show the low-temperature shrinkage or any other abnormalities in the physical and mechanical behavior, in detail described above.

Thus, the deformation of a glassy polymer, even in the early stages, is very uneven. Well-defined discrete zones of plastically deformed polymer, i.e., shear bands and crazes, appear in the polymer. The above data indicate that both shear bands and crazes, which arise in the deformation of amorphous glassy polymers, have very unusual structural and mechanical properties. It seems reasonable to assume that, in the mechanical behavior of glassy polymers, all of the above anomalies are related to the emergence and development of structural formations.

7. STRUCTURE OF SHEAR BANDS AND CRAZES OCCURRING DURING DEFORMATION OF GLASSY POLYMERS

In the context of this review, we should elaborate on the structure and properties of the above inhomogeneities (shear bands and crazes) that arise from the inelastic, plastic deformation of polymer glasses. These inhomogeneities may occur simultaneously in a glassy polymer under deformation [51] (Fig. 18). At the same time, there is a fairly simple method to deform the polymer through the development of only
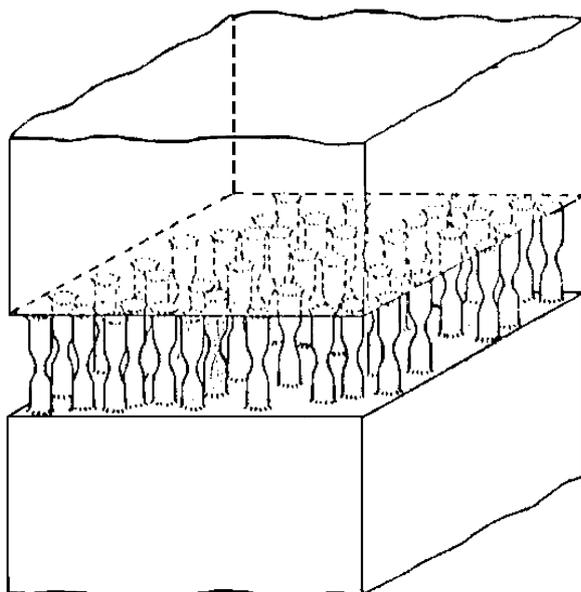
Fig. 21. Schematic diagram of structure of a craze; tension axis is vertical [56].

crazes without shear bands. For this purpose, it is sufficient to carry out the deformation of the polymer in the so-called adsorption-active media (AAM). This allows us to study both the crazing process in the polymers and the structure of crazes in detail [55].

7.1. Structural Aspects of Polymer Crazing

Numerous studies have shown that the deformation of a glassy polymer in AAM occurs exclusively by the emergence and development of crazes. Indeed, structural studies show that a disordered amorphous polymer during its deformation in AAM is spontaneously transformed into a surprisingly ordered, regular structure [54, 55, 61]. This structure is presented schematically in Fig. 21 [56]. It is clear that, in deformation by the crazing mechanism, the orientation transformation of the polymer occurs within the fibrillar aggregates that connect fragments of the original amorphous unoriented polymer.

An electron micrograph of a PET sample deformed in adsorption-active medium is shown in Fig. 22. It is clear that this sample does contain many areas of plastically deformed, fibrillated material containing microvoids. It is important to note that, with the development of inelastic deformation of the polymer by the crazing mechanism, the polymer in the initial block-oriented state is continuously transformed into a highly ordered state (the craze material). This means that the ratio between these parts of the polymer constantly changes, which is clearly reflected in the properties of the deformed polymer as a whole.

The process of the formation and development of crazes can easily be detected and studied using direct microscopic experiments [62]. In this way, the multistage character of crazing process and its relationship with the mechanical response of the deformed polymer were found in [63]. The main structural changes that accompany the crazing of the polymer in a liquid medium during its stretching are schematically shown in Fig. 23. The obtained data were compared with the corresponding stress–strain curve. It is clear that, in the early stages of stretching of the polymer (up to the yield stress, that is, region *I* of the stress–strain curve), a certain number of crazes appear on the polymer surface. These crazes grow in the direction perpendicular to the axis of elongation of the polymer (region *II* of the stress–strain curve), while its width remains nearly constant and very small (fractions of a micron); this is the stage of craze growth. As can be seen from Fig. 23, the formation of crazes begins long before reaching the yield point of the polymer, which once again shows the inelastic nature of the so-called Hooke section of the stress–strain curve.

The process continues until the growing crazes pass through the cross-sectional area of the sample. At this point, the stress–strain curve reaches the plateau (Fig. 23). After crazes penetrate the cross section of the polymer, the next stage of crazing of the polymer in a liquid medium begins, namely, the craze broadening, when crazes intergrown across the entire cross section of the polymer increase their size in the

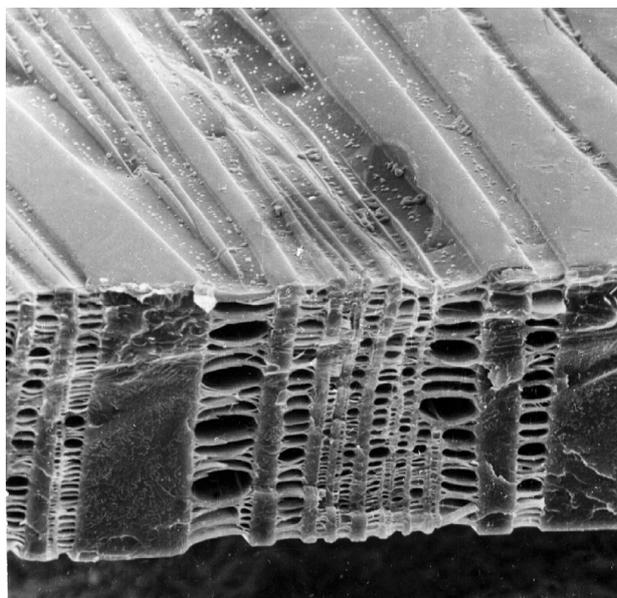**Fig. 22.** Scanning electron micrograph of a sample of glassy polymer (PET) deformed in the AAM at 100% (tensile axis is horizontal) [51].
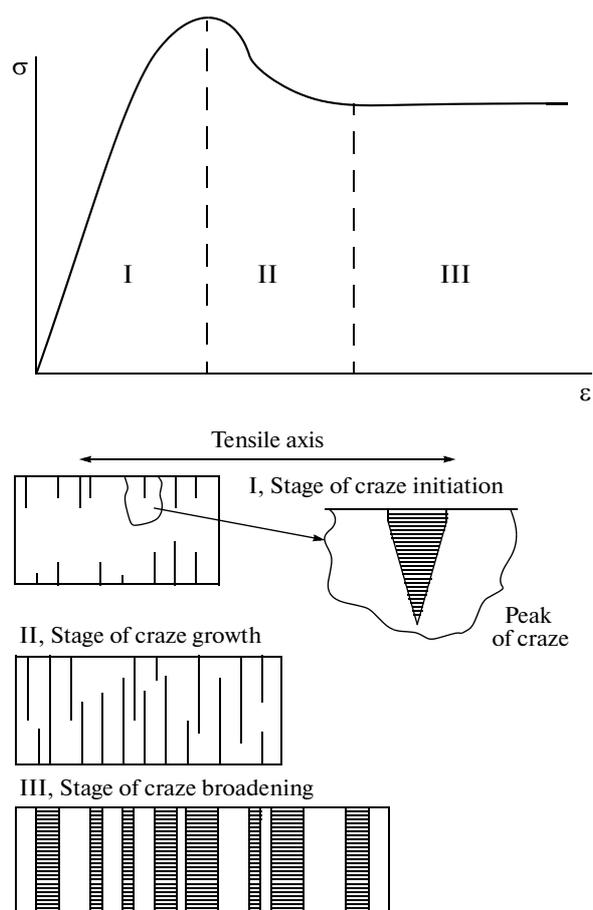

Fig. 23. Stress-strain curves of the polymer in AAM and schematic representation of the individual stages of the development of crazes: I, region of craze initiation; II, region of craze growth; and III, region of craze broadening [51].
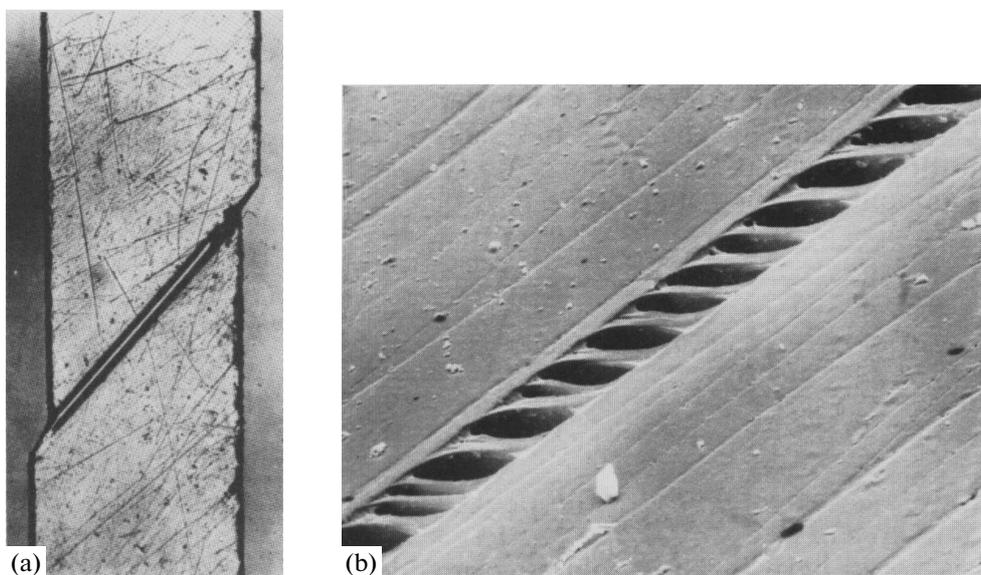
Fig. 24. (a) Appearance of PS sample containing shear band and (b) electron micrograph of this band showing its internal structure [64].

direction of the stretching axis of the polymer (region *III* in the stress–strain curve). It is obvious that the basic transformation of the polymer into the highly ordered fibrillated state occurs.

It is important to note that the crosscut dimensions of such fibrillar aggregates of oriented macromolecules ranged from 2 to 20 nm, which, as will be shown below, is crucial for understanding their properties and the properties of glassy polymers containing crazes. Thus, the deformation of glassy polymer can occur by the crazing mechanism, resulting in the polymer acquires a specific structure and an unusual set of physicochemical, physicomechanical, adsorption, and other properties [55].

7.2. Structure Features of Shear Bands Arising in the Deformation of Glassy Polymers

As noted above, the crazing of polymers is just one of the alternatives of the development of inelastic deformation of glassy polymer (Figs. 21–23). Another form of the inelastic deformation of the polymer consists of the appearance and development of shear bands. A photograph of a polymer sample in which a shear band is triggered at the initial stage of stretching is presented in Fig. 24. It can be seen that, as in low-molecular-weight solids, this band grows through the sample at an angle of 45–50° to the direction of the tensile stress. However, this is where the similarity of shear bands in polymers and in low-molecular-weight solids ends.

It turns out that shear bands in polymers have a complex structure [64, 65]. They are filled with highly dispersed oriented fibrillated material that is completely the same as the corresponding material filling the volume of crazes [54–56].

This important similarity is confirmed by direct microscopic observations. When material containing shear bands is subjected to a small stretch in the direction of the normal plane of the shear bands, the latter are revealed (Fig. 24b), exposing a craze-like structure (compare Figs. 22 and 24b). In this case, the similarity with the craze structure is so strong that these revealed shear bands were called "shear-band crazes" [64]. Some morphological difference of a shear-band craze from a conventional craze is that the fibrils in its structure are tilted with respect to the plane of the shear band (Fig. 24b).

The complex structure of shear bands in glassy polymers has a specific effect on the surface morphology of their destruction. A photograph of a PS sample in which a band shift was initiated is presented in Fig. 25. With further strain, the sample was destroyed along this shear band. It can be seen that, in this case, a significant amount of plastically deformed polymer appears in the volume of the shear band. It is clearly seen at higher magnifications that this material consists of parallel plates constructed by fibrils stuck together (Fig. 25b). This kind of structure is morphologically strikingly similar to the craze material, revealed by brittle cleavages of crazed polymers [51]. As shown in [64], this material can easily be separated from the sample with tweezers and investigated by DSC. It turned out that the material of the shear bands is responsible for the exothermic low-temperature (below T_g) effect detectable using DSC in the
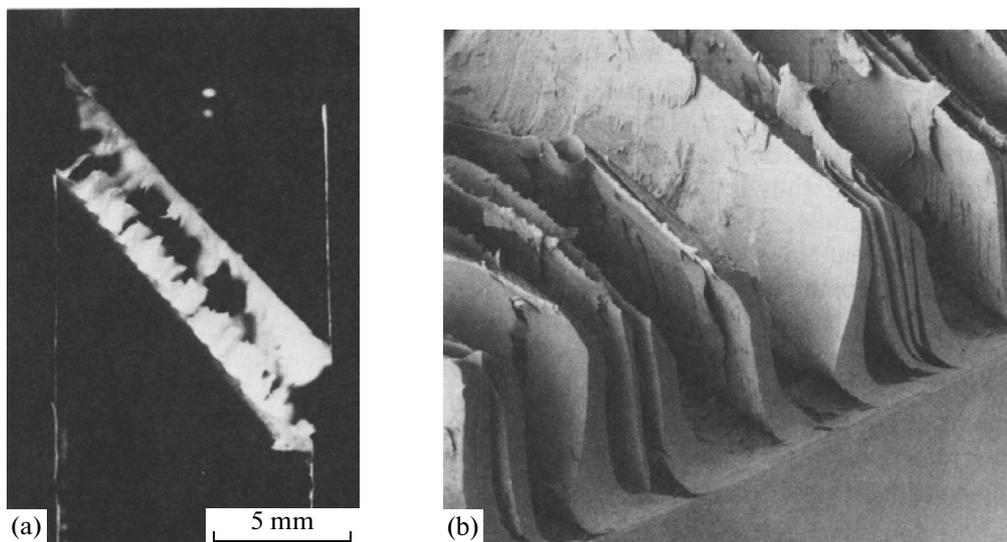
Fig. 25. (a) Appearance of PS sample after destruction at shear band and (b) electron micrograph of fracture surface at shear band [64].

deformed glassy polymer (Fig. 15b). At the same time, the material located between the shear bands is undeformed and, therefore, indistinguishable from the original block polymer. In particular, it does not show the low-temperature exothermic effect during annealing.

Both the shear band and craze were obtained in one PS sample [64]. An electron micrograph of the sample is presented in Fig. 26. It can be clearly seen that the difference between a shear-band craze and a conventional craze is that the fibrils in its structure are tilted with respect to the plane of shear bands. The rest of the morphological features of these two structures are completely analogous.

Another important aspect of the structure of microinhomogeneities (shear bands and crazes) that arise during the deformation of glassy polymers is the question of the presence of real microcavities in them. The presence of a microporous structure in crazes is now beyond doubt [54, 55]. At least in the early stages, the development of the deformation in the polymer in AAM occurs by the growth in its total porosity. At the same time, the significant overall contraction of the stretched polymer is observed under shear flow and, despite the presence of shear bands with real interfaces, the question of the development of real total porosity of the polymer is not so obvious.

It was shown that the transport of methanol into PMMA samples subjected to uniaxial compression by 23−24% was in sharp contrast to its transport to the original undeformed PMMA [66]. The diffusion rate was twofold higher at 40°C and fivefold higher at 25°C than for the undeformed PMMA. These data sug-
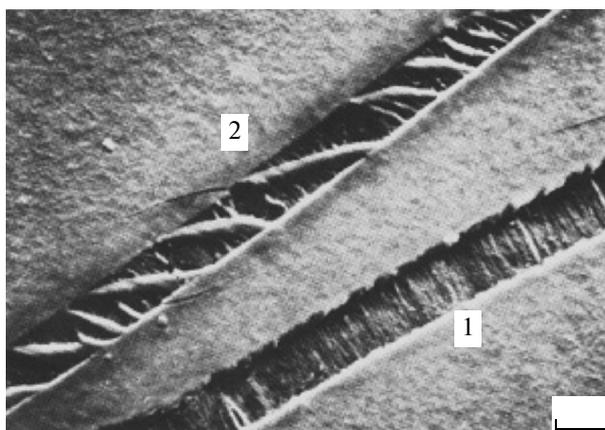

Fig. 26. Electron micrograph of the PS sample containing (*1*) a craze and (*2*) a shear band [64].
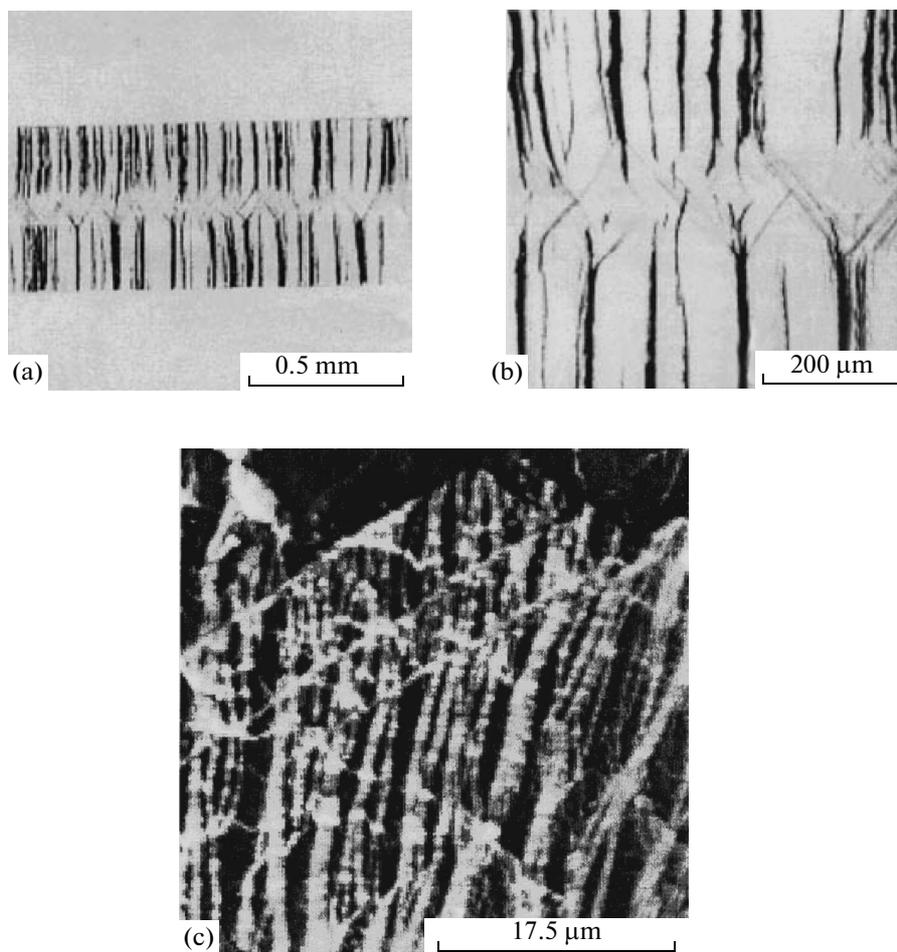
Fig. 27. Light micrograph of thin cross cut of PET sample containing (a) crazes and (b) shear bands; (c) low-temperature scanning electron micrograph of a cleaved PET sample given in Figs. 27a and 27b after its use as a membrane in the dialysis cell containing aqueous solutions of NaCl and AgNO₃ [67]. See explanations in text.

gest that there are some areas in the shear bands of glassy polymers in which the filling material is so loosened that the transport of low-molecular-weight substances is facilitated.

It can be simply demonstrated that under the same conditions, the polymer is deformed either by the crazing mechanism or through the development of shear bands [67]. In the tension of bulk PET samples in AAM, crazes appear on their surface and begin to spread to the depth of the sample. Naturally, with their growth, the hydrodynamic resistance to the flow of fluid to their top increases. Eventually, a situation develops when the fluid cannot be supplied efficiently and in sufficient quantity to the sites of the orientational transformation of the polymer (peaks of crazes). As the presence of AAM in the areas of active deformation is necessary for the development of crazes, the polymer selects an alternative path of the development of deformation, that is, by the mechanism of growth of shear bands.

Namely, this situation is shown in Fig. 27. This illustration shows a light micrograph of a thin cross section of the PET sample with thickness of 0.7 mm stretched at room temperature in AAM (*n*-hexanol) by 50% at a rate of ~100% min. It is clear that, under these conditions, crazes could not cross the entire cross section of the polymer and start the phase of their broadening (Fig. 27a). However, the polymer in its core continues to be deformed by the development of shear bands, which does not require the presence of AAM. At a higher magnification of micrographs (Fig. 27b), some important features of this type of deformation of the polymer can be noted. Shear bands, like crazes, are perfectly visible in the light microscope, which shows clearly that they have a well-defined interface.

The film, whose structure is shown in Figs. 27a and 27b was placed as a membrane into a dialysis cell whose chambers were filled with an aqueous solution of NaCl on one side and with a solution of AgNO₃ on the other side. It was shown earlier [68] that, if the crazes penetrated across the polymer film from one

side to another, solutions of NaCl and AgNO$_3$ diffusing towards each other through a system of interconnected pores in their structure met in the pore volume and formed AgCl crystals, which were easily detected by electron microscopy. As can be seen in Figs. 27a and 27b, the massive PET film deformed in AAM is characterized by an unusual layered structure. Crazes containing real microvoids do not cross the entire cross section of the polymer, which leaves a layer of polymer in the core of the film that is not affected by crazes, but is penetrated by shear bands.

An electron micrograph of brittle cleavage of the same sample of PET after the treatment with solutions of NaCl and AgNO$_3$ is presented in Fig. 27. It can be clearly seen that, as a result of the procedure described above, clear crystals of AgCl are deposited in the volume of crazes, which indicates that the solutions of NaCl and AgNO$_3$ penetrate through the PET film. Moreover, it follows from Fig. 27 that AgCl crystals are deposited, not only in the microvoids of crazes, but also in the shear bands (straight channels that cross the polymer at an angle of ~45°), distinctly contrasting them. This result indicates that the, if they do not contain real microcavities, shear bands have such a low density that a low-molecular-weight liquid can diffuse through them like through channels.

To summarize this section, an important similarity between the above two structures, crazes and shear bands, should be noted, i.e., both shear bands and crazes are through channels in the polymer filled with a highly dispersed fibrillated material. As shown below, this similarity is the basis of many anomalies in the physicomechanical, physicochemical, and other properties of deformed glassy polymers.

8. ON THE NATURE OF STRUCTURAL AND MECHANICAL ABNORMALITIES IN THE PROPERTIES OF DEFORMED GLASSY POLYMERS

To explain the full range of features of the structural and mechanical behavior of deformed polymers, several mechanisms are suggested that do not take into account or identify the role of the above-mentioned structural units (shear bands and crazes) in the development of large inelastic deformations.

For the first (chronologically) of these approaches, consider a series of works carried out to study the thermally stimulated recovery of deformed polymer glasses (Figs. 10 and 11) [32, 33, 69, 70]. In these works, abnormalities in the mechanical behavior of polymer glasses (low-temperature recovery of size under annealing) are attributed to the original heterogeneity of their structure. It is assumed that the mechanism of high-temperature recovery is associated with the entropic relaxation of the excited stretched macromolecular coils and passing them to their original state due to the release of segmental mobility at T_g of the polymer. The nature of the low-temperature component of the recovery was associated with conformational rearrangements of macromolecules stimulated by the combined action of temperature and internal stresses accumulated in the deformation process [32, 33, 69, 70].

Similar to the term "forced-elastic deformation", this phenomenon has been called "forced-elastic relaxation," which implies that the mechanisms of deformation and subsequent recovery of the sizes of the deformed polymer have a common nature; in fact, the deformation of the polymer is activated by externally applied stress, while the recovery is activated by internal stresses. Later, within this model, it was suggested that the low-temperature relaxation of the deformed polymer glass is due to the heterogeneity of the structure of the initial polymer glasses, and the mechanism of this phenomenon is associated with sequential devitrification of local structural domains under increasing temperature, a set of which occur in the original undeformed material [71, 72].

The main features of this approach areas follows:

(1) the assumption that the observed molecular motion responsible for abnormalities in the low-temperature recovery of residual deformation of the deformed glassy polymers is entropic in nature;

(2) the assumption that these abnormalities are incorporated in the structure of the original polymer glass with a heterogeneous structure and a set of the glass transition temperatures.

Note that, in this model, the suggestion that the original undeformed polymer contains areas that are so different in their glass transition temperatures seems the most controversial. This provision is contrary to numerous experimental data, where only one rather narrow region of the glass transition temperature is recorded in the glass transition temperature of amorphous polymers using various methods.

Another approach to explaining the same structural and mechanical characteristics of polymer glasses is presented in [34–36]. These studies are based on the concept in which all inelastic deformation and a steady plastic flow occur in the structure of the polymer saturated with small-scale intensive plastic shear transformations (PST), rather than in the original structure. This structure is excited and metastable. The formation of PST begins at the earliest stages of loading and reaches a steady state at low strains (20–35%). PSTs are the main source of the macroscopic deformation of the polymer. Conformational rearrangements in chains at $T < T_g$ do not come directly under the influence of stress, as they are the products of the

termination of PST. PSTs are nonconformational, nonvolume shear formations surrounded by elastic stress fields. The entire energy accumulated by the sample during the deformation is concentrated in these fields. The processes of relaxation and physical aging and the molecular mobility in a deformed glass are closely associated with the birth and termination of PST. The mass transfer during the deformation of the glass occurs through small-scale movements of the γ-, β-, and, probably, δ-types rather than via segmental motions.

The main features of this approach are (1) a provision stating that all the abnormalities in the structural and mechanical behavior of polymer glasses are associated with structural changes that the polymer acquires during inelastic deformation and (2) certain structural transitions in shear transformations not related to the entropic elasticity of the macromolecules are responsible for the low-temperature recovery of the deformed polymer glasses.

As a disadvantage of this approach, the suggestion should be considered that certain energy transitions in the PST and elastic mechanical stresses around them are responsible for the reversibility of large deformation in the deformed polymer. At the same time, today, there is no doubt that large reversible strains is a privilege of polymeric bodies, and the nature of such an elasticity is due to the entropic reduction of the polymer chains during their transition to the most probable state [31]. For example, the increase in tension in the deformed glassy polymer during its isometric heating at temperatures below T_g cannot be explained usingf PST (Fig. 9). The existence of PST has not been detected by any experimental method.

In some studies [21, 73, 74], the plasticity of polymers below their glass transition temperature is associated with β-molecular motion. However, the data in Fig. 12 indicate that the molecular motion introduced into the glassy polymer by deformation does not affect the β-peak; it is located on the temperature scale above the β-molecular motion, but lower than the α-transition.

Works [75] may also be noted, in which the process of plastic deformation of a solid polymer is described using the concept of free volume. In all the studies cited above, the mechanism of plastic deformation is seen at the microscopic, submolecular level. It is assumed that plastic deformation is delocalized over the volume of the polymer, and its elementary act takes place in the volumes of the size of tens to hundreds of angstroms. Finally, in a number of publications, the authors suggest that the anomalous low-temperature molecular motion that enters into the glassy polymer through mechanical deformation is localized in certain zones dispersed in a glassy matrix [76–80]. Unfortunately, the authors of the cited papers did not specify what these zones are, how they arise, and what are their morphology and properties.

In our opinion, the coexistence of multiple points of view on the mechanism of the deformation of polymer glasses is due to the lack of direct experimental data on the elucidation of structural rearrangements that accompany this process.

It is important to note that there is another aspect of the problem of the deformation of polymer glasses, which was not considered or taken into account until recently. Any deformation of a solid material and, in particular, a polymer, in addition to a change in geometric dimensions, is accompanied by a change in their surface area. While the volume of the deformed polymer can remain constant [31], its surface area is always changing.

Let us illustrate this phenomenon using the example of a well-studied process, such as the orientation stretching of synthetic fibers. Recall that the cold stretching of the polymer is accompanied by the emergence and development of a neck. A photograph of a sample of polyester fiber in its transition to the neck is presented in Fig. 28. This photo is associated with elementary calculations of changes in the surface area that take place in such a strain. Indeed, it follows from Fig. 28a that the diameter of the molded fiber before its orientation stretching was approximately 15 μm and, after the stretching, the neck diameter is approximately μm; that is, it is decreased by almost half. Using elementary calculations, we can show that the surface area of a fiber fragment 1 cm in length before its stretching (the radius can be determined from the upper part of Fig. 28) is 47.8×10^{-3} cm^2 and, after the deformation, taking into account the fiber radius in Fig. 28 (the lower part), this surface will be 100.8×10^{-3} cm^2. This means that the simple orientation stretching of the fiber doubles its surface. It is obvious that an increase in the total surface area of the polymer is only possible if the material from the bulk polymer partially migrates to the surface. This kind of transportation in the bulk polymer has also not been studied or characterized to date, despite that it obviously plays an important role in the structural rearrangements of the deformed polymer.

The reasons for the lack of reliable information about such an important phenomenon as mass transfer during deformation of polymers and related changes in the interfacial surface area lie mainly in the absence of a reliable method of investigation. The task of obtaining information about the phenomena of mass transfer in a deformed polymer is rather complex. Indeed, it follows from Fig. 28 that, before and after the orientational stretching, the polymer fiber has a smooth cylindrical shape and one cannot conclude anything about the mass transfer in the bulk polymer based on this observation.
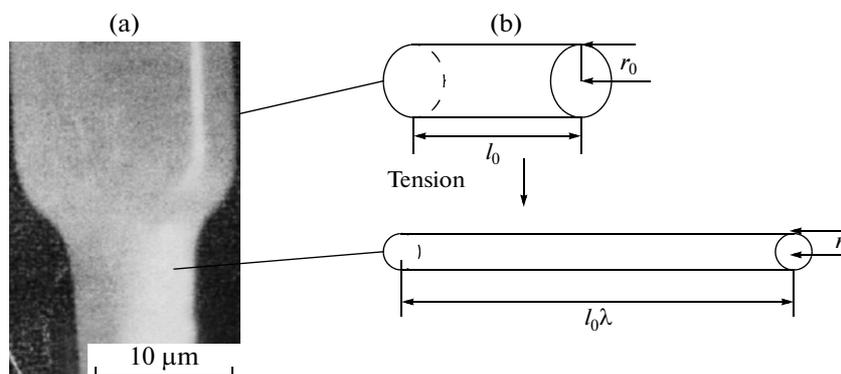
Fig. 28. (a) Appearance of section of synthetic polymer fibers deformed with the formation of a neck and (b) diagram to assess the change in the surface area of the polymer during its deformation [86].
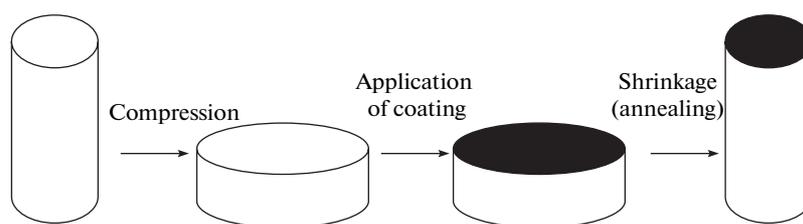

Fig. 29. Schematic diagram of the experiment for visualization of structural rearrangements in thermally stimulated shrinkage of polymer deformed under uniaxial compression (in-plane tension) [51].

In this context, direct microscopic studies that could shed light on this problem become important. A method for visualizing the structural changes that accompany the deformation of glassy polymers has been proposed and justified in [81−85]. The potential of this method was illustrated above by a study of the deformation of an amorphous polymer (PET) in uniaxial tension at a constant rate (Fig. 17).

This technique is no less effective in the visualization of the mass transfer processes during the restoration of the size of the deformed glassy polymer under annealing. A cylindrical sample was subjected to uniaxial compression when its surfaces adjacent to the contracting surfaces are free to slip on them (Fig. 29) [86]. As a result of this compression, the polymer takes the form of a cylinder of a lower height, but with a larger diameter (and area) of its round bases. After that, a thin metallic coating was applied to these bases. Next, the sample was subjected to annealing, and the metal-coated surfaces were investigated. It is obvious that during annealing, which is accompanied by the restoration of the original sample size (Fig. 29), the bases of the cylinder are decreased in the surface area, which is only possible if the material of the surface partially migrates into the bulk polymer. The microscopic examination of the coated polymer surface provides important information about the process of this kind of migration.

Figures 30a and 30b show two micrographs obtained by the above method in the study of the mechanism of thermally stimulated recovery of the size of deformed amorphous PET. The results of the study of two PET samples predeformed under uniaxial compression by about the same amount (22−24%) are presented. The only difference between samples (a) and (b) lies in the fact that one of them (a) was deformed above the glass transition temperature (100°C), and the other (b) was deformed below the glass transition temperature, i.e., at room temperature. It should be noted that, in the restoration of the size of the examined samples during annealing in the absence of a coating, in both cases, the surface remains smooth at all stages, regardless of the temperature of preliminary deformation.

In particular, the presence of coating enables the identification and characterization of the structural changes of the polymer during the thermally stimulated recovery of its size.

It can be seen that the decrease in the coated area of the sample (shrinkage) in the case of the deformation of the polymer above the glass transition temperature gives the platinum coating a regular and pronounced microrelief (Fig. 30a). The mechanism of the emergence and development of this relief may be considered as a special kind of loss of mechanical stability of the hard cover under its planar contraction on an elastic foundation. This process was considered in detail in [87−89]. Upon the annealing of the
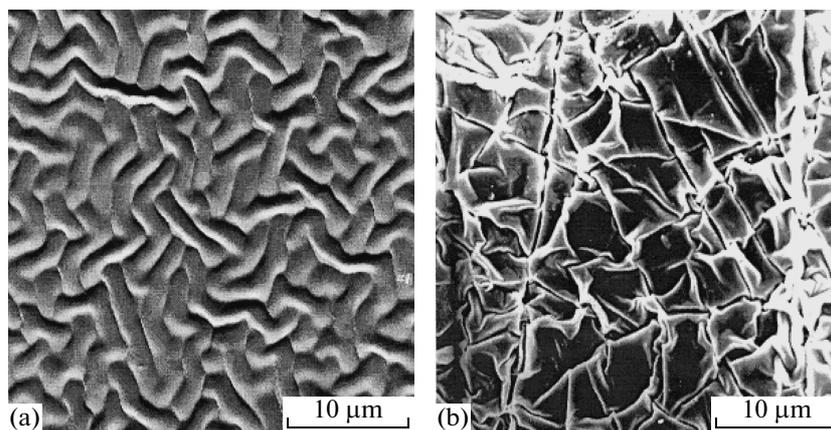
Fig. 30. Electron micrographs of PET samples deformed by uniaxial compression (a) at 100°C and (b) at room temperature. After deformation, thin (10-nm) layers of platinum were deposited on surfaces of samples and samples were subjected to annealing at 105°C [51].
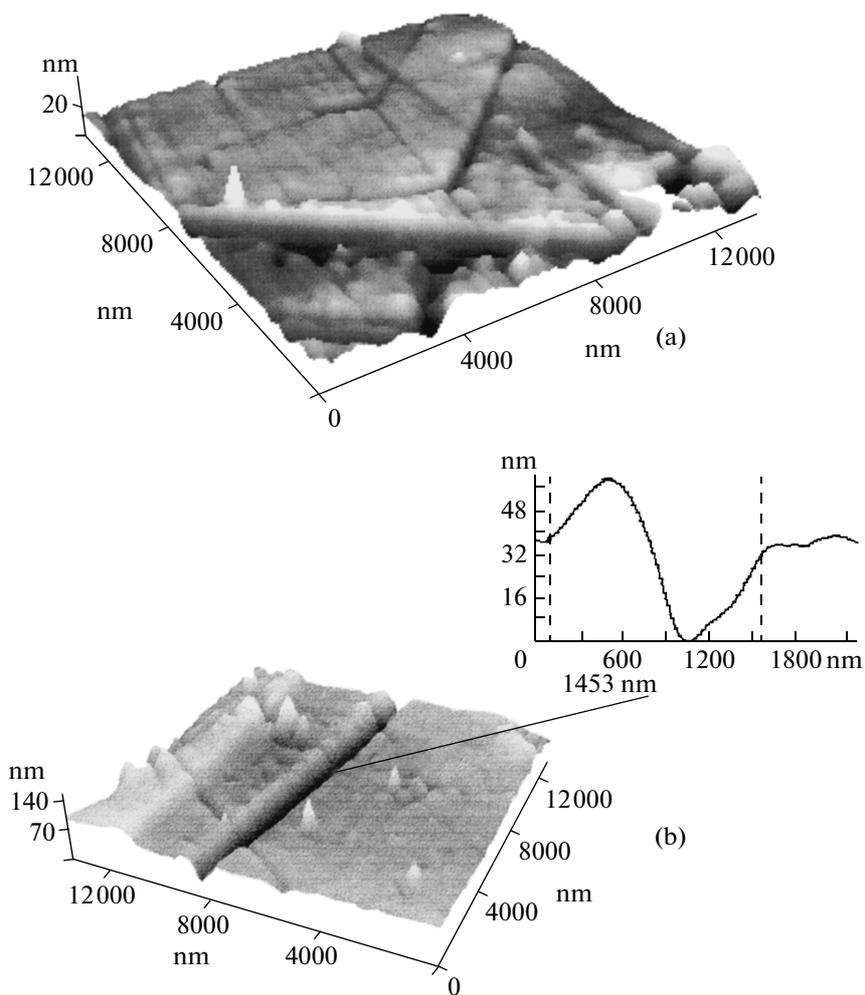
Fig. 31. Three-dimensional reconstruction of atomic force image of surface of PET sample that restored its size due to annealing. Sample was deformed by 18% as shown in Fig. 29. After applying to surface of a thin (10-nm) layer of platinum, the sample was heated to 105°C, as a result of which it was restored its original dimensions. (a) General view of surface; (b) image of individual shear band [51].

deformed polymer, the surface area on which the metallic coating is applied decreases via the diffusion of the polymer from the surface into the bulk (Fig. 29). In this case, this process occurs homogeneously, causing the coating on the polymer surface to be uniformly compressed, lose stability, and acquire a microrelief shown in Fig. 30a. It is important to note that this microrelief is uniformly distributed over the entire surface of the sample, which indicates the overall homogeneity (affinity) of the plane strain and, consequently, the restoration process of the sizes of PET when it is annealed above the glass transition temperature. The latter is quite obvious, since the polymer is subjected to uniaxial compression at temperatures above its T_g; that is, the polymer was in the highly elastic state, and the uniformity (affinity) of deformation is an inherent property of rubbery polymers [31].

Let us now consider how the metal coating responds to the recovery of the size during the annealing of PET deformed below the glass transition temperature. As can be seen from Fig. 30b, the thermally stimulated recovery of the sizes of the polymer is accompanied by a dramatically different structural rearrangements in the surface layer than for the polymer deformed above its T_g. It is clear that, during annealing, the entire sample surface is covered with straight lines that cover the entire surface and intersect each other at different angles. The data of atomic force microscopy show that these lines are grooves in the surface layer of the polymer (Fig. 31a). Since the observed lines cross the entire surface of the examined samples, one can assume that they occupy all the cross section of the deformed polymer. These lines are straight channels (Fig. 31b) in which the polymer is drawn from the surface into the bulk during annealing.

The method developed in [81–85] for the visualization of structural rearrangements that occur in the restoration of the size of the deformed glassy polymers enables the characterization of the structural changes that accompany the process in its various stages. The results of the studies of the evolution of the surface structure in the process of restoring the sizes of another strain glassy polymer PS are given in Fig. 32. In this case, the experiment was carried out somewhat differently. All samples were deformed to the same compression ratio (~25%), and different values of recovery (shrinkage) of the sizes were achieved by varying the annealing temperature.

It turned out that the way in which some degree of shrinkage was achieved did not crucially affect the structural rearrangements of the polymer. Thus, at a relatively low annealing temperature of 70°C, the shrinkage of the sample is small (1.7%) and the sample surface is covered with a grid of shear bands (Fig. 32a). Increasing annealing temperature (80°C) realizes the magnitude of shrinkage of 7.5% (Fig. 32b). In this case, shear bands are more in relief and their density increases. Finally, annealing in the region of the glass transition temperature (90°C) leads to the total shrinkage of the entire deformed material. It is clear that, in this case, the shear bands emerged in the early stages of deformation (shrinkage) of the polymer remain (Fig. 32c). The entire surface of the polymer is involved in the process of shrinkage. Moreover, we note the undoubted similarity of the relief, implemented in the thermally stimulated shrinkage of PS and PET (compare Figs. 30b and 32c), which indicates the generality of the observed phenomena. A folded relief localized between the shear bands is very similar to the microrelief, the mechanism of the formation of which was discussed above. This relief, which is detectable using a microscopic procedure, looks similar to the relief that arises from the shrinkage of the polymer deformed above the glass transition temperature (Fig. 30a). Recall that the shrinkage of the polymer deformation above the glass transition temperature is uniform and, therefore, the polymer surface acquires a regular microrelief that is uniformly distributed over the entire surface of the sample.

Thus, the data of direct visualization of the process of thermally stimulated recovery of the original dimensions of the deformed glassy polymer yield two conclusions. First, the thermally stimulated recovery of the initial size of the polymer deformed below its T_g also occurs in the temperature range below T_g of the polymer, which is in full agreement with other studies discussed above [32–36] and, second, this process is concentrated in specific areas (shear bands).

It is important to note that this type of thermomechanical behavior is even more pronounced for polymers deformed in AAM by the crazing mechanism. Since crazes contain microvoids in the structure, their evolution during annealing can easily be studied by light microscopy. For example, using light microscopy, the distance between the walls of the crazes in PC was measured during heating [90]. The results of these experiments are shown in Fig. 33. It is clear that, long before T_g (practically from room temperature), a significant decrease in the width of the crazes (shrinkage) begins, while the nonoriented areas between them even slightly increase its sizes due to thermal expansion. Therefore, the observed total recovery of the sizes of the deformed polymer (low-temperature shrinkage) is due to the processes occurring within the crazes or, in other words, due to the properties of highly dispersed oriented polymer filling the crazes. Upon reaching T_g of the block polymer, crazes whose widths are reduced by 90–95% are healed and become invisible under a microscope.
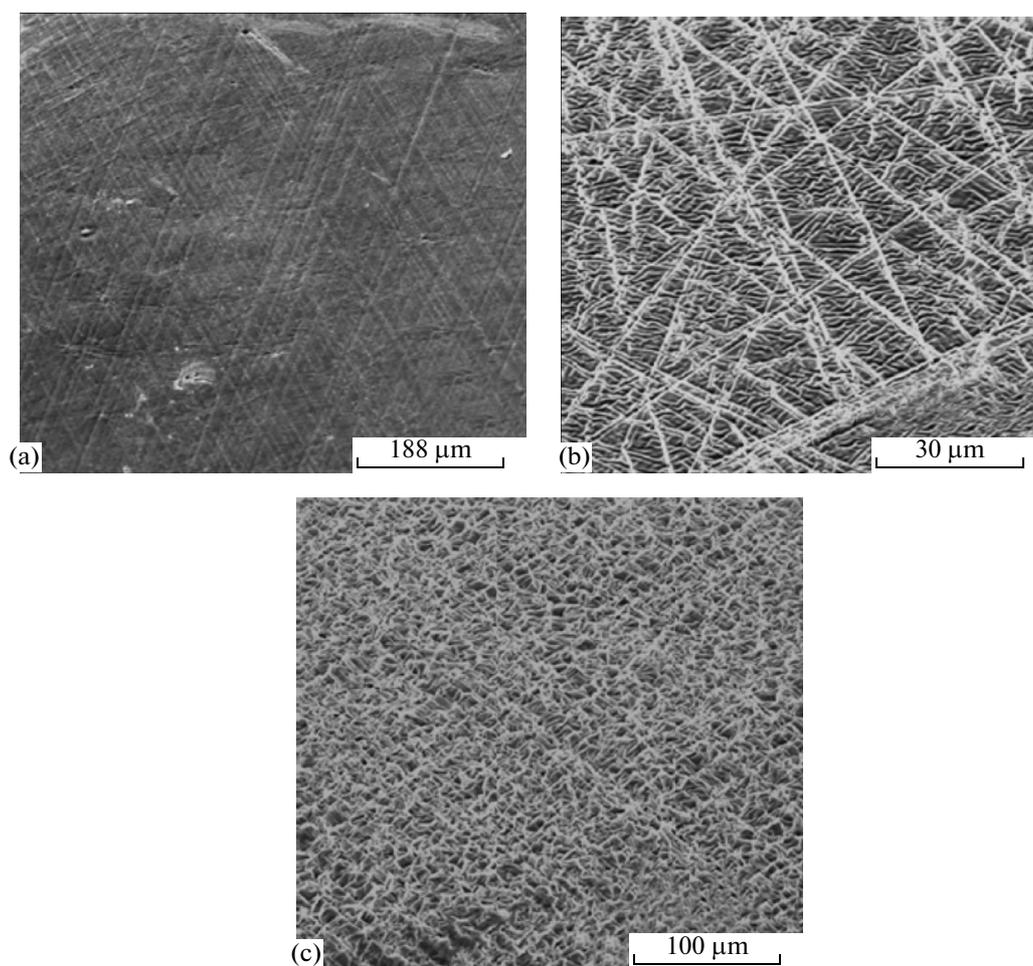
Fig. 32. Scanning electron micrographs of PS samples subjected to uniaxial compression by ~25% at room temperature and shrunk by (a) 1.2, (b) 7.5, and (c) 25% after the annealing at 70, 80, and 90°C, respectively [51].
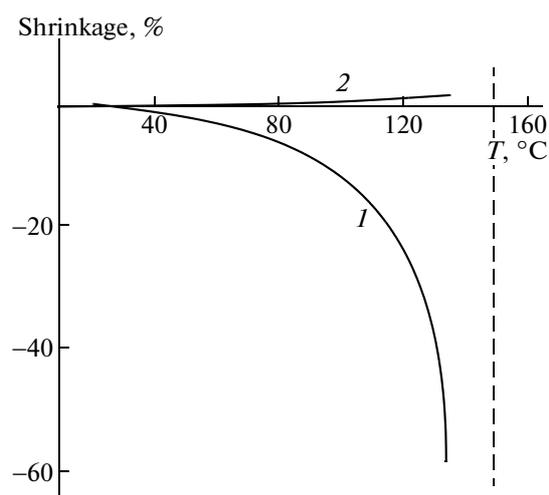
Fig. 33. Temperature dependence of relative change in linear distance between (*1*) the walls of crazes and (*2*) nonoriented areas between crazes in direction of tensile axis for the PC samples stretched in AAM. Vertical dashed line is glass transition temperature of PC [90].
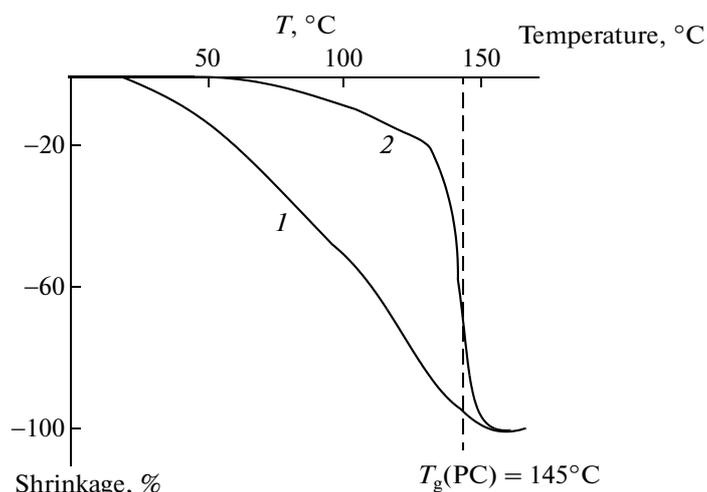
Fig. 34. Relative change in size of PC samples deformed (*1*) by crazing mechanism in AAM and (*2*) in air with formation of a neck [51].

The existence of special zones in deformed glassy polymers that contain highly dispersed oriented material (shear bands and/or crazes) imparts very unusual thermomechanical properties to the polymer as a whole. The size restoration curves of PC deformed (*2*) in air to form a neck and (*1*) in AAM by the crazing mechanism are compared in Fig. 34. It can clearly be seen that, during the annealing of the sample deformed in the air, there is a pronounced low-temperature contribution to the restoration of the sizes of the polymer. This contribution is ~20%, which approximately corresponds to the yield strength of PC in tension. This result is in line with data from other studies [32−36]. At the same time, the polymer deformed by the crazing mechanism restores its size almost completely at temperatures below T_g of the block polymer. This difference is apparently due to the fact that, during the deformation of the polymer in AAM, the free surface of the fibrillated craze material is developed in a wide range of the degrees of stretching of the polymer rather than being limited by the deformation corresponding to the yield point (see Figs. 22 and 23). In the case of shear flow, this process only takes place at small strains both before and in the vicinity of the yield stress (Fig. 11). It is not a surprise that, e.g., the abnormal low-temperature recovery of the size of the deformed polymer during annealing is observed for crazed polymers over the entire range of deformation [55], while for the polymers deformed by the mechanism of shear stress, it only occurs in the strain range up to the yield stress (Fig. 11).

It is interesting to note that the low-temperature contribution to the restoration of the size of the polymer deformed in air has been the subject of numerous long-term studies [32−36], while the much more pronounced effect of the low-temperature recovery of the size of crazed polymers (Fig. 34) has not attracted serious attention.

8.1. Mechanism of Low-Temperature Recovery of Size of Deformed Glassy Polymers During Annealing

The set of data presented above lead to a conclusion that the anomalous thermomechanical behavior of deformed glassy polymers is due to the processes that take place in specific areas of plastically deformed polymer embedded in the original polymer matrix. However, the important question remains unclear, i.e., what are the physical reasons for the low-temperature (below T_g) restoration of the size of deformed polymer glasses at their annealing or, in other words, what types of molecular motion in polymers is responsible for these structural adjustments proceeding spontaneously?

It is important to note that, since the mid-1990s, a new direction of research has been developed in connection with the study of the properties of amorphous glassy polymers in thin (nanometer) films and surface layers. The fundamental dependence of T_g of amorphous polymer films on their thickness was found [91]. It turns out that, in thin layers of about 50−60 nm, T_g of amorphous polymers begins to decrease rapidly with decreasing length of the polymer phase. A typical plot of this kind for amorphous PS is presented in Fig. 35 [92]. It can clearly be seen that the fall in T_g of the polymer with a decrease in its thickness reaches several tens of degrees. The physical reasons for this phenomenon have not yet entirely studied, although there were several hypotheses about its mechanism.
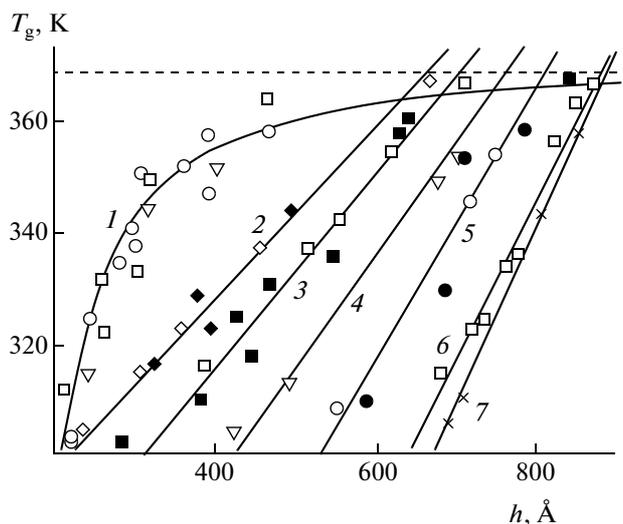
Fig. 35. Dependence of glass transition temperature of PS free films (T_g) on their thickness (h). Molecular weight of PS $M \times 10^{-3}$: (*1*) 116–347, (*2*) 541, (*3*) 691, (*4*) 1250, (*5*) 2077, (*6*) 6700, and (*7*) 9000 [92]. Dashed line shows the glass transition temperature of block PS.

One hypothesis is related to the peculiarities of the vitrification process of the polymer in a limited volume (this is a situation when the polymer phase is so small that there are difficulties in the implementation of the equilibrium conformations of the chains and the nature of large-scale molecular motion changes). It is known that the process of vitrification is due to the cooperative type of molecular motion, for which a rather extended polymer phase is required [93]. Using second-harmonic generation, the mobility in the surface layers of low-molecular-weight glass-forming liquids was measured [94]. It was shown that, in the surface layers, the collective dynamics of molecular motion is violated (the intensity of molecular motion increased compared to this value in the bulk polymer), which leads to a glassy state.

The point of view that the reason for lowering the glass transition temperature in thin films and surface layers is the segregation of end groups in these macromolecules is no less popular [95–102]. The concept of segregation at the interface of the terminal groups is based on the fact that, according to the Fox–Flory theory [103], the ends of the chains are in fact a plasticizer that lowers the T_g of the polymer. It is believed that the increased concentration of the end groups in the surface layers of polymers compared with their concentration in the bulk polymer increases the local concentration of free volume in them and, thus, lowers the glass transition temperature.

A more detailed discussion of the mechanism of this phenomenon can be found in the reviews on this topic [91, 92, 104]. In the context of this review, the very fact of the fundamental lowering of the glass transition temperature of polymer in thin films and surface layers is important. It is important to recall that the inelastic deformation of glassy polymers by the development of shear bands or crazes is essentially a process of dispersing it into the smallest aggregates of oriented macromolecules, that is, fibrils with diameters of units to tens of nanometers. This kind of fibrillation of a block polymer means that the polymer is transferred into a thin surface layer, since the fibrillar assembly of macromolecules of such a diameter contains only a few tens of oriented macromolecules [105]. Considering the data in [55, 64], we can say with confidence that the material of the shear bands and crazes has a much lower T_g than that of the original block polymer. The latter fact is a real physical basis to explain the existence of a large-scale molecular mobility in deformed glassy polymers at temperatures much lower than T_g of the block polymer [51].

In the case of the deformation of the polymer in the air, the polymer is deformed in two stages. In the first stage (up to the yield point), the inelastic deformation of the polymer is localized in shear bands, the interface of which blocks the original unoriented polymer.

At the second stage (the plateau region of the curve of tension or compression), the polymer totally transferred in the oriented state. It is important to note that, according to direct microscopic observations (Fig. 17), shear bands appeared in the early stages of deformation are included in the oriented structure of the polymer, which is implemented at the second stage of deformation. This inclusion occurs in a way that the shear bands retain their individuality and a set of properties. In the case of crazing, this dispersion of polymer in discrete zones (crazes) is expressed even more intensely because it is not limited by the deformation that corresponds to the yield strength of the polymer (Fig. 23).

(a)   (b)

Fig. 36. Schematic representation of structure of (a) craze and (b) shear band [65].

The data on the structure of shear bands and crazes [51, 64], as well as the data established in [95–102] on the fundamental relationship between the glass transition temperature and the length of the polymer phase, allow a reasonable guess about the structure of deformed glassy polymers. As a result of deformation, the glassy polymer acquires a two-phase structure. Shear bands and/or crazes that contain superfine fibrillated material become embedded in a glassy matrix block. It is important to note that these zones of the plastically deformed polymer permeate (percolate) all the cross section of the polymer.

A comprehensive review of structural changes that accompany the deformation of a glassy polymer suggests the following picture of inelastic deformation of the polymer and thermally stimulated restoration of its size. The deformation of glassy polymers at the initial stages (before and in the yield stress) provides a structure constructed of two interrelated components, i.e., the part of the oriented polymer localized in shear bands and/or crazes and the undeformed polymer blocks located between them (Figs. 16–20). As shown above, the shear bands and crazes are filled with a fibrillated, highly dispersed polymer with a significantly lower T_g than the surrounding block polymer. Further inelastic deformation of the polymer in the air (the plateau region in the strain—strength curves) leads to the molecular orientation of the polymer blocks located between the shear bands. The orientation of this part of the polymer occurs without the formation of new interfaces and, in essence, is no different from the orientation of the polymer in a highly elastic state. In the case of the deformation of the glassy polymer in AAM, a two-phase structure containing a zone of highly dispersed fibrillated material embedded in the polymer matrix also arises. In this case, the effects of the anomalous thermomechanical behavior are even more pronounced. This is caused by the fact that, unlike the deformation of the polymer in the air, the zone of highly oriented material (crazes) occurs not only in deformations before and at the yield strength of the polymer block, but also in the entire range of deformations (Fig. 23).

The annealing of this binary system that arises in the inelastic deformation of glassy polymer is accompanied by the following structural rearrangements. The heating of the deformed polymer in the temperature range below its glass transition temperature causes the devitrification and shrinkage of the material in shear bands, which has a reduced glass transition temperature over a wide temperature range (low-temperature contribution to the thermally stimulated recovery). As a physical phenomenon, this part of the thermally stimulated shrinkage of the deformed polymer is associated with an entropy reduction in the oriented material that fills the shear bands and has a lower glass transition temperature.

Further heating leads to the relaxation of the main part of the oriented polymer (bulk component), which, in essence, is no different from the shrinkage of a rubbery block polymer and, therefore, occurs in the glass transition temperature of the block polymer (high-temperature contribution to the thermally stimulated recovery). In the case of a highly crazed glassy polymer, the high-temperature contribution to the thermally stimulated restoration of size fully degenerate (Fig. 34). The latter circumstance is due to the fact that, during crazing, the zones that contain highly dispersed oriented material (crazes) are developed throughout the range of deformations and, therefore, the transition of the polymer in the oriented state as occurs in a block (in the tension through the development of a neck) hardly occurs.

Thus, all the anomalies in the mechanical behavior of deformed glassy polymers (stress relaxation in the initial part of the curve of tension (compression), including the increase in tension under the isometric heat of the deformed glassy polymer; the existence of low-temperature contribution to the thermally stimulated recovery of the deformed polymer glasses; and the appearance of a soft, pliable phase in the deformation of the glassy polymer detectable in the study of the dynamic mechanical properties) can be easily explained if two fundamental facts are considered. First, the inhomogeneous character of inelastic deformation in glassy polymers, which stands behind the development of zones (shear bands and/or crazes) in the initial polymer and, second, a marked decrease in T_g of highly dispersed oriented material filling both

shear bands and crazes. As can be seen, all of the above anomalies in the mechanical behavior of glassy polymers are due to their polymeric nature and, therefore, are not observed in low-molecular-weight solids.

8.2. Physical Reasons for the Abnormalities in Thermophysical Properties of Deformed Glassy Polymers

Thus, the analysis of structural studies allows us to formulate the physical reasons for the anomalies in the mechanical behavior of deformed polymer glasses. Let us now consider the data regarding anomalies in the thermophysical properties of deformed glassy polymers. Recall that these anomalies are related, first, to the deformation calorimetry data, according to which at the first stages of deformation of a glassy polymer, it accumulates a significant amount of internal energy of an unknown nature (Fig. 14) [34—36]. Second, as a result of the deformation of a glassy polymer, a broad exothermic peak appears in its DSC thermograms in the temperature range below T_g (Fig. 15) [21].

The energy balance of deformation of glassy polymers is fundamentally different from the corresponding characteristics of low-molecular-weight plastics. Whereas in the deformation of a low-molecular-weight plastic material (such as copper metal), all the mechanical energy expended is converted into heat [106], in the deformation of a glassy polymer, the mechanical energy is accumulated in the polymer in the form of internal energy (Fig. 15). Obviously, this effect is associated with some irreversible changes in the structure of the deformed polymer. It was shown above that the structure of a glassy polymer does in fact undergo major changes during its deformation. These changes are associated with the formation of discrete zones in the polymer (shear bands and crazes) that contain highly dispersed fibrillated material. According to some estimates [55], this material has a specific surface area of several hundred square meters per gram. It is obvious that the presence of an excess of free surface cannot but affect the internal energy of the polymer. In this regard, it is important to evaluate the possibility of the accumulation of internal energy by the deformable polymer by increasing its surface energy.

The question arises as to whether the experimentally determined accumulation of such significant amounts of internal energy during the deformation of the polymer can be associated with the development of interfaces typical of shear bands and/or crazes? To answer this question, the internal energy that the polymer can accumulate solely due to the development of the interface arising in the deformation through the development of shear bands and/or crazes in it was quantitatively estimated [107]. The basis of this assessment is the assumption that, in the stretching of a glassy polymer to (approximately) its stress yield, the entire deformation occurs through the formation and development of discrete zones (shear bands and/or crazes) containing a plastically deformed fibrillated polymer. This assumption is based on a substantial array of available experimental data. First, the experimental data on the deformation mechanism of glassy polymers in the air show that when the deformation is performed before and at its yield point, the process does occur through the development of shear bands (Figs. 16—18) [28, 51]. In the case of the deformation of the glassy polymer in AAM (through the crazing mechanism), the development of crazes with highly developed interfacial surfaces causes no doubts, even in a wider range of the deformation magnitudes [55]. Second, all of the anomalies in the mechanical behavior of glassy polymers deformed in air (Figs. 10 and 11) are observed in the strain range that correspond to the values before and at the yield point.

As has been repeatedly noted above, there is no fundamental difference between the structure of crazes and shear bands. In both cases, structural formations with fibrillar morphology and, consequently, a high level of the interface are developed. In a relatively recent paper [65], this fact was illustrated in the following way (Fig. 36). In this context, it does not really matter whether the strain is developed through the development of shear bands or crazes. In both cases, the polymer acquires an excess of the interface surface characteristic for the fibrillar structure of shear bands or crazes.

Assume that all inelastic deformation at the first stage (before and at the yield point of the polymer) occurs by the appearance and development of the zones containing plastically deformed fibrillated material. Schematically, this case of deformation is shown in Fig. 23, which implies that the inelastic deformation takes place through the transition (spent) of a block polymer into the material of crazes (shear bands). Considering this deformation mechanism of the polymer, the interfacial surface area that the polymer acquires during deformation can be reasonably estimated.

Indeed, the deformation corresponding to the yield stress of glassy polymers (ε) is known from experiment (~10%) [1, 28]. Take the ratio of elongation of a fibrillated polymer in shear bands and crazes (λ_s) equal to 2, which corresponds to direct microscopic evaluations [21]. According to the available experimental data [55, 58, 64], a polymer that fills the shear zones and the crazes is divided into a system of fibrils with diameter D_f, which is ~10^{-6} cm [55]. In this case, the total surface area of fibrils (S_f) of the polymer in the shear zones (crazes) is [51]

$$S_f = 4\varepsilon/(\lambda_s - 1)D_f.$$

This relation enables us to estimate the surface energy U accumulated by a glassy polymer during its deformation in the first stage, when the inelastic deformation takes place mainly through the development of shear bands or crazes (before and at the yield stress) as follows:

$$U = S_f \gamma = 4\gamma\varepsilon/(\lambda_s - 1)D_f,$$

where γ is the specific surface energy of the polymer.

The value of specific surface energy γ of common glassy polymers, such as PS, PET, and PMMA, is $0.04-0.05$ J/m^2. If the shear strain of the polymer ε to be 10% (the approximate value of the deformation of the yield point of most glassy polymers), the total surface area of the fibrillated material in the shear bands is ~40 m^2/cm^3, while the corresponding value of the surface energy is $1.6-2.0$ J/cm^3. Note that, according to the deformation calorimetry data [34–36], the magnitude of the internal energy accumulated in the polymer in its deformation to the yield point is $2-3$ J/cm^3 for such polymers as PS, PC, and PMMA.

This result, in spite of the coarseness of assessments allows a reasonable guess about the existence of other (in addition those mentioned in [21]) contributions to the internal energy accumulated by the glassy polymer during its deformation (change in chain conformation, i.e., the intramolecular energy due to the $T-G$ transitions, changes in molecular packing and intermolecular interaction energy, and the distortion of valence angles and bonds and the energy of breaking chemical bonds). In addition to the above factors, the excess internal energy can be associated with the development of advanced interfaces. Moreover, as shown above, this contribution to the internal energy of the deformed polymer can be so great that it completely provides the value of the experimentally measured value of the internal energy accumulated by the deformed polymer.

Now consider what happens during the annealing of deformed polymer glasses. As shown above, the deformed glassy polymer is a heterogeneous system in terms of structure and contains discrete zones (shear bands and crazes), which have a highly developed interfacial surface (Figs. 22 and 24). The annealing of the deformed polymer leads not only to the restoration of its size, but also is accompanied by a complete disappearance (healing) of these interfaces (Fig. 20) [54, 55]. In fact, this kind of annealing takes place in the experiments on DSC [21]. It can be seen from the data presented in Fig. 20 that, in deformed glassy polymers, the healing of phase boundaries in low-temperature annealing (below T_g) is accompanied by the appearance of a broad exothermic peak on the DSC thermograms that extend almost from the β-transition to T_g. Note that the extension of this DSC peak almost coincides with the ranges of the anomalies in the mechanical behavior of deformed polymers (compare Figs. 11 and 15).

In light of the above-developed ideas on the role of excess interfacial surface in discrete zones (shear bands and crazes) that arise from the inelastic deformation of polymer glasses, the existence of the low-temperature exothermic DSC peak becomes clear (Fig. 15) [21]. Upon heating a deformed glassy polymer at temperatures below its T_g, the local T_g of highly dispersed oriented material of shear bands and crazes is consistently achieved.

This has two consequences. First, the shrinkage of the oriented material of shear bands and crazes occurs, which is accompanied by the restoration of the size of the polymer according to the usual entropic mechanism, as discussed in the previous section. Second, since the devitrified material of shear bands and crazes that experienced shrinkage is above its local T_g (but below the T_g of the block polymer), the process of healing begins in the excess interface [108]. The healing (self-adhesion [109]) of the interface is only possible if the polymer is in a highly elastic state. The mechanism of the healing process consists of the mutual diffusion of chain segments across the interface, which is possible when this kind of segmental mobility in the polymer exists [110]. The processes of the decrease (healing) of the interface are thermodynamically favorable and, therefore, occur spontaneously, when the necessary molecular mobility is provided. Obviously, the healing of the interface is always an exothermic process accompanied by a general decrease as the free energy of the system. Namely, this effect is observed in the DSC thermograms (Fig. 15b) in the form of a localized exothermic peak between the β- and α-transitions of a block polymer.

The value of the internal energy accumulated by the polymer in the first stages of deformation is released as heat during its subsequent annealing as a result of healing of the interface. Not surprisingly, the thermal energy determined by DSC is $2-3$ J/cm^3; it is fully corresponds to the amount of internal energy accumulated during the deformation of the glassy polymers (Fig. 14) [35].

Thus, all of the known features in the mechanical and thermophysical behavior of glassy polymers that do not fit into conventional ideas about their properties are explained as follows. First, the deformation of a glassy polymer is principally nonuniform, which causes the deformed glassy polymer to be a structure built from two related phases, i.e., a block polymer in which the zones of plastically deformed material (shear bands and/or crazes) are integrated. Second, these areas (shear bands and crazes) are filled with highly dispersed oriented material, in which the glass transition temperature has decreased in comparison
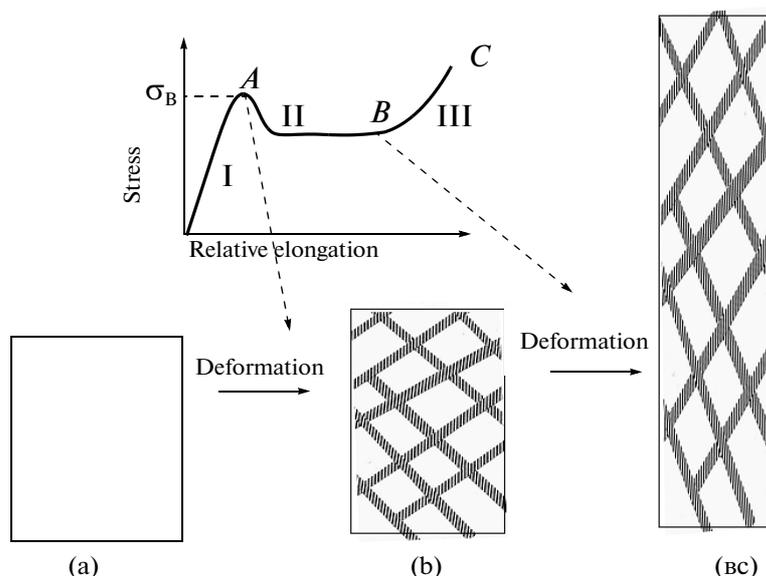
Fig. 37. Schematic diagram of structural changes accompanying the deformation of glassy polymers in air (see explanations in the text).

with the block polymer and high interfacial surface. The latter two factors can consistently explain all the abnormalities in the mechanical and thermophysical properties of deformed glassy polymers from a unified position. It is important to note that the above representations of the structural and mechanical behavior of glassy polymers, in contrast to other studies [32−37, 69−80, 106] are based on the results of direct structural studies [82−91].

9. CONCLUSIONS

In light of the above ideas, the process of deformation of the glassy polymer during its stretching can be described as follows (Fig. 37). In the early stages of deformation (before and at the yield stress), shear bands with a specific structure emerge. The polymer located between the shear bands is undeformed and is no different from the original unoriented polymer in the structure and properties. The further inelastic deformation of the polymer (the plateau region in the strain−strength curves) leads to the molecular orientation of the polymer blocks located between the shear bands. The orientation of this part of the polymer occurs without the formation of new interfaces and, therefore, the accumulation of internal energy at this stage of deformation is hardly observed. It is important to note that the shear bands that appeared in the early stages of deformation of the polymer are included in the polymer structure and, even after the full transition to the oriented state, retain their individuality, interphase boundaries, and properties.

The reverse process of restoring the size and structure of the deformed glassy polymer can also be depicted graphically with respect to the developed representations (Fig. 38). In particular, heating of the deformed polymer in the temperature range below its glass transition temperature causes the shrinkage of the material in shear bands, which has a reduced glass transition temperature over a wide temperature range (low-temperature contribution to the thermally stimulated recovery of sizes). As a physical phenomenon, this part of the thermally stimulated shrinkage of the deformed polymer is associated with not only entropy reduction in the oriented material that fills the shear bands and has a lower glass transition temperature, but also the healing of interfaces in the structure of shear bands. The healing process of the interfaces during the annealing of such a system is characterized by an exothermic effect and the complete relaxation of the accumulated internal energy.

Further heating leads to the relaxation of the main part of the oriented polymer, which, in essence, is no different from the shrinkage of a rubbery block polymer and, therefore, occurs at the glass transition temperature of the block polymer (high-temperature contribution to the thermally stimulated recovery of size).
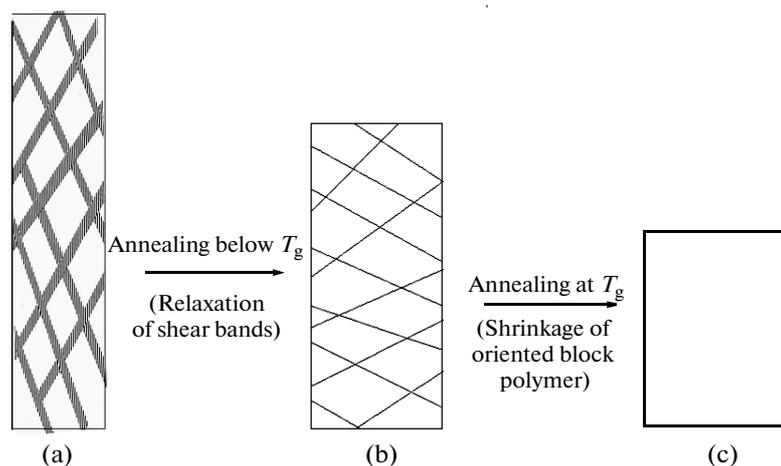
Fig. 38. Schematic diagram of structural rearrangements that accompany the thermally stimulated restoration of the size of deformed glassy polymer (see explanations in the text).

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REFERENCES

1. Kuleznev, V.N and Shershnev, V.A., *Khimiya i fizika polimerov* (Chemistry and Physics of Polymers), Moscow: KolosS, 2007.
2. Struik, L.C.E., *Physical Aging in Amorphous Glassy Polymers and Other Materials*, Amsterdam: Elsevier, 1978.
3. Tant, M.R. and Wilkes, G.L., *Polym. Eng. Sci.*, 1981, vol. 21, no. 14, p. 874.
4. Petrie, S.E.B., *J. Macromol. Sci., Part B: Phys.*, 1976, vol. 12, no. 2, p. 225.
5. Kargin, V.A. and Slonimskii, G.L., *Kratkie ocherki po fizikokhimii polimerov* (Short Essays on the Physical Chemistry of Polymers), Moscow: Khimiya, 1967.
6. Shlyapnikov, Yu.A., *Usp. Khim.*, 1997, vol. 66, no. 1, p. 1.
7. Belousov, V.N., Kozlov, G.V., Mikitaev, A.L., and Lipatov, Yu.S., *Dokl. Akad. Nauk SSSR*, 1990, vol. 313, no. 3, p. 630.
8. Bove, L., D'Aniello, C., Gorrasi, G., Guadagno, L., and Vittoria, V., *Polym. Bull.*, 1997, vol. 3S, p. 579.
9. Balta-Calleja, F.J., Santa Cruz, C., and Asano, T.J., *J. Polym. Sci., Polym. Phys. Ed.* 1993, vol. 31, p. 557.
10. Vittoria, V., Petrillo, E., and Russo, R., *J. Macromol. Sci., Part B: Phys.*, 1996, vol. 35, p. 147.
11. Neki, K. and Geil, P.H., *J. Macromol. Sci., Part B: Phys.*, 1973, vol. 8, no. 12, p. 295.
12. Hwang, Y., Inoue, T., Wagner, P.A., and Ediger, M.D., *J. Macromol. Sci., Part B: Phys.*, 2000, vol. 38, p. 68.
13. Capodanno, V., Petrillo, E., Romano, G., Russo, R., and Vittoria, V., *J. Appl. Polym. Sci.,* 1997, vol. 65, p. 2635.
14. D'Amore, A., Cocchini, F., Pompo, A., Apicella, A., and Nicolais, L., *J. Appl. Polym. Sci.*, 1990, vol. 39, p. 1163.
15. D'Amore, A., Pompo, A., and Nicolais, L., *Macromol. Chem. Macromol. Symp.*, 1993, vol. 68, p. 203.
16. Michele, A., Vittoria V, *Polymer*, 1993, vol. 34, p. 1898.
17. Moynihan, C.T., Easteal, A.J., DeBolt, M.A., and Tucker, J., *J. Am. Ceram. Soc.*, 1976, vol. 59, p. 12.
18. Williams, G. and Watts, D.C., *Trans. Faraday Soc.*, 1970, vol. 66, p. 80.
19. Bailey, R.T., North, A.M., and Pethrick, R.A., *Molecular Motions in High Polymers*, Oxford: Clarendon, 1981.
20. Davis, J.W. and Pethrick, R.A., *Polymer*, 1998, vol. 39, no. 2, p. 255.
21. Bershtein, V.A. and Egorov, V.M., *Differentsial'naya skaniruyushchaya kalorimetriya v fizikokhimii polimerov* (Differential Scanning Calorimetry in Physical Chemistry of Polymers), Leningrad: Khimiya, 1990.
22. Shantarovich, V.P., Oleinik, E.F., Arazhakov, M.S., Salamatina, O.B., Kevdina, I.B., Azamatova, Z.K., and Gustov, V.V., in *Nauchnaya konferentsiya Instituta khimicheskoi fiziki im. N.N.Semenova RAN*, (Sci. Conf. of The Semenov Inst. of Chemical Physics, Russ. Akad. Sci.), Moscow, 1998, p. 78.
23. Govaert, L.E., van Melick, H.G.H., and Meijer, H.E.H., *Polymer*, 2001, vol. 42, p. 1271.
24. Narisawa, J. and Jee, A.F., *Mater. Sci. Technol., Struct. Prop. Polymers*, 1993, vol. 12, p. 701.

25. Gurevich, G. and Kobeko, P., *Rubber. Chem. Tec.*, 1940, vol. 13, p. 904.
26. Haward, R.N., *Trans. Faraday Soc.*, 1942, vol. 38, p. 394.
27. van Melick, H.G.H., *PhD Thesis*, Eindhoven: Eindhoven University of Technology, 2002.
28. Lazurkin, Yu.S., *Doctoral (Phys.-Math.) Dissertation*, Moscow: Vavilov Inst. of Phys. Problems, Akad. Nauk SSSR, 1954.
29. Laius, L.A. and Kuvshinskii, E.V., *Vysokomol. Soedin., Ser. A*, 1964, vol. 6, no. 1, p. 52.
30. Shoshina, V.I., Nikonovich, G.V., and Tashpulatov, Yu.T., *Izometricheskii metod issledovaniya polimernykh materialov* (Isometric Method for Studying Polymer Materials), Tashkent: Akad. Nauk Uzb. SSR, 1989.
31. Treloar, L.R.G., *The Physics of Rubber Elasticity*, Oxford: Oxford University Press, 1967, 2nd ed.
32. Arzhakov, S.A., *Doctoral (Chem.) Dissertation*, Moscow: Karpov Research Inst. of Physics and Chemistry, 1975.
33. Arzhakov, M.S., Arzhakov, S.A., and Zaikov, G.E., *Structural and Mechanical Behavior of Glassy Polymers*, New York: Nova Science, 1997.
34. Oleynik, E.F., in *High Performance Polymers*, Baer, E. and Moet, S., Eds., Berlin: Hauser Verlag, 1991, p. 79.
35. Oleinik, E.F., Salamatina, O.B., Rudnev, S.N., and Shenogin, S.V., *Vysokomol. Soedin., Ser. A*, 1993, vol. 35, no. 11, p. 1819.
36. Shenogin, S.V., Homme, G.W.H., Salamatina, O.B., Rudnev, S.N., and Oleinik, E.F., *Polym. Sci., A*, 2004, vol. 46, no. 1, p. 21.
37. Arzhakov, M.S., *Doctoral (Chem.) Dissertation*, Moscow: Moscow State Univ., 2004.
38. Gauthier, C., Pelletier, J.-M., David, L., Vigier, G., and Perez, J., *J. Non-Cryst. Solids*, 2000, vol. 274, p. 181.
39. Trzadnel, M. and Kryszewski, M., *Polymer*, 1988, vol. 29, p. 619.
40. Munch, E., Pelletier, J.B., and Vigier, G., *Phys. Rev. Lett.*, 2006, vol. 97, p. 207801.
41. Wallace, M.L. and Joos, B., *Phys. Rev. Lett.*, 2006, vol. 96, p. 025501.
42. Warren, M. and Rottler, J., *J. Chem. Phys.*, 2010, vol. 133, p. 164513.
43. Munch, E., Pelletier, J.-M., and Vigier, G., *J. Polym. Sci., Part B: Polym. Phys.*, 2008, vol. 46, p. 497.
44. Havriliak, S.Jr. and Shortridge, T.J., *Polymer*, 1990, vol. 31, p. 1782.
45. Starkweather, J., *Polymer*, 1991, vol. 32, p. 2443.
46. Bauwens-Crowet, O., *J. Mater. Sci.*, 1999, vol. 34, p. 1701.
47. Berensa, R. and Hodge, I.M., *Macromolecules*, 1982, vol. 15, p. 756.
48. Parisot, J., Rafi, O., and Choi, W.J., *Polymer Eng. Sci.*, 1984, vol. 24, no. 11, p. 886.
49. Shu-Sing Chang, *J. Chem. Thermodyn.*, 1977, vol. 9, p. 189.
50. Volynskii, A.L., Efimov, A.V., and Bakeev, N.F., *Polym. Sci., C*, 2007, vol. 49, no. 7, p. 816.
51. Volynskii, A.L. and Bakeev, N.F., *Strukturnaya samoorganizatsiya amorfnykh polimerov*, (Structural Self-Organization of Amorphous Polymers), Moscow: Fizmatlit, 2005.
52. Volynskii, A.L., Kulebyakina, A.I., Panchuk, A., Moiseeva, S.V., Bol'shakova, A.V., Grokhovskaya, T.E., Yarysheva, L.M., Kechek'yan, A.S., Bazhenov, S.L., and Bakeev, N.F., *Polym. Sci., A*, 2007, vol. 49, no. 12, p. 1265.
53. Kechek'yan, A.S., *Vysokomol. Soedin., Ser. B*, 1987, vol. 29, no. 11, p. 804.
54. Kambour, R.P., *J. Polym. Sci., Part D: Macromol. Rev.*, 1973, vol. 7, p. 1.
55. Volynskii, A.L. and Bakeev, N.F., *Solvent Crazing of Polymers*, Amsterdam, New-York: Elsevier, 1996.
56. Passaglia, E., *J. Phys. Chem. Solids,* 1987, vol. 48, no. 11, p. 1075.
57. Nadezhin, Yu.S., Sidorovich, A.V., and Asherov, B.A., *Vysokomol. Soedin., Ser. A*, 1976, vol. 18, no. 12, p. 2626.
58. Bowden, P.B. and Raha, S., *Philos. Mag.*, 1970, vol. 22, p. 463.
59. Oleinik, E.F., Rudnev, S.N., and Salamatina, O.B., *Dokl. Akad. Nauk SSSR*, 1986, vol. 286, no. 1, p. 1235.
60. Kechek'yan, A.S., Rodionova, Yu.A., and Bazhenov, S.L., *Polym. Sci., A,* 2005, vol. 47, no. 2, p. 126.
61. *The Physics of Glassy Polymers*, Haward, R.N. and Young, B.Y., Eds., London, New-York: Chapman and Hall, 1997.
62. Volynskii, A.L., Aleskerov, A.G., and Bakeev, N.F., *Vysokomol. Soedin., Ser. B*, 1977, vol. 19, p. 218.
63. Volynskii, A.L., Loginov, V.S., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A*, 1981, vol. 23, no. 5, p. 1059.
64. Li, J.C.M., *Polym. Eng. Sci.*, 1984, vol. 24, no. 10, p. 750.
65. Friedrich, K., *Adv. Polym. Sci.*, 1983, vols. 52−53, p. 266.
66. Harmon, J.P., Lee, S., and Li, J.C.V., *Polymer*, 1988, no. 7, p. 1221.
67. Volynskii, A.L., Yarysheva, L.M., Mironova, A.A., Arzhakova, O.V., Kechek'yan, A.S., Ozerin, A.N., Rebrov, A.V., and Bakeev, N.F., *Polym. Sci., A,* 1996, vol. 38, no. 2, p. 152.
68. Volynskii, A.L., Yarysheva, L.M., Arzhakova, O.V., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A*, 1991, vol. 33, no. 2, p. 418.
69. Arzhakov, S.A. and Kabanov, V.A., *Vysokomol. Soedin., Ser. B*, 1971, vol. 13, no. 5, p. 318.
70. Arzhakov, S.A., Bakeev, N.F., and Kabanov, V.A., *Vysokomol. Soedin., Ser. A*, 1973, vol. 15, no. 10, p. 1154.
71. Arzhakov, M.S., Lukovkin, G.M., and Arzhakov, S.A., *Dokl. Chem.*, 1999, vol. 369, nos. 4−6, p. 289.
72. Arzhakov, M.S., Lukovkin, G.M., and Arzhakov, S.A., *Dokl. Chem.*, 2000, vol. 371, nos. 4−6, p. 57.
73. Brady, T.E. and Yeh, G.S.Y., *J. Macromol. Sci., Part B: Phys.*, 1974, vol. 9, no. 4, p. 659.
74. Bershtein, V.A., Peschanskaya, N.N., Halary, J.L., and Monnerie, L., *Polymer*, 1999, vol. 40, p. 6687.
75. Sanditov, D.S. and Sangadiev, S.Sh., *Polym. Sci., A,* 1999, vol. 41, no. 6, p. 643.

76. Johari, J.P., *J. Chem. Phys.*, 1973, vol. 58, p. 1766.

77. Boyce, M., *Polym. Eng. Sci.*, 1995, vol. 35, p. 331.

78. G'Sell, C., El Bari, H., Perez, J., Cavaille, J.Y., and Johari, G.P., *Mater. Sci. Eng., A*, 1989, vol. 110, p. 223.

79. Perez, J., Cavaille, J.-Y., and David, L., *J. Mol. Struct.*, 1999, vol. 479, p. 183.

80. David, L., Quinson, R., Gauthier, C., and Perez, J., *J. Polym. Eng. Sci.*, 1997, vol. 37, p. 1633.

81. Volynskii, A.L., Kechek'yan, A.S., Grokhovskaya, T.E., Lyulevich, V.V., Bazhenov, S.L., Ozerin, A.N., and Bakeev, N.F., *Polym. Sci., A*, 2002, vol. 44, no. 4, p. 374.

82. Volynskii, A.L., Grokhovskaya, T.E., Kechek'yan, A.S., Bazhenov, S.L., and Bakeev, N.F., *Dokl. Phys. Chem.*, 2000, vol. 374, nos. 4−6, p. 200.

83. Volynskii, A.L., Grokhovskaya, T.E., Kechek'yan, A.S., and Bakeev, N.F., *Polym. Sci., A*, 2003, vol. 45, no. 3, p. 265.

84. Volynskii, A.L., Grokhovskaya, T.E., Lyulevich, V.V., Yarysheva, L.M., Bol'shakova, A.V., Kechek'yan, A.S., and Bakeev, N.F., *Polym. Sci., A*, 2004, vol. 46, no. 2, p. 130.

85. Volynskii, A.L., Kulebyakina, A.I., Panchuk, D.A., Moiseeva, S.V., Bol'shakova, A.V., Grokhovskaya, T.E., Yarysheva, L.M., Kechek'yan, A.S., Bazhenov, S.L., and Bakeev, N.F., *Polym. Sci., A,* 2007, vol. 49, no. 12, p. 1265.

86. Volynskii, A.L., Yarysheva, L.M., and Bakeev, N.F., *Polym. Sci., A*, 2011, vol. 53, no. 10, p. 871.

87. Volynskii, A.L., Grokhovskaya, T.E., Sembaeva, R.Kh., Bazhenov, S.L., and Bakeev, N.F., *Dokl. Phys. Chem.*, 1998, vol. 363, nos. 4−6, p. 416.

88. Volynskii, A.L., Grokhovskaya, T.E., Sembaeva, R.Kh., Yaminskii, I.V., Bazhenov, S.L., and Bakeev, N.F., *Polym. Sci., A*, 2001, vol. 43, no. 2, p. 124.

89. Volynskii, A.L., Grokhovskaya, T.E., Sembaeva, R.Kh., Bazhenov, S.L., and Bakeev, N.F., *Polym. Sci., A*, 2001, vol. 43, no. 6, p. 625.

90. Grokhovskaya, T.E., Volynskii, A.L., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A*, 1977, vol. 19, no. 9, p. 2112.

91. Volynskii, A.L. and Bakeev, N.F., *Polym. Sci., B*, 2003, vol. 45, nos. 7−8, p. 195.

92. Forrest, J.A. and Dalnoki-Veress, K., *Adv. Colloid Interface Sci.*, 2001, vol. 94, p. 167.

93. Rostiashvili, V.G., Irzhak, V.I., and Rozenberg, B.A., *Steklovanie polimerov* (Glass Transition of Polymers), Leningrad: Khimiya, 1987.

94. Jerome, B. and Commandeur, J., *Nature*, 1997, vol. 386, p. 589.

95. Tanaka, K., Takahara A., Kajiyama T, *Macromolecules*, 1997, vol. 30, no. 21, p. 6626.

96. Kajiama, T., Tanaka, K., and Takahara, A., *Proc. Japan Acad.*, 1997, vol. 73B, no. 7, p. 132.

97. Tanaka, K., Kajiyama Ò., Takahara A, *Acta Polym.*, 1995, vol. 46, p. 476.

98. Kajiyama, T., Tanaka, K., and Takahara, A., *Macromolecules*, 1995, vol. 28, no. 9, p. 3482.

99. Kim, J.H., Jang, J., Lee, D-Y., and Zin, W-C., *Macromolecules*, 2002, vol. 35, no. 6, p. 311.

100. Bollinne, C., Stone, V.W., Carlier, V., and Jonas, A.M., *Macromolecules*, 1999, vol. 32, no. 14, p. 4719.

101. Frank, B., Gast, A.P., Russel, T.R., Brown, H.R., and Hawker, C., *Macromolecules*, 1996, vol. 29, no. 20, p. 6531.

102. Zheng, X., Sauer, B.B., Van Alsten, J.G., Schwartz, S.A., Rafailovich, M.H., Sokolov, J., and Rubinstein, M., *Phys. Rev. Lett.*, 1995, vol. 74, p. 407.

103. Fox, T. and Flory, P., *J. Polym. Sci.*, 1954, vol. 14 P, p. 315.

104. Forrest, J.A., *Eur. Phys. J. E: Soft Matter Biol. Phys.*, 2002, vol. 8, p. 261.

105. Yang, A.S.M. and Kramer, E.J., *J. Polym. Sci., Part A: Polym. Chem.*, 1985, vol. 23, p. 1353.

106. Shenogin, S.V., Hone, G.W.H., and Oleinik, E.F., *Thermochim. Acta*, 2002, vol. 391, p. 13.

107. Volynskii, A.L., Efimov, A.V., Grokhovskaya, T.E., Yarysheva, L.M., and Bakeev, N.F., *Polym. Sci., A*, 2004, vol. 46, no. 7, p. 708.

108. Volynskii, A.L. and Bakeev, N.F., *Polym. Sci., A*, 2009, vol. 51, no. 10, p. 1096.

109. Voyutskii, S.S., *Autogeziya i adgeziya vysokopolimerov* (Autohesion and Adhesion of High Polymers), Moscow: Khimiya, 1960.

110. Kuleznev, V.N., *Smesi polimerov* (Polymer Blends), Moscow: Khimiya, 1980.

SPELL: 1. tetracene, 2. causingthe, 3. cooperativity, 4. inducate, 5. particulr, 6. usingf, 7. nonoriented