Structural Aspects of Inelastic Strain in Glassy Polymers[1]

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Abstract—The specific behavior of mechanical and physicochemical properties of undeformed polymer glasses and those subjected to mechanical deformation was analyzed. The range of phenomena observed in the first steps of deformation (before and at the yield point), such as a growth in stress upon isometric heating, strong low-temperature shrinkage of strained polymers, buildup of internal energy, etc., are discussed in detail. Particular attention is given to analysis of structural rearrangements that accompany inelastic deformation of polymer glasses.

INTRODUCTION

The structure, properties, and deformation mechanism of glassy polymers are the subject of thorough investigation for many years. The material concerning the specifics of the glassy state of amorphous polymers is so tremendous that we do not intend by any means to completely cover these topics within the framework of one review paper. The aim of this paper was to survey experimental data published to date on the abnormal physicochemical and mechanical behavior of glassy polymers. Particular attention in this review will be given to analysis of the structural–mechanical behavior of glassy polymers in the small-strain region (before and at the yield point).

The interest in studying the problem of the glassy state of polymers is due to at least two circumstances. First, a wide practical use of glassy polymers requires the maximum possible understanding of their mechanical behavior. Second, some fundamental properties of glassy polymers have certain specific features that have not been clearly understood yet.

In turn, these specific features may be divided into two categories: (1) there is a certain type of large-scale molecular motion in a temperature range below the glass transition temperature of amorphous polymers, which is responsible for the processes of their physical aging, and (2) mechanical deformation imparts to glassy polymers a variety of general properties that have not been unequivocally explained to the present.

In this context, we briefly discuss available data on the specific features of physical aging of glassy polymers and the problem of the influence of mechanical deformation on the structure and properties of glassy polymers.

STRUCTURAL INHOMOGENEITY AND NONEQUILIBRIUM STATE OF AMORPHOUS GLASSY POLYMERS

First studies on the problem date to mid-XX century and are associated with the name of Academician V.A. Kargin, the founder of polymer science in the USSR [1]. On the basis of a variety of experimental data that embraced a wide range of polymer chemistry and polymer physics phenomena, he advanced a fundamental concept according to which amorphous polymers should be considered as molecular systems that are ordered to a certain degree.

According to modern concepts, amorphous polymers are structurally inhomogeneous solids with inhomogeneity sizes of the order of a few angstroms to a few tens of angstroms [1–3]. It is the structural inhomogeneity that actually implies the presence of a certain ordered structure. However, the inhomogeneity of the structure of amorphous polymers does not relate to phases but is fluctuative, nonequilibrium in character [4, 5], thus creating considerable experimental difficulties in the determination of the mechanism of structural rearrangements in amorphous polymers. The reasons behind these difficulties consist in the impossibility of using well developed structural investigation methods based on the phase contrast of subjects to be studied (X-ray diffraction analysis, electron diffraction). Multiply repeated attempts [6, 7] at using direct microscopic methods for solving this problem failed to develop a universal model of the structure of amorphous polymers and the mechanisms of their deformation with allowance for structural inhomogeneity.

Nonetheless, the aforementioned structural disequilibrium is easy to reveal by studying the influence of low-temperature (below T_g) annealing on the mechanical and thermal properties of amorphous glassy polymers.

Figure 1 shows tensile stress–strain curves for amorphous PET subjected to annealing at 60°C for various periods of time [5]. Note that this annealing tempera-

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Fig. 1. Tensile stress–strain curves for glassy PET at room temperature. The time of low-temperature (T = 60°C) annealing is (*1*) 0.16, (*2*) 1.5, (*3*) 16.6, (*4*) 166.6 and (*5*) 1166.6 h [5].

Fig. 2. DSC curves for (*1*) quenched PS and PS annealed at 60°C for (*2*) 0.2, (*3*) 1, (*4*) 10, (*5*) 90, and (*6*) 170 h [8].

ture is well below the PET glass transition temperature (75–78°C). Low-temperature annealing leads to a considerable increase in the elastic modulus and the yield point of the glassy polymer. These changes in the mechanical properties during the physical aging of the polymer are also accompanied by a substantial change in its thermophysical properties. These changes are unequivocally demonstrated by DSC data. Figure 2 shows typical data relevant to this case. It is distinctly seen that the endothermic peak in the glass transition region becomes progressively more intense during annealing. A comprehensive analysis of the effect of physical aging of polymer glasses on the evolution of DSC thermograms is given in a book [8].

The emergence of the nonequilibrium structure of polymer glass and its relaxation under low-temperature annealing conditions are usually associated with the evolution of free volume on the transition of a polymer from the rubbery to the glassy state. A decrease in the fractional free volume upon cooling of a rubbery polymer corresponds to equilibrium conditions only far from its glass transition temperature. With approaching the glass temperature, the viscosity of the polymer begins to drastically increase; as a result, the polymer structure characteristic of the rubbery state is "frozen-in" upon polymer transition to the glassy state. The process of physical aging is the spontaneous transition of polymer glass to the state of thermodynamic equilibrium. The evolution of free volume plays a central role in the physical aging process. On the basis of these ideas, several models were proposed to describe the mechanism of this phenomenon. All of the stem from the experimental finding that allows physical aging to be separated into two components, the thermally activated contribution described by the Arrhenius equation and the process whose driving force is the excess free

volume in the system, which determines how far is the system from equilibrium. In other words, the process of physical aging of a polymer depends, first, on a certain type of molecular motion in the temperature range of the glassy state and, second, on the migration of free volume. Despite a wealth of studies on the revealing of the mechanism of physical aging, no complete understanding has been reached yet. Let us cite just a few studies that have been performed recently. Cangialosi *et al.* [12] studied a change in free volume in PC by the positron annihilation technique at three aging temperatures 25, 100, and 128°C. A decrease in free volume depending on the aging time was measured in all cases. The obtained results were interpreted as a decrease in the number of free-volume holes during aging. The results agree well with the Struik free-volume model [9].

Quite opposite results were obtained by McGonigle *et al.* [13]. They also studied the free-volume content of PET and related polymers by positron annihilation technique. It was found that the effect of physical aging upon annealing below T_g was distinctly displayed in all cases. Nonetheless, the free volume did not change under these conditions.

A more complex picture of physical aging was observed in a study [14] on the physical aging processes in PC Changes in the elastic modulus, rigidity, and creep of PC during its aging at ambient and elevated temperatures were studied with the use of the indentation technique in combination with DSC. It was found that both the elastic modulus and the rigidity of PC varied in an abrupt manner after aging for approximately equal times at different temperatures. It is believed that free volume has a certain gradient throughout the polymer volume, being distributed in PC to have a higher concentration or a greater size of

free-volume holes closer at the surface than in the bulk. As a consequence, the consolidation of PC during annealing occurs inhomogeneously with a more significant decrease in free volume in the regions adjacent to the polymer surface and a smaller decrease or even without a change in the bulk. A comparison of mechanical testing and DSC data showed that there is no direct (linear) correlation between a change in the mechanical properties of the polymer during annealing and the corresponding evolution of enthalpy. This finding agrees well with the data reported in [15]. It is believed that changes in the mechanical properties and enthalpy during aging are due to different reasons. The change in the mechanical properties is due to a decrease in the polymer free volume upon annealing, whereas the shift in the position and the height of the endothermic DSC peak are determined by the value of internal energy of the polymer.

Hwang *et al.* [16] studied the specific features of molecular-probe reorientation processes in the PC matrix during its physical aging. They could explain the obtained results only by assuming that the aging process is not uniform—the process in some polymer microregions is considerably faster than in other regions.

The viewpoint [8] that β-molecular motion is responsible for the observed effects of physical aging of polymer glasses is also noteworthy. It should be specified that like α relaxation, β relaxation is segmental in nature; but this is a noncooperative motion of a segment, which can be realized at sites of loose molecular packing (free volume) in the case of a glassy solid. The disturbance of cooperativity of molecular motion suggests certain structural inhomogeneity of a glassy polymer. This means that polymer glass has a nonuniform structure. In some regions, a glassy polymer has such a structure that the cooperativity of large-scale molecular motion is violated in there. It is for this reason that molecular motion is displayed in temperature regions below the glass temperature [8]. Summarizing the above considerations, it may be concluded that glassy polymers are thermodynamically nonequilibrium systems. As a consequence, they are characterized by the processes of structural rearrangements within the temperature range of the glassy state, which are determined as the physical aging of polymer glasses. Despite of numerous studies, the physical causes of aging have not been completely understood yet and they should be taken into account in the analysis of molecular processes accompanying inelastic deformation of polymer glasses.

EFFECT OF MECHANICAL LOADING ON THE STRUCTURE AND PROPERTIES OF GLASSY POLYMERS

Large strains in glassy polymers, which are called forced elastic strains by Lazurkin [17], are their unique property and actually lead to the global transition of a polymer into an oriented state. The achievement of such a strain forms the basis for a fundamental engineering method aimed at optimizing the mechanical properties of polymer films and fibers, namely, orientation drawing. Under uniaxial tension, such strain is macroscopically displayed as neck initiation and propagation in the polymer during deformation. The process of cold drawing of glassy polymers is described in detail and analyzed in comprehensive monographs [17–19]. For this reason, we will not dwell on the detailed mechanism of this phenomenon. In this paper, we will consider in detail processes that precede the global transition of a polymer to the oriented state; although these processes have also been studied well, they are understood to a lesser extent. It turns out that the global transition to the oriented state by necking is preceded by a number of preparatory processes. These processes occur in the small-strain region corresponding to the so-called Hookean portion of the tensile (compressive) stress–strain curve for a glassy polymer and in the yield point region. Lazurkin noted that there are relatively fast relaxation processes occurring in the temperature range of the glassy state and at strains below the yield point. "These strains continuously decrease in magnitude after unloading and ultimately vanish to zero for a relatively short time without heating above T_g." [17]. He called the phenomena observed elastic-aftereffect strain. The basic features of such strains are well known, although they have not been explained to a full extent. First, this is the effect of strain rate and loading frequency on the elastic modulus and mechanical loss. It is well known [20, 21] that polymer loading rate affects to the strongest extent the initial elastic modulus of the polymer, which is not characteristic of the true elastic behavior of solids.

Second, the substantial stress relaxation in a glassy polymer in the so-called Hookean region of the tensile (compressive) stress–strain curve seems very unusual. Figure 3 shows a set of such stress relaxation curves for glassy PMMA [17]. It is well seen that the glassy polymer under these conditions exhibits mechanical behavior that is quite untypical of an elastic Hookean solid. Note that stress relaxation is displayed in both the force and temperature sets below T_g and below the yield point.

Third, Lazurkin [17] found that strong birefringence, which relaxed with time, appeared in a strained glassy polymer in the Hookean region. The signs of birefringence are always the same for the polymer subjected to elastic aftereffect deformation and forced elastic deformation; i.e., for the neck-oriented polymer. At the same time, the birefringence sign for elastic strain does not coincide with that of birefringence acquired by the polymer as a result of its molecular orientation. In light of this finding, Lazurkin concluded that there is no fundamental difference between elastic aftereffect strain and forced elastic strain. Both types of strain are associated with large-scale structural rearrangements

Fig. 3. Stress relaxation curves for PMMA in the glassy state. The test temperature was (*1*) 18, (*2*) 25, (*3*) 40, (*4*) 54, (*5*) 71, and (*6*) 83°C. The initial stress was ~0.5 of the yield stress [17].

Fig. 4. Isometric heating curves for PMMA specimens deformed to λ of (*1*) 1.5, (*2*) 2.5, (*3*) 3.25, and 3.9 at 105°C [22].

due to conformational changes in polymer chains. On the basis of obtained data, Lazurkin came to the conclusion that, first, a deformed amorphous polymer possesses a certain molecular mobility with the limits of the glassy state and, second, "both strain types—forced elastic and elastic aftereffect—are orientational in character. They are associated with rearrangements of molecular chains resulting in the appearance of preferable orientation." These results were not interpreted in a comprehensive manner at that time, since it was believed that large-scale molecular motion in the glassy state is frozen-in and any spontaneously occurring molecular processes are impossible on this scale.

Later, a variety of phenomena were discovered that suggested the feasibility of large-scale molecular motion in amorphous polymers below their glass transition point. Such experimental findings include a rise in stress upon isometric heating of a deformed glassy polymer. It turns out [22, 23] that the stress in a stretched specimen increases when the specimen is heated under isometric conditions. It is noteworthy that the stress begins to be detectable well below the glass transition temperature. This finding indicates the possibility of large-scale molecular motion in the glassy state of amorphous polymers. An example of such mechanical behavior is given in Fig. 4. It is well seen that the deformed polymer (PMMA) exhibits a substantial increase in stress in the region of temperatures that are considerably lower than its glass transition temperature (115°C). The feasibility of large-scale molecular motion is revealed even better by studying the thermally stimulated shrinkage of deformed glassy polymers. Numerous works showed that a deformed glassy polymer recovers its dimensions in a rather peculiar

manner upon annealing. This kind of heat shrinkage (Fig. 5) comprises two components.

First, a part of residual strain relaxes in a temperature range below the polymer glass transition temperature during annealing and, second, there is a contribution to the thermally stimulated recovery of the polymer that relaxes at the glass transition temperature. In the works cited above, a number of very important observations were made; in particular, it was shown that the low-temperature component of residual strain is associated with the deformation of a polymer to strains that do not exceed its yield point (Fig. 5) [24].

If a polymer is deformed below its yield point, the material completely recovers its dimensions in a tem-

Fig. 5. (*1*) Stress–strain curve for uniaxial compression of PMMA at room temperature and (*2*) low-temperature and (*3*) high-temperature contributions to heat shrinkage upon annealing [24].

Fig. 6. DSC curves for PS (*1*) deformed by uniaxial compression by 30% and then annealed at 70°C for (*2*) 0.003, (*3*) 0.08, (*4*) 1.5, (*5*) 6, (*6*) 11, and (*7*) and 50 h [8].

Fig. 7. Dependence of (*1*) heat, (*2*) mechanical work, and (*3*) stored internal energy on the strain in the uniaxial compression of PS at 30°C and a strain rate of 5×10^2 min^{-1} [29].

perature range below the glass transition temperature. As the strain increases to values that exceed the yield point, the high-temperature component of heat shrinkage begins to build up in the polymer; i.e., the part of shrinkage that relaxes in the glass transition range of the polymer. In this case, the low-temperature contribution to the size recovery of the specimen does not disappear but just stops to change in magnitude.

If a polymer is deformed above the glass transition temperature, the low-temperature contribution to the thermally stimulated recovery of residual strain com-

pletely disappears, and shrinking entirely occurs in the polymer glass transition region [24, 25].

After deformation of a polymer, there remains a part of strain that relaxes at the experimental temperature immediately after unloading. It turned out that this contribution to thermally stimulated size recovery by a specimen could be fixed by the deep cooling of the polymer in the deformed state [24–26]. After unloading and annealing of such a specimen, this part of residual strain relaxes during annealing in a temperature range below the deformation temperature. This finding is an additional proof of the earlier assumption [17] that the strain of glassy polymer in the Hookean region is not true elastic (reversible) strain.

Another experimental fact that needs to be explained in the context of the data discussed above is an abnormally high value of internal energy stored by a glassy polymer at the initial deformation steps (in regions before and at the yield point). Park and Uhlman [27] found that the difference in enthalpy between deformed and undeformed PC, PE, and PP is of the order of a few joules per gram.

By the DSC technique, it was found [28] that PVC deformed below the glass transition temperature contains a considerable amount of internal energy. An important observation was made that the stored energy begins its release during annealing 30–40°C below T_g. For PS and some of styrene copolymers with methacrylic acid, it was reported [8] that specimens deformed by 40% also store internal energy (6.3 J/g), and the excess of internal energy was associated with the weakening of intermolecular interaction in a polymer, which is due to its inelastic strain.

The influence of strain on the thermal properties of a glassy polymer is displayed in a specific manner. A deformed polymer exhibits a broad exothermic DSC peak below the glass transition temperature (Fig. 6). Above, we have noted that an undeformed polymer "acquires" an endothermic peak during physical aging.

It is noteworthy that these peaks undergo evolution during low-temperature annealing. It turns out that the exothermic peak (curves *1–3*) gradually decreases during low-temperature annealing and disappears at all (curves *4–7*) at long annealing times. At the same time, the endothermic peak due to the physical aging of the glassy polymer increases with the annealing time. In other words, although a spontaneous process accompanied by a decrease in the free energy of the system takes place on annealing, the thermal effects that accompany the physical aging and the structure relaxation of the deformed glassy polymer have opposite signs. Moreover, a comparison of Figs. 2 and 6 shows that both of the aforementioned thermal processes seem not to "notice" one another and evolve independently. In many thermodynamic studies by means of deformation calorimetry [18–31], it was shown that the plastic deformation of polymer glasses is fundamentally different from the corresponding process in low-molecu-

lar-mass solids. It turns out that a considerable portion of deformation work (mainly before and in the yield-point region) is consumed to be stored, not be converted into heat, by the polymer (Fig. 7) [29].

It may be assumed that the aforementioned specific features of the structural–mechanical and thermal behavior are interrelated and manifest the same general mechanism of relaxation of a glassy polymer under temperature–force impact.

Several mechanisms were proposed for explaining all the basic features of the structural–mechanical behavior of glassy polymers. As a first approximation, we may consider a series of studies on thermally stimulated recovery of deformed polymer glasses [24, 25, 32, 33]. In these works, anomalies in the mechanical behavior of polymer glasses are associated with their initial structural inhomogeneity. It is assumed that the mechanism of high-temperature recovery is determined by the entropic relaxation of excited stretched macro-molecular coils and their transition to the initial state via freezing-out the segmental mobility at the T_g of the polymer. In other words, the recovery of an oriented polymer is observed at T_g. The nature of the low-temperature component of recovery was associated with conformational rearrangements in macromolecules induced by the joint action of temperature and internal stresses stored during deformation [24, 25, 32, 33].

By analogy with the term "force-induced elastic strain" this phenomenon was called force-induced elastic relaxation, implying the commonness of the mechanisms of the deformation and subsequent recovery of a deformed polymer, which consists in that the deformation of the polymer is activated by an applied external stress and the recovery, by internal stresses. Later [34, 35], it was proposed in terms of this model that the low-temperature relaxation of deformed polymer glass is due to the heterogeneity of the structure of the initial polymer glasses, and the mechanism of this phenomenon involves the devitrification of local structural regions, which are in abundance in the virgin unde-formed polymer, upon a rise in temperature.

The basic characteristics of this approach are the assumptions on the entropic nature of the observed molecular motion responsible for anomalies in the low-temperature recovery of residual deformation of glassy polymers and the assumption that these abnormalities are predetermined by the nature itself of the initial poly-mer glass having a heterogeneous structure and the set of glass transition temperatures.

Note that the most disputable point in this model is the concept that the initial undeformed polymer con-tains regions with different glass transition tempera-tures. This assumption is conflicting with numerous experimental data, which show that only one glass tem-perature is recorded in measurements on the glass tran-sition temperature of amorphous polymers by various techniques.

Another approach to explaining the same structural–mechanical peculiarities of polymer glass is advanced in [29–31]. The model is based on the concept that all inelastic deformation and steady plastic flow occur in a polymer structure saturated with small-scale plastic-shear strains, not in the initial structure. This structure is excited and metastable. The generation of plastic-shear transformations begins at the very early steps of loading and reaches a steady state at small strains (20–35%). Plastic-shear transformations are the main source of macroscopic deformations. Conformational rearrangements in chains at $T < T_g$ are not immediately induced by stress but result from the decay of plastic-shear transformations. Plastic-shear transformations are nonconformational volumeless shear entities sur-rounded by elastic-stress fields. All the energy stored by a specimen on deformation is concentrated in these fields. The relaxation and physical aging processes and molecular mobility in glass subjected to deformation are closely related to the generation and decay of plas-tic-shear transformations. Mass transfer during glass deformation is effected by small-scale motions of γ, T_g, and probably δ types, not by segmental motions.

The basic characteristic features of this approach are as follows: the assumption that all anomalies in the structural–mechanical behavior of polymer glasses are due to structural changes imparted to the polymer dur-ing its inelastic deformation; responsible for the low-temperature recovery of deformed polymer glasses are certain structural transitions in shear transformations, which are not associated with the entropic elasticity of macromolecules.

A disadvantage of this approach is the assumption that it is certain energy transitions in plastic-shear transformations and the surrounding elastic mechanical stresses that are responsible for the reversibility of large strain in the deformed polymer. At the same time, it is undoubted today that large reversible deformation is the privilege of polymeric solids, and this elasticity origi-nates from the entropic contraction of polymer chains upon their transition to the most probable state [36].

Some authors [8, 37, 38] believe that the plasticity of polymers below their glass transition temperature is due to β-molecular motions.

It is also worth mentioning that the plastic deforma-tion of a solid polymer may be described in terms of the free-volume concept [39, 40].

Note that in all the works cited above, the mecha-nism of plastic deformation was considered on the microscopic submolecular level. It was assumed that plastic deformation in all cases is delocalized in the bulk of the polymer, and its elementary event takes place in a volume of a few tens to a few hundreds of angstroms.

Concluding this section, it should be pointed out that all the abnormalities in the mechanical behavior discussed above are observed in the small-strain region. Indeed, the elastic-aftereffect strain discovered by

Fig. 8. Stress–strain curves for uniaxial compression at 293 K of (*1*) PMMA and PMMA crosslinked with (*2–4*) ethylene glycol dimethacrylate and (*2'–4'*) triethylene glycol dimethacrylate at a crosslinker concentration of (*2, 2'*) 2.5, (*3, 3'*) 5.2, and (*4, 4'*) 11.2 mol % [25].

Lazurkin appears at strains that do not go beyond the yield point. The same strain range is characterized by the buildup of the low-temperature component of the shrinkage of the deformed polymer. The major portion of stored internal energy is also released in the region of small strains that do not go beyond the yield point of the deforming polymer (Figs. 5, 7).

Moreover, the mechanism of inelastic deformation of a glassy polymer at this stage substantially differs from that in the large-strain region (the region of stress decay and the plateau region on the tensile (compressive) stress–strain curve). This, in particular, becomes clear from data reported in [25] on the mechanical properties of PMMA under room-temperature uniaxial compression conditions. The obtained specimens were crosslinked with various amounts of ethylene glycol dimethacrylate. The introduction of the crosslinking agent has a very strong effect on the mechanical behavior of polymer networks occurring in the rubbery state, which is completely consistent with the concepts of the statistical theory of rubber elasticity [36]. As follows from the data presented in Fig. 8, the situation radically changes below the glass transition temperature. The difference in the degree of crosslinking is reflected in the mechanical behavior of the polymer only at strains exceeding the yield strain. Below the yield point, the mechanical properties of the polymer do not depend on the presence or absence of covalent-bonding network at all. This result directly evidences that the mechanisms of deformation of a glassy polymer are substantially different before and after the yield point.

SPATIAL INHOMOGENEITY OF STRAIN IN POLYMER GLASSES

The experimental data considered above raise several important questions. First, what are the reasons behind the anomalies in the mechanical behavior of glassy polymers? Second, is the initial inhomogeneous labile structure of a glassy polymer related in any manner with the abnormalities in its mechanical and thermal behavior?

Recall that these specific features of the mechanical and thermal behavior of glassy polymers are revealed mainly upon their deformation to small elongations.

There are several alternative models used to explain these phenomena. The coexistence of these different points of view is due to the fact that all of them are based on the data obtained with the use of indirect experimental techniques. Indeed, the thermodynamic, kinetic, mechanical, and other investigation techniques themselves do not provide direct information on the mechanism of the phenomena of interest. In order to create a real physical picture in all of the cases discussed above, it is necessary to attract certain model concepts, which inevitably involve some inherent assumptions. It is obvious that these questions cannot be answered unless direct information on structural rearrangements accompanying inelastic deformation of a glassy polymer is available. In this context, it is necessary to consider the available experimental structural data concerning these characteristic features of the structural–mechanical behavior of polymer glasses.

The first thing to be noted is the fundamental difference between the processes occurring in deformed and undeformed polymer glass during low-temperature annealing. Besides this difference in the thermal behavior (cf. Figs. 2, 6), there is another fundamental difference. In fact, the processes of physical aging of polymer glasses occur simultaneously throughout the bulk of a glassy polymer. The observed change in the structure and properties of the polymer also refers to all elements of its volume (the so-called affinity of properties).

At the same time, numerous direct microscopic observations showed that inelastic deformation of a glassy polymer always occurs inhomogeneously throughout its volume. The affinity is characteristic of deformation of amorphous polymers that occur in the rubbery state (in a temperature region above the corresponding glass transition temperature). What is inherent in glassy polymers is the distinct inhomogeneity of deformation by volume. This inhomogeneity is manifested at least in the fact that a neck appears in the polymer under uniaxial tension conditions. However, the structural inhomogeneity of deformation is also observed before necking at strains that do not exceed the strain at yield point in the polymer; i.e., at the point where all the aforementioned abnormalities take place.

Inhomogeneities in the plastic deformation of a glassy polymer, for example, are easy to reveal in the

region of strains that do not exceed the strain at yield point. Nadezhin *et al.* [41] found that high-intensity diffuse X-ray scattering appears at 3–5% elongation of PS and PVAC in the range 10–20°C below the respective glass transition temperatures. This finding unequivocally indicates that certain violation of the continuity of a glassy polymer and the emergence of interfaces that become the source of small-angle X-ray scattering take place under these conditions in the region corresponding to the Hookean portion of the tensile stress–strain curve.
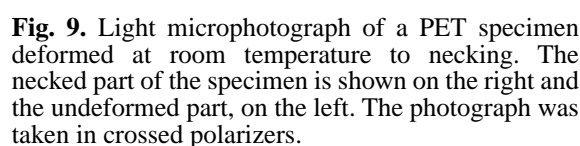
Lazurkin [17] seems to have been the first who noted that polymer deformation becomes nonuniform by volume in the region of the yield point. A system of inhomogeneities appears in the polymer, which are easy to detect with a light microscope and even by unaided eye. These inhomogeneities were rectilinear lines crossing the polymer at an angle of 45°–55° to the draw axis. By analogy with low-molecular-mass solids, Lazurkin called them shear bands and noted that the presence of microscopic inhomogeneities, the stress concentrators, is needed for their emergence.

These shear bands are easy to detect by direct microscopic examination. Figure 9 shows an optical microphotograph of a PET specimen deformed at room temperature with necking. As is seen from this figure, shear bands run through the part of specimen that has not passed to the oriented state (neck). The neck material, at first glance, does not contain such bands. Nonetheless, this material "remembers" that the transition to neck is made by the polymer that contains shear bands. If the PET neck is treated with a solvent in which the polymer swells, shrinking due to this treatment will result in a system of shears in the material [42].
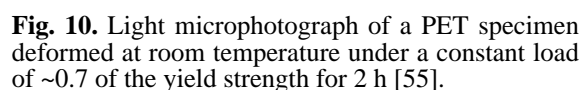
Figure 10 shows a light microphotograph of a glassy PET specimen held at a constant tensile load of 0.6 of the yield strength. It is well seen that inhomogeneities appear in the polymer. Along with the system of shear bands oriented at an angle of ~45° to the direction of tensile stress, other zones of plastically oriented polymer are seen, which propagate normally to the draw axis. These are so-called crazes. They are known [43] to differ from shear bands not only in the direction of propagation but also in the presence of microvoids in their structure.

To summarize, deformation of a glassy polymer is realized in an extremely inhomogeneous fashion at the first steps of its development. Distinct discrete zones of plastically deformed material—shear bands and crazes—appear in the polymer. It is reasonable to assume that the above-discussed abnormalities in the mechanical and thermal behavior of glassy polymers loaded in the region of the Hookean portion of the tensile (compressive) stress–strain curve and in the polymer yield point region are due to structural rearrangements in the polymer at this stage of its deformation.

To establish this correlation, it is of paramount importance to perform direct structural investigation of

Fig. 9. Light microphotograph of a PET specimen deformed at room temperature to necking. The necked part of the specimen is shown on the right and the undeformed part, on the left. The photograph was taken in crossed polarizers.

Fig. 10. Light microphotograph of a PET specimen deformed at room temperature under a constant load of ~0.7 of the yield strength for 2 h [55].

the deformation mechanism. In [43], we showed that this relation is easy to reveal by a direct structural study of solvent crazing of polymers.

In the case of shear (forced elastic) deformation, the generation and development of plastically deformed polymer zones (shear bands), which are freely detectable by direct structure investigation techniques, also take place (Figs. 9, 10).

STRUCTURAL FEATURES OF SHEAR FLOW OF GLASSY POLYMERS

Under uniaxial compression conditions at which many anomalies in the behavior of glassy polymers were revealed [24, 25, 29–35], it is much more difficult to observe the development of shear bands, since a cylindrical specimen takes a barrel-like shape after deformation, so that the detection of individual shear bands in this specimen becomes extremely difficult.

Nonetheless, the use of well-known procedures of sample preparation for direct microscopic examination makes it possible to solve the problem. For example, Bowden and Raha [44] made microscopic sections of samples of some glassy polymers deformed in uniaxial compression and investigated these sections in a polarizing light microscope. It turned out that a deformed glassy polymer (PS, PC, PET, PMMA at 130°C) contains rectilinear bands of ~ 1 μm in width that exhibit strong birefringence and are separated by blocks of the virgin, undeformed material. In other words, a polymer is deformed under these conditions by developing shear bands accompanied by slipping of blocks of unoriented material along these bands. This finding unambiguously indicates that the aforementioned anomalies in the mechanical and thermal behavior of deformed glassy polymers are due to the processes occurring in plastic-deformation zones (crazes and shear bands). This is rather obvious, since the undeformed polymer blocks separated by shear bands have nothing to differ from the initial polymer; i.e., they do not possess an excess internal energy, do not undergo low-temperature shrinking, and do not show any other abnormalities of their physicochemical behavior.

What is important is the undoubted resemblance of craze generation and propagation to the corresponding process of generation and development of shear bands. In particular, it was shown [44] that the amount of shear bands increased with an increase in strain. The buildup of crazes takes place in a similar manner with the increasing strain. Data on craze buildup were obtained by direct microscopic examination, inasmuch as the detection of crazes is considerably facilitated by the presence of real microvoids in their structure [43].

There is another structural variety of nonuniform deformation of glassy polymers. This variety was named diffuse shear zones. Such zones are microscopic shears united into broad regions capable of propagating as a single whole to the entire cross section of a specimen during strain development. An increase in the strain rate and a decrease in the deformation temperature facilitates the transition of strain development from the mechanism of growth of diffuse shear zones to that of growth of individual shear bands. It was found that shear bands more readily appear in annealed and slowly cooled, rather than quenched, specimens [44].

Later, wealth of studies on various aspects of generation, development of structure of shear bands in polymer were performed. The formation of thick, large shear bands (0.1–0.6 mm) was thoroughly studied in [45]. It turned out that there are two steps of this process. In the first step, a batch of thin bands (0.01–1 μm) appears on a stress concentrator, for example, such as an orifice in a polymer plate. These thin bands grow at a rate of the order of 80 mm/s. When the batch of bands reaches the side surface, the second step of the process begins. This is a large-scale shift in the batch of bands towards the formation of a thick shear band and a surface step. The rate of propagation of such a step is about 5 mm/s. Note that the two-stage development of shear bands is very similar to the development of crazes. Indeed, the development of crazes may be divided into two stages, their growth that continues until the crazes traverse the polymer cross section and craze broadening [43].

As has been noted above, the rate of propagation of thick shear bands is very high, of the order of 10 cm/s. This makes it difficult to measure the temperature or the force dependence of the rate. However, Kramer [46] managed to observe the growth of a batch of thin bands in the shear zone of PS, since the zone moved at a significantly lower rate (10^{-5}–10^{-3} cm/s). By measuring the temperature and force dependence of this rate, he obtained an enthalpy of activation of ~273 kJ/mol and an activation volume of 2300 ± 500 Å^3. The latter quantity was found to be close to the corresponding values obtained in the study of dynamics of inelastic deformation of bulk PS (2650 Å^3) [47]. The large values of activation volume indicate that the growth of thin shear bands or shear zones is a cooperative process involving many molecular segments.

Argon *et al.* [48] also made an important observation. They revealed the complete healing (relaxation) of shear bands when the specimen was heated above T_g. During the isothermal annealing of samples subjected to shear deformation [49], its gradual relaxation with time was detected. This process follows the second-order rate law. The Arrhenius plot of the rate of this process allows its activation enthalpy for PS to be calculated (672 kJ/mol). The value thus found is in good agreement with a value of 739 kJ/mol obtained in studying the relaxation kinetics of bulk PS [50]. This result suggests that the processes responsible for the recovery of residual strain in a deformed bulk polymer and the healing of shear bands upon annealing process are the same.

Above, we have noted that a glassy polymer stored a considerable amount of internal energy upon its plastic deformation. Since the accumulation of internal energy takes place mainly at the initial steps of deformation of the glassy polymer, it is reasonable to assume that this process is also due to the generation and growth of shear bands in the polymer.

The results of experimental measurements of stored energy in shear bands are surveyed in [51]. Polystyrene blocks were cut from a thick plate and annealed at 115°C for 20 h ($T_g = 101°C$) with subsequent cooling to

Fig. 11. Electron microphotographs of (a) the shear band structure of PS subjected to small deformation [51], (b) the fibrillar structure of the same shear band after its degradation and (c) the fibrillar structure of a craze in PET deformed in an adsorption-active solvent.

room temperature. Specimens containing an orifice were compressed to obtain thick shear bands originating from the orifice. If compression were not stopped at a proper time, the fracture would occur along the boundary between a shear band and the undeformed matrix. After failure, the material of the shear band was readily lifted from the interface with pincers. Then, the shear-band material was examined by the DSC technique. As was found, it was the shear-band material that contained a large amount of internal energy, whereas the material occurring between shear bands turned out to be undeformed and, thus, to contain no stored internal energy.

The most important thing that required for understanding the phenomena occurring upon inelastic deformation is the structure of shear bands. Note that the shear bands appearing in polymers are fundamentally different from those produced in low-molecular-mass solids. It turns out [51, 52] that the bands have a complex structure. They are filled with a dispersed ori-

ented fibril material that is completely analogous to the material that fills the space of crazes.

This important resemblance is corroborated by direct microscopic examination. When a material containing shear bands is subjected to small stretching, these bands open, exposing a crazelike structure. The similarity to the craze structure is so striking that such open shear bands were called "shear-band crazes" [51]. A certain morphological difference between the shear-band craze and the classical craze is that fibrils in the craze structure are tilted at an angle to the craze plane (Fig. 11a). Figure 11b presents a microphotograph of the structure of shear-band material, which was taken after the fracture of a PS specimen [51]. It is well seen that this material is composed of parallel plates formed by stuck fibrils. Figure 11c shows a microphotograph of the structure of craze material in PET. This micrograph was taken for a brittle-fractured crazed PET specimen. Unlike cleaved surfaces examined in the traditional studies on the structure of crazes [43], the surface to be

Fig. 12. Light microphotographs of (a) sections of a PET specimen of 0.7 mm in thickness subjected to uniaxial extension in *n*-hexanol by 50% at a rate of 100%/min at room temperature to necking, (b) the central part of this specimen at a large magnification and (c) the same in crossed polarizers [55]. See the text for more detail.

studied in this case was cleaved perpendicularly to the polymer draw axis (along the craze wall). Under these conditions, the crack propagates along the boundary between the craze wall and its fibrillar material, thus allowing its viewing from one side (on the side of craze wall). As follows from comparison of Figs. 11a, 11b, and 11c, the craze material and the shear-band material possess a striking morphological similarity. The assumption that both crazes and shear bands contain oriented fibrillar polymer is also corroborated by direct microscopic examinations [51, 52].

It is relatively simple to demonstrate that a polymer can be deformed under the same conditions via either the crazing mechanism or the growth of shear bands [43]. When monolithic PET specimens are stretched in an adsorption-active liquid medium (AALM), crazes are generated on their surface and begin to propagate into the bulk of a specimen. Evidently, as crazes grow, the hydrodynamic resistance to the liquid flow toward their tips increases. Finally, there comes a time when the liquid cannot be supplied effectively and in a sufficient amount anymore to the sites of orientational trans-

formation of the polymer (craze tips). Since the growth of crazes requires the presence of AALM at the sites of active deformation, the polymer "chooses" the alternative mechanism of strain development via the formation of shear bands.

It is this situation that is illustrated in Fig. 12. This figure shows a light microphotograph of a thin section of a 0.7-mm thick PET specimen drawn at room temperature by 50% at a rate of ~100%/min in a hexanol-1 medium (Fig. 12a). It is well seen that crazes under these conditions could not traverse the entire cross section of the polymer for the step of their broadening to start. Nonetheless, the polymer continues to deform in its kernel via the development of shear bands, which does not require the presence of AALM. At a larger magnification of the microphotographs (Fig. 12b), certain important features of this mode of polymer deformation may be noticed. First, the shear bands are excellently seen through a light microscope, thus indicating the presence of well-defined interfaces. Second, the shear bands start from the tips of sprouted crazes, thus indicating that it is the sharp tips of crazes that are the

seeds of shear bands. To summarize, the data presented above give another piece of evidence that the process of their generation has a certain resemblance to the craze generation process. In both cases, in order to generate a zone of localized strain, it is necessary to have a certain inhomogeneity (seed, stress concentrator) in the material.

And third, strong birefringence in shear bands is seen in crossed polarizers (Fig 12c), which indicates that the bands are filled with the oriented polymer. The presence of oriented material in shear bands was also demonstrated in [53, 54], where not only the orientation of a polymer in shear bands was detected but also the degree of its orientation was measured.

A very important question is the structure and properties of the polymer localized in shear lines. It was repeatedly noted that oriented material filling shear zones has a lower density as compared with the surrounding undeformed polymer. Direct evidence for this is a substantial acceleration of methanol diffusion into PMMA shear bands [51].

The results of the experiment reported in [55] also showed that the density of material in PET shear bands is lower as compared with the surrounding block polymer. In that study, we mounted a film with a structure resembling the one shown in Fig. 12, as a membrane in a dialysis cell whose chambers were filled with an aqueous NaCl solution on one side and by an $AgNO_3$ solution on the other side. Earlier [56], it was shown that if crazes run through the film from one side to another, NaCl and $AgNO_3$ solutions, diffusing countercurrently, meet in the craze space and form AgCl crystals, which are easy to detect with an electron microscope. As is seen from Fig. 12, the monolithic PET film deformed in AALM has an unusual layered structure. Crazes containing real microvoids do not traverse across the entire polymer cross section, leaving in the kernel of the film a layer of polymer that has not suffered from crazes but is penetrated by shear bands. Figure 13 presents an electron micrograph of the same PET specimen after treatment with NaCl and $AgNO_3$ solutions. It is well seen that as the result of the procedure described above, AgCl crystals are indeed deposited in precipitate in the craze space, thus indicating the penetration of the NaCl and $AgNO_3$ solutions through the PET films. Moreover, from Fig. 13 it follows that AgCl precipitated not only in microvoids of crazes but also in shear bands, rendering them contrast. This result unequivocally indicates that even though shear bands do not contain real microvoids, they have so insignificant density that a low-molecular-mass liquid can diffuse along these bands as by channels.

In summary, it may be concluded that inelastic deformation of glassy polymers develops in an extremely inhomogeneous manner, being localized in shear bands or crazes depending on external conditions.

Fig. 13. Electron microphotographs of a freeze-fractured surface of a 0.7-mm thick PET specimen subjected to uniaxial extension in *n*-hexanol by 50%. After deformation, the specimen was used as a membrane in a dialysis cell containing aqueous NaCl and $AgNO_3$ solutions [55]. See the text for details.

In both cases, these zones contain a fibrillar polymer and have distinct interface boundaries.

VISUALIZATION OF STRUCTURAL REARRANGEMENTS ACCOMPANYING DEFORMATION AND SHRINKING OF GLASSY POLYMERS

As has been noted above, there are currently several points of view on the mechanism of inelastic deformation and heat shrinkage of deformed polymer glasses. The reason for this is the lack of direct experimental data to disclose the mechanism of observed phenomena. In this context, it is extremely important to develop new investigation techniques that would provide an opportunity for gaining direct information on structural rearrangements accompanying inelastic deformation of a glassy polymer.

In recent studies [55, 57–59], we elaborated a direct microscopic examination procedure that enables this problem to be solved in many respects. In the most general sense, a structural-rearrangement imaging procedure is based on the most fundamental property of solids. All solids change their surface area upon deformation. While the volume of a solid may remain constant, its surface area practically *always* varies. The sign of this variation may be different, the surface increases upon stretching (uni- or biaxial) and decreases upon shrinking.

Fig. 14. Schematic of uniaxial compression of a polymer under conditions when its surface is firmly attached to the compressing surface or the surface freely slides during compression [57].

Fig. 15. Schematic of the experiment on visualization of structural rearrangements upon heat shrinkage of a polymer deformed by uniaxial compression [57] (*1*) uniaxial compression, (*2*) decoration, and (*3*) annealing.

It is on this property of polymers that our procedure for the imaging of structural-rearrangements is based. In order to use this procedure properly, it is necessary to deform a specimen in such a manner that it would be possible to accomplish targeted and controllable changes in its surface area. The principal feature of the "preparation" of specimens to suit this structural-rearrangement visualization procedure is as follows. In [29–35], we subjected to uniaxial compression a cylindrical polymer specimen under conditions when there was the firm joint of the polymer to the compressing surface; as a result, the specimen took a barrel-like form. The process of shape recovery of such a specimen is studied by measuring the dependence of its height on annealing temperature. The polymer deformation that allows specimens for direct microscopic examination to be obtained is conducted under conditions when a specimen can freely slip along compressing surfaces. In this case, the height of the specimen decreases to compensate for the increase in the area of its surface that contacts the compressing surface. It is these specimen surfaces that change their area during the deformation or shrinkage of the specimen (Fig. 14). Obviously, an increase in the surface area implies the carrying over of a part of the polymer from the bulk to the surface upon deformation or, vice versa, a decrease in the surface

area upon shrinkage manifests the transfer of the polymer from the surface to the bulk. The magnitude of change in the surface area is easy to determine by measuring the diameter of a specimen before and after its deformation (shrinkage).

If a thin solid coating is deposited on this surface before deformation (shrinkage), it will reflect structural rearrangements occurring in the substrate upon its subsequent deformation (shrinkage). The mechanism of deformation (shrinkage) of the substrate determines the character of the surface structuring of the coating. In turn, the surface structuring of the coating contains information on the mechanism of deformation of the polymer. Relief formation in the coating is easy to study by direct microscopic examination. The scheme of sample preparation for such a study is given in Fig. 15.

The experimental data considered above show that shear bands, in which the entire inelastic strain of the glassy polymer is in fact concentrated, are developed at the first steps of its deformation. This is indicated by the results of direct microscopic observations [44, 51]. Between the shear bands, blocks of the undeformed bulk polymer are located. As regards the mechanism of the heat shrinkage of deformed glassy polymers, nothing had been known on the structural rearrangements accompanying this process until our studies were published [55, 57–59].

The procedure described in [55, 57–59] made it possible to obtain important information just on the shrinkage mechanism for deformed glassy polymers in the first place. Specimens used in the cited studies were prepared by uniaxial compression followed by decoration in the manner described above. Then the specimens were annealed and the occurring size recovery was recorded.

Let us consider the process of thermally stimulated shrinkage of two PET specimens, of which one was deformed by uniaxial compression above the polymer glass transition temperature (100°C) and the other was deformed below it (at room temperature). In other respects, the both samples were treated in the same manner. Note that despite the fact that both samples were annealed to the same temperature (105°C), the paths they followed to acquire their initial dimensions were substantially different. As is seen in Fig. 16, the specimen deformed at 100°C recovers its size in the PET glass transition region. However, the PET specimen deformed at room temperature recovers its size almost completely in the temperature range below the glass temperature. Another amorphous polymer PS behaves in an exactly similar manner [58]. This thermomechanical behavior of the polymer is fully consistent with the results of studies reported in [24, 25, 29–35].

Figure 17 presents two microphotographs obtained using the above-described procedure in studying the mechanism of heat shrinkage of deformed amorphous PET. The pictures refer to two PET samples that shrunk

Fig. 16. Recovery of the initial dimensions during the annealing of PET specimens deformed by uniaxial compression at (*1*) 100°C and (*2*) room temperature [55].

by approximately the same value (22–24%) by annealing. As we have already noted, the only difference between specimens a and b is that one was deformed above the glass transition temperature (100°C) and the other was deformed at room temperature. It should be noted that during the shrinkage by annealing in the absence of decoration, the surface of the deformed specimens remained smooth in all of its steps regardless of the temperature of preliminary deformation.

It is the presence of coating that allows structural rearrangement in a polymer during its heat shrinkage to be revealed and characterized. Recall that the area of the metal-decorated surface decreases upon heat shrinkage by annealing. In other words, a part of the polymer occurring at this surface diffuses into the bulk. Evidently, the coating cannot "follow" this "surface" polymer. As a result of decrease in the surface area, the contraction of the coating and (owing to good interfacial adhesion) its pulling into the bulk of the polymer take place, which in turn facilitates relief forming on the metal-decorated surface.

Let us consider in more detail what are the consequences of the response of decoration to compression of the substrate polymer deformed above and below its glass transition temperature. From Fig. 17a, it is seen that the shrinking of the polymer deformed above the glass temperature imparts a regular and distinct microrelief to the platinum coating. The process of formation and development of such topography is essentially a special kind of loss in mechanical stability of the hard coating upon its biaxial compression on a compliant substrate. This mechanism was thoroughly discussed in [57–59]. Without dwelling on the details of topography formation, let us note that the microrelief is uniformly distributed throughout the surface of the specimen, thus indicating the general homogeneity of biaxial deformation and, correspondingly, shrinkage of PET above its glass transition temperature. The latter conclusion is rather obvious since the uniformity (affinity) of deformation is an intrinsic property of rubbery polymers [36].

Let us now consider how the applied metal coating responds to the biaxial shrinkage of PET deformed below the glass temperature. As follows from Fig. 17b,

Fig. 17. Electron microphotographs of PET specimens deformed by uniaxial compression at (a) 100°C and (b) room temperature. After deformation, the surface of specimens decorated with a thin (10 nm) platinum layer and the specimens were subjected to annealing at 105°C [57].

Fig. 18. Three-dimensional AFM images of (a) the surface of a PET specimen deformed by biaxial compression (after decoration with a thin (10 nm) platinum layer, the specimens was subjected to biaxial shrinking by 18% in annealing) and (b) a single shear band and (c) the corresponding profilogram [55].

the thermally stimulated shrinkage of the polymer is accompanied by radically different structural rearrangements in the surface layer as compared with the shrinkage of the polymer deformed above its glass transition temperature. At this annealing temperature, the entire surface of the sample is covered by rectilinear bands, which cross the whole surface and each other at various angles. Their lateral sizes are not identical, so that there is quite a broad width distribution of the bands. The atomic force microscopy data (Fig. 18a) show that the bands are furrows of various widths in the polymer surface. Since the detected bands cross the entire sample surface examined, it may be assumed that they traverse the entire cross section of the deformed polymer as well. It is clearly seen that the broader the bands, the greater the depth they penetrate into the polymer surface, and vice versa. It is in this linear grooves (Fig. 18b) that the polymers is drawn from the surface into the bulk.

The experimental conditions are such that in both cases (above and below the glass transition temperature), the polymer surface increases in dimensions as a result of biaxial stretching. The rise in the surface area is inevitably accompanied by the carry over of material from the depth (bulk) of the polymer to the surface. The obtained results corroborate the well-documented ideas that this process above the glass transition temperature occurs homogeneously (affinely) throughout the entire surface, as in the case of deformation of a liquid. The specifics of a polymer as compared with a low-molecular-mass liquid consist in that plane orientation takes place in the polymer, which is evidently responsible for the subsequent heat shrinkage observed in this case.

During shrinkage, the recovery of the former initial surface also proceeds in the homogeneous manner; as a result, the applied coating is also uniformly contracted over its entire area. The affinity of deformation of a rubbery polymer is one of the principal prerequisites of the statistical theory of rubber elasticity [36]. It is this reason that is behind the formation of the homogeneous topography (Fig. 17a) described in detail above [60–62].

In the case of the biaxial deformation of a glassy polymer, the growth in surface area is not uniform. The increment is localized in discrete zones of inelastic strain, the shear bands containing the oriented material. This process is effected by the sprouting and subsequent broadening of shear bands, seemingly, as in the case of generation and growth of crazes [43]. This similarity is emphasized by the results of direct microscopic examination according to which the deformation process during the development of both shear bands [51] and crazes [43] is accompanied by a rise in the number of zones of localized inelastic strain (shear bands and crazes) in the polymer. As a result, a material representing unoriented polymer blocks separated by narrow zones, which contain the highly oriented polymer and are separated from these blocks by well-

Fig. 19. Electron microphotographs of PET specimens deformed by uniaxial compression to different extension ratios—(a) 2.1, (b) 4.2, (c) 9.3, and (d) 14.6%—at room temperature and shrunk by annealing at 80°C [58].

defined interfaces, is formed at the first deformation step in both cases.

The reverse process of heat shrinkage of the polymer deformed below the glass transition temperature also occurs inhomogeneously, since the oriented polymer located in shear bands is responsible for the reversibility of deformation. The data obtained with the use of the new microscopic measurement procedure [55, 57–59] directly show that the shrinking of the polymer primarily takes place in shear bands, as indicated by pulling the coating into the bulk of the polymer in shear zones (straight lines in Fig. 18). In other words, the transfer of material from the surface to the bulk during shrinkage is effected by its diffusion in shear bands, which are excellently "memorized" by the deformed polymer.

The further development of this procedure made it possible to obtain important data on structural rearrangements in a polymer at different stages of its deformation. The procedure [55, 57–59] allows structural rearrangements that accompany the shrinking of the polymer deformed to different degrees to be monitored. Typical results of such an investigation are presented in Fig. 19. At small strains (~2%), the polymer shrinks during annealing, by "pulling" into the surface in straight zones crossing the entire sample, i.e. the shear bands. At the same time, the whole space between these bands remains smooth and undeformed (Fig. 19a). An increase in the preliminary deformation of the polymer to large values (4.2%) noticeably changes the picture of polymer heat shrinkage (Fig. 19b). In addition to shear bands, the formation of "wrinkles" on the sample surface between shear bands is observed. The further increase in the value of preliminary deformation (9.3%) leads to greater and greater involvement of the material located between shear bands in the thermal shrinkage of the polymer (Fig. 19c). At last, at high uniaxial-compression values that knowingly exceed the yield point of the polymer, its all surface acquires a regular microrelief (Fig. 19d). Nonetheless, shear bands that were produced at the late steps of shrinking appear against the background of this topography in the visualized pattern of deformation. The folded relief located between shear bands resembles very much the topography whose formation mechanism was discussed previously (Fig. 17a, [60–62]). This relief revealed by means of the microscopic examination procedure used is similar in outward appearance to that produced by the shrinkage of the polymer deformed above the glass

temperature (Fig. 17a). Recall that the shrinking of a polymer deformed above its glass transition temperature occurs homogeneously; as a consequence, the polymer surface acquires a regular microrelief uniformly distributed over the whole sample surface.

Figures 19c and 19d clearly show, against the background of topography due to the total orientation of the polymer, shear bands that were produced at the first step of polymer deformation. In other words, the development of shear bands takes place at the beginning of polymer deformation (before and at the yield point). In the reverse process, i.e., heat shrinkage by annealing above the glass transition temperature, the polymer first shrinks in shear bands and then in the bulk of the oriented material. The direct microscopic measurement data discussed above allow us to state that the oriented material located in shear bands is responsible for the low-temperature (below glass transition) recovery of oriented glassy polymers. It is obvious that low-temperature shrinkage is due to molecular processes occurring in shear bands.

The structural data presented above for the mechanism of heat shrinkage of a glassy polymer are general in character. Similar results were obtained in the study of thermally stimulated shrinkage of deformed PS specimens. In this case, the experiment was carried out in a somewhat different manner. All samples were deformed to the same degree of compression (~25%), and different shrinkage values were achieved by varying the annealing temperature (Fig. 16).

It turned out that the path by which a certain degree of shrinking is reached does not exert a determining effect on structural rearrangements in the polymer. For example, at a relatively low annealing temperature of 70°C, the shrinkage of a PS specimen is small (1.7%) and its surface is covered by a grid of shear bands (Fig. 20a). An increase in the annealing temperature to 80°C (Fig. 20b) leads to a shrinkage of 7.5%. The shear bands become more pronounced and their density increases. The annealing of PS specimens at 85°C increases the shrinkage to strain values that approximately correspond to the yield point (11%). This process is accompanied by the formation of microrelief between shear bands (Fig. 20c). At last, annealing in the glass transition region (90°C) brings about a shrinkage that noticeably exceeds the polymer yield point and leads to the total shrinkage of the whole of deformed material. It is well seen that the shear bands that appeared at the early steps of polymer deformation (shrinkage) are preserved in this case (Fig. 20d). At large magnifications, it is clearly seen that the shrinking process engages the entire polymer surface (Fig. 20d). Furthermore, note the undoubted similarity in the topography produced by the heat shrinkage of PS and PET (Figs. 19e, 20e), which indicates the commonness of the observed phenomena.

In summary, the obtained data show that a glassy polymer is deformed as though the deformation has two steps. In the first step (before the yield point), inelastic strain is localized in shear bands separated by blocks of unoriented initial polymer.

In the second step (the plateau region on the tensile or compressive stress–strain curve), the total transition of the polymer to the oriented state takes place. It is very important that, according to direct macroscopic observations (Fig. 20d), shear bands generated at the first deformation step are incorporated into the oriented polymer structure, which is created at the second deformation step. The inclusion occurs in such a manner that the shear bands retain their individuality and the set of properties.

Despite of the aforementioned commonness in the mechanisms of inelastic deformation of different glassy polymers, there are certain differences in the sample preparation procedure between this work and numerous studies performed earlier [29–35]. Usually, the deformation of polymers by uniaxial compression is studied on cylindrical specimens. As a result of such deformation, the polymer takes the barrel-shaped form. The reverse process of thermally stimulated size recovery is studied by measuring the height of deformed samples during annealing.

The data on structural rearrangements accompanying the shrinkage of deformed glassy polymers, which we have discussed above, were obtained under somewhat different conditions [55, 57–59]. Recall that the uniaxial compression in these experiments was carried out under the conditions of free sliding of the sample surfaces that contacted the compressing surfaces. As a result of this preparation procedure, the sample did not take the barrel-shaped form [24, 25, 29–35]. This sliding was achieved with the use of pliant (metal or polymer) gaskets that separated the compressing surface from the surface of samples to be studied. Obviously, a required degree of compression of the polymer is easy to reach under these conditions; however, it is not possible to obtain its uniaxial compression curve, since the mechanical response in this case is due to both the polymer per se and the gasket material. This circumstance somewhat complicates the interpretation of results, especially, in the cases when attempts are made at revealing the differences in the structural rearrangements of the polymer upon its deformation before and after the yield point, and (which is important) also complicates a comparison of results obtained by different investigators.

To overcome this difficulty, we developed a new procedure for studying structural rearrangements in a polymer under deformation [59]. As in other works [29–35], a test specimen was a cylinder. However, unlike commonly used monolithic specimens, this cylinder was assembled from disks of ~1 mm in thickness (Fig. 21). After deformation, such a specimen could be disassembled into individual elements and studied using the direct microscopic examination procedure

Fig. 20. Electron microphotographs of PS specimens uniaxially compressed by ~25% at room temperature and shrunk by (a) 1.7, (b) 7.5, (c) 11, and (d, e) 25% by annealing at 70, 80, 85, and 90°C, respectively [58].

described above. Actually, this is the technique of structural tomography of polymers.

The deformation of such samples revealed two aspects to make it clear that the given tomographic procedure does not bring about radical changes in the mechanism of deformation of the polymer as a whole. First, a multilayer specimen whose structure is shown in Fig. 21 is deformed as a single whole by uniaxial compression; as a result, its form changes from cylindrical to barrel-shaped in full agreement with the change observed in [29–35] upon the deformation of a monolithic specimen. Second, the uniaxial compres-sion curve of the multilayer specimen exactly corresponds to that of the monolithic polymer.

This procedure makes it possible to obtain new important information on the polymer subjected to deformation, which is analogous to the information that is usually provided by tomography. Figure 22 depicts the strain in each polymer layer depending on its place (distance) relative to the compressing surface. These experimental data indicate that the polymer deformed by uniaxial compression is very inhomogeneous in terms of structure. Indeed, the PMMA sample deformed by 30% in uniaxial compression contains regions that substantially differ from one another in the

mechanical behavior is practically the same as that of the initial undeformed PMMA (lower curve); for this reason, they are not given in Fig. 23. Layer 4 exhibits a well defined low-temperature components of thermally stimulated size recovery, which appears after reaching an annealing temperature of ~50–55°C. It is from this temperature that the size recovery of all other disks composing the multilayer specimen begins. Moreover, the high-temperature (in the PMAA glass transition region) component of thermostimulated size recovery appears and becomes progressively more significant in samples 5–9. As the distance from the barrel bottom increases, this contribution to heat shrinkage continuously increases and begins to gradually exceed the low-temperature component in absolute value.

To summarize, the cylindrical specimen that is commonly used in experiments on uniaxial compression of polymers is deformed very inhomogeneously. Inside the sample subjected to uniaxial compression, there are zones deformed to different extents. As follows from Fig. 23, these layers not only differ in the value of strain but also respond in different manners to subsequent heating in annealing experiments.

The advantages of the tomographic approach are not exhausted by gaining new information on the mechanical and thermomechanical response of test systems. The combination of the tomographic approach with the procedure of visualization of structural rearrangements developed earlier [55, 57–59] makes it possible to "look into" the interior of the polymer subjected to deformation. Indeed, after deformation of the multilayer specimen, it may be disassembled into constituent elements. The surface of each element can be decorated by applying a hard coating and investigated by direct

Fig. 21. Sketches of specimens used in tests on uniaxial compression in (a) [29–35] and (b) [59].

value of strain. The first three to four layers adjacent to the compressing surfaces practically do not contain residual strain. However, the polymer strain exceeds 70% in the central part formed as a result of compression of the "barrel."

The proposed procedure makes it possible to study the thermally stimulated size recovery of every layer that composes the barrel. In Fig. 23, these data are represented as the absolute change in the height of each layer correlated with the annealing temperature. It is well seen that there are three types of thermomechanical behavior depending on the place of the layer. Layers 1–3, counting from the compressing surface, very little change their size during annealing. Their thermo-

Fig. 22. Uniaxial compressive strain in individual PMMA layers (initial layer thickness of 1 mm each), depending on their position with respect to the compressing surface. The total value of uniaxial compression of the multilayer specimen is 30% [59].

Fig. 23. Change in the absolute value of the height of individual PMMA layers after deformation of the multilayer specimen by 30% at room temperature. The numbering of curves corresponds to the position of each layer with respect to the compressing surface. The vertical line marks the PMMA glass transition temperature [59].

microscopic examination after annealing and associated shrinking.

Such experiments were performed; their results are given in Fig. 24. It is seen that layer 3, which is relatively close to the compressing surface, has a small strain and, correspondingly, a low degree of shrinking (1.7%). This specimen shrinks by pulling the polymer occurring on its surface into the bulk in distinct shear bands. An increase in strain and, hence, shrinkage to 20.8% (layer 5) leads to the engagement of the material occurring between the shears bands in the process of thermostimulated size recovery in the sample (Fig. 24b). Figure 24b shows the initial stage of this engagement; for this reason, the appearing topography looks imperfect and irregular. An increase in the compression of the coating to 45% (layer 7) is accompanied by the appearance of so regular and perfect topography that it becomes difficult to distinguish it from the microrelief produced by shrinking the polymer deformed above the glass transition temperature (cf. Figs. 17a and 24c). The striking resemblance between these figures indicates the extreme similarity, if not identity, of the mechanisms of the development of these topographies. At large strains, a glassy polymer shrinks in the same manner as the polymer deformed above its glass transition temperature. The main feature of such deformation is its homogeneity (affinity). It is not surprising that the involvement of the bulk of the polymer in heat shrinkage takes place in its glass transition range.

VIRGIN STRUCTURE OF GLASSY POLYMER AND ITS EFFECT ON THE MECHANISM OF PLASTIC DEFORMATION

Thus, we have considered two groups of problems related to the specifics of molecular motion in glassy polymers. First, this is a certain type of low-temperature (below the corresponding glass temperature) molecular motion, which is observed in virgin glassy polymers. This type is responsible for the process of physical aging of polymer glasses [8]. The second is molecular motions occurring in the deformed polymer material. They are responsible for the set of physical and mechanical properties that have been considered in detail above: the elastic-aftereffect strain [17], stress rise upon isometric heating [22, 23], low-temperature shrinking of deformed polymer glasses [24, 25], etc.

The question arises of how these types of molecular motion are connected, if at all? Are the structure and properties of a virgin polymer responsible for the observed anomalies in the physicomechanical behavior of deformed glasses, or should they be associated with certain structural entities that appear immediately during inelastic deformation of the polymer?

At present, both points of view are coexisting; a part of researchers relate all anomalies in the physicomechanical behavior of polymer glasses to their original

Fig. 24. Atomic-force-microscopy images of individual layers after deformation of a multilayer PMMA specimen by 30%. The layers were decorated with a thin (15 nm) platinum coating and annealed at 130°C to be shrunk by (a) 1.7, (b) 20.8, and (c) 45% [59].

structure [14, 25, 32–35] and some, to the appearance of certain structures immediately during deformation [29–31].

To answer the questions raised, let us consider the results obtained by some workers who used a combination of several experimental techniques for studying the mechanism of deformation. For example, Parisot *et al.* [63] studied inelastic deformation in PC under uniaxial tension and simultaneously measured the processes of

Fig. 25. (*1*) Tensile stress–strain curve and (*2*) corresponding mechanical losses in PC at room temperature. After reaching the elongation corresponding to point *A* in the stress–strain curve, the stress was released to zero and the sample rested in this state for 1 h. After the rest, stretching was resumed [63].

internal friction. Figure 5 collates the stress–strain curve for PC with corresponding mechanical losses measured simultaneously with uniaxial stretching at a constant rate. It is seen that the loss is first (before applying a mechanical stress) small as, should be expected for polymer glass. After applying the load and well before the polymer yield point (beginning from an elongation of ~2%), a certain new "phase" appears in the polymer, which has a much higher compliance and, correspondingly, greater mechanical losses. The amount of this "phase" continuously increases, since the continuous rise in internal friction is observed, which stops rather sharply after reaching the yield point. The further deformation of the polymer (in the necking region) is not accompanied by an increase in mechanical losses, nor their noticeable decrease takes place. If the deformation of the polymer is terminated in this region of the tensile stress–strain diagram, an abrupt drop in mechanical losses is observed together with stress relaxation. This finding unequivocally testifies to the relaxation (healing) of the new "phase" that has appeared upon polymer deformation. Resuming deformation dramatically increases the level of mechanical loss again, thus indicating the "reanimation" of relaxed regions with an increased level of mechanical loss or, alternatively, the appearance of new regions but in the same amount as in this initial state, after reaching the polymer yield point.

These data distinctly correlate with the results of direct thermodynamic investigations performed using deformation calorimetry [29–31]. In these calorimetric studies, it was shown that the buildup of internal energy by a deformed polymer also takes place only until strains that approximately correspond to the yield point; after this, the energy stops to change substan-

tially. It is also important that the data presented in Fig. 25 are consistent with the results of studies on the thermally stimulated size recovery of deformed polymer glasses. Indeed, a comparison of Figs. 25 and 5 shows that the low-temperature contribution to thermostimulated recovery is realized only until the yield point; i.e. just at the point where losses for internal friction of the deformed polymer emerge and grow. As soon as the yield point is reached, the growth in mechanical losses ceases (Fig. 25) and the low-temperature contribution to the thermostimulated recovery of deformed polymer glass stops increasing (Fig. 5).

The experimental data discussed above indicate that a certain second "phase" having substantially different properties appears in polymer glass during its inelastic deformation. This phase emerges even in the region of the Hookean portion of the tensile stress–strain curve, and its amount continuously increases until the polymer reaches the yield point. As soon as the yield point is reached, i.e., the stress in the polymer ceases to increase, the amount of the generated new phase also reaches a limit and, simultaneously, the stored internal energy stops growing. Consequently, the deformed glass has another structure as compared with its initial state and it may be assumed that the initial nonequilibrium structure is not responsible for the physicochemical and physicomechanical abnormalities exhibited by deformed polymer glass.

Above, we have shown that the deformation of polymer glass in the region of the yield point is accompanied by the development of directly detectable zones of plastically deformed polymers—the shear bands. These bands contain an oriented fibrillar polymer, and it is this polymer that is responsible for the anomalies in the physicomechanical behavior of polymer glasses. The mechanism of deformation and shrinking of deformed polymer glass will be considered in detail below.

To answer the second question about the interrelation between the structure and properties of the initial and deformed glassy polymer, we need to remember another important circumstance. In fact, molecular processes responsible for the physical aging of polymer glass develop simultaneously throughout the bulk of the glassy polymer, i.e., these are affine processes.

At the same time, it should be noted that the deformation of polymer glasses is localized in special zones (shear bands, crazes). All anomalies in the physicochemical and physicomechanical behavior of deformed polymer glasses are due to processes that occur just in these special zones of localization of inelastic strain. Note that these zones are generated and grow directly in the glassy matrix in which the processes of physical aging are inherent. The processes of initiation and propagation of both crazes and shear bands have been thoroughly studied and characterized. In particular, it was shown [43] that both types of such entities in a polymer are developed linearly by the action of mechanical stress. They look as if they "do not notice" that the

polymer matrix itself, in which they propagate, is structured. Moreover, both crazes and shear bands during their growth look as through they do not notice even more serious obstacles. It is well known that both types of entities linearly grow even in more structured media—crystalline polymers in which both crazes [52] and shears [51] propagate rectilinearly, traversing the entire cross section of the specimen.

Taking into account the affinity of the physical aging processes, we may try to evaluate the size of space in which they take place. It is obvious that these volumes are commensurable with the size of the free-volume holes determined by the positron annihilation technique. The amount of such holes is of the order of $(1–2) \times 10^{19}$ cm^{-1}, and their size is ~2 Å [64]. Since these processes occur in the bulk of the polymer throughout, it is clear that the number of such zones is very large and comparable with the number of macromolecules in unit volume of the polymer.

At the same time, the number of zones of localized deformation (shear bands and crazes) is relatively small. This number is easy to estimate by a direct microscopic experiment and it depends on the values of stress, strain, temperature, etc. [43]. The number of zones of inelastic deformation is incommensurable with the amount of microheterogeneities characteristic of the structure of amorphous polymers. In other words, the generation and development of these zones of plastically deformed polymer is not directly related to its internal structural inhomogeneity. Such a small number of generated crazes or shear bands is due to certain occasional structure imperfections (defects, stress concentrators) that are inherent in a real polymer and differ in the extent of "hazard" from the viewpoint of initiation of plastic-deformation zones [43].

Summarizing the material discussed in this section, it may be concluded that the physicochemical and physicomechanical anomalies in the behavior of initial and deformed polymer glasses seem to be due to the fundamentally different processes determined by different kinds of molecular motion. In the former case, molecular motion takes place throughout the bulk of the polymer, leading to its transition to a more equilibrium structural–physical state. In the latter case, the motion is localized in special zones (shear bands and crazes). Its realization leads to the complete recovery of the initial structure and properties of a glassy polymer and the complete healing of the regions of the plastically deformed polymer.

MECHANISM OF DEFORMATION AND THERMOSTIMULATED RECOVERY OF POLYMER GLASSES

The data that have been obtained in direct structural measurements and discussed in the previous sections permit us to take a fresh look at the mechanism of deformation of polymer glasses. In order to have an adequate understanding of experimental data, it is necessary to return to consideration of another type of plastic deformation of polymers, crazing, which has been comprehensively described in our book [43]. Although there is no fundamental difference between crazing and generation of shear bands, it is substantially easier to obtain direct data on the mechanism of crazing as a physical phenomenon. This is due to the fact that a craze contains microvoids in its structure, thus allowing various types of microscopy and small-angle X-ray scattering to be employed for its investigation.

Numerous experimental data concerning the abnormal behavior of crazed polymers could be self-consistently explained using two important peculiar qualities that accompany their inelastic deformation. The first is the experimentally established fact that inelastic deformation of a glassy polymer via the crazing mechanism is accompanied by its dispersion into tiny aggregates of oriented macromolecules, the fibrils, which range from nanometers to tens of nanometers in size. The polymer fibrillization of this kind actually means its transfer to a certain surface layer, since a fibrillar aggregate contains only a few tens of macromolecules, as noted above [65]. Second, numerous studies performed in recent years have established that polymers in thin films and surface layers exhibit special properties, in particular, a substantially reduced glass transition temperature [66–68]. In fact, only these two fundamental features of deformation of glassy polymers made it possible to rationalize the entire set of anomalies in the physicomechanical and physicochemical behavior of crazed polymers.

As has been noted above, crazing is only one of the variety of types of inelastic deformation of glassy polymers. Another type is the forced rubber elasticity or shear flow discussed above. It is noteworthy that there is no fundamental difference between these two types of plastic deformation. Both shear flow and crazing are thermally activated plastic-deformation processes leading to the dispersion of a polymer into fibrillar aggregates of macromolecules. The principal similarity between these types of plastic deformation of glassy polymers was repeatedly emphasized in the literature. The structure of inelastic-strain zones in the polymer in the case of crazing and shear is sketched in Fig. 26. It is seen that there is undoubted morphological similarity between crazes and shear bands [52]. This similarity allows the earlier developed structural approach to be used for describing crazing as a physical phenomenon and for treating the mechanism of shear flow.

In this context, the essential difference between shear flow and crazing, which is revealed by consideration of structural data on both types of plastic deformation of polymers, is also worthy of attention. Figure 27 depicts the size recovery curves for annealing of PC specimens stretched at room temperature in air up to necking (curve *4*) and in AALM via the classical crazing mechanism (curve *3*), as well as PMMA deformed by classi-

Fig. 26. Schematic of the (a) craze and the (b) shear band structure [52].

Fig. 27. Temperature dependence for the size (ε) recovery of (*1*, *2*) PMMA and (*3*, *4*) PC specimens deformed by uniaxial tension: (*1*, *3*) PMMA and PC samples deformed by solvent crazing in *n*-propanol and (*2*, *4*) PMMA and PC sample stretched in air at 100°C (PMMA) or room temperature (PC). The vertical dashed lines refer to the glass transition temperatures of (I) PC and (II) PMMA [43].

cal crazing (curve *1*) and uniformly at 100°C (curve *2*). It is clearly seen that PC deformed to necking exhibits an insignificant shrinkage (~12%) below the glass transition temperature. This thermomechanical behavior is fully consistent with the data that demonstrate two contributions to the heat shrinkage of deformed glassy polymer [43]. In general, the size recovery of such a sample takes place in the polymer glass transition region, as should be expected. However, the crazed specimen shrinks completely (by 95%) below its glass transition temperature. In the case of PMMA, the entire shrinkage of the crazed sample is accomplished in a temperature range below the glass transition temperature, whereas the sample stretched by the mechanism of shear flow at 100°C completely shrinks at T_g of the polymer. Note that the molecular motion responsible for the low-temperature recovery of crazed polymers manifests itself in a temperature range that is more than 100°C lower than the T_g of the bulk polymer.

Direct microscopic experiments showed that the low-temperature shrinking of crazed polymers is due to

structural rearrangements occurring inside crazes. Figure 28 depicts the plots of relative variation in the linear dimensions of crazes and distances between them against the annealing temperature, as obtained in direct microscopic measurements on PC samples deformed in AALM via the classical crazing mechanism. It is seen that the edges of individual crazes almost completely close before the PC glass temperature. At the same time, unoriented fragments of the initial polymer located between crazes not only lack any sign of shrinking but even insignificantly grow in size as a result of thermal expansion. Similar results were obtained by annealing crazed PMMA samples [43].

During crazing in an adsorption-active solvent, the free surface of the fibrillized craze material develops over a wide range of polymer extension ratios. In the case of shear flow, the process occurs only in the small-strain region—before and in the vicinity of the yield point. It is not surprising therefore that, for example, abnormal low-temperature shrinkage upon annealing is observed for crazed polymers over the entire range of deformation (Fig. 27) and for polymers deformed by the shear flow mechanism only in the strain range below the yield point (Fig. 5).

In order to understand the mechanism of plastic deformation of glassy polymers, it is also necessary to analyze data concerning the energy balance for this process. In thorough thermodynamic studies, it was repeatedly shown that accumulation of a significant amount of internal energy of somewhat vague nature takes place at the early steps of deformation (before and at the yield point) of glassy polymers. This effect, in particular, is manifested in a DSC-detectable increase in the enthalpy of a deformed glassy polymer [18], as well as is directly determined by means of deformation calorimetry [29–31]. The reliable detection of the effect of buildup of internal energy by a polymer does not answer, as such, the question of what is the factor responsible for the change in the polymer energy state upon deformation. Bershtein and Egorov [8] believe that a change in intermolecular interaction in a polymer upon its deformation makes a determining contribution to the change in sit internal energy.

In light of the discussed similarity between crazing and shear flow, it is important to determine the feasibility of internal-energy buildup in a polymer subjected to deformation, by increasing its surface energy. In connection with this, two central features of deformation of glassy polymers should be pointed out. First, the buildup of internal energy at the initial steps of plastic deformation is characteristic exceptionally of glassy polymers. In the case of inelastic deformation of low-molecular-mass crystalline solids, all work of deformation dissipates as heat in the first step [31]. Second, the structure of shear bands developed in polymers is radically different from the structure of shear bands observed in low-molecular-mass solids. Shear bands in polymers are filled with a fibrillar oriented polymer [51].

The question now arises as to whether the internal energy accumulated in so significant amounts upon polymer deformation is due to the development of interfaces characteristic of shear bands? To answer it, let us make use of the available experimental data on the structure of shear bands. According to data reported in [51], shear bands are filled by fibrillized polymer material. Taking this circumstance into account, we attempted in [69] to estimate the internal energy that a polymer can accumulate at the first steps of inelastic deformation. This estimation involved contemporary ideas on the structure of shear bands in glassy polymers.

Let the magnitude of inelastic strain in a polymer be given by ε. Assume that at the first deformation steps, all strain is concentrated in shear bands. This assumption is completely consistent with numerous experimental data, which show that a polymer deformed approximately to its yield point is a set of shear bands separated by blocks of the undeformed polymer [44]. Let the draw ratio of the polymer inside shear bands be λ_s. It is easy to show that the specific volume of polymer material in shear bands V_s (volume of polymer material in shear zones referred to the volume of undeformed polymer) is given by

$$V_s = \varepsilon/\lambda_s - 1. \tag{1}$$

According to available experimental data [44, 51, 55], the polymer that fills the shear zones is subdivided into set of fibrils with a diameter D_f. In this case, the total surface area of the polymer in shear zones will be

$$S_f = 4V_s/D_f.$$

Or, taking account of Eq. (1),

$$S_f = 4\varepsilon/(\lambda_s - 1)D_f. \tag{2}$$

The relationship obtained makes it possible to determine the value of surface energy U stored by a glassy polymer during its deformation at the first step when inelastic deformation is effected primarily by the development of shear zones (before and at the yield point):

$$U = S_f\gamma = 4\gamma\varepsilon/(\lambda_s - 1)D_f, \tag{3}$$

where γ is the specific surface energy of the polymer.

The value of the specific surface energy λ_s of the most popular glassy polymers, such as PS, PET, and PMMA, is 0.04–0.05 J/m². Let the polymer draw ratio in shear zones be equal to two. This value agrees with the known experimental data obtained by direct measurement of the polymer draw ratio in shear bands [8]. A typical diameter of fibrils D_f in shear bands and crazes is 10^{-6} cm [43].

If the shear strain ε of a polymer is assumed to be 10% (an approximate value of strain at yield point for many glassy polymers), the specific surface area of the

Fig. 28. Temperature dependence for the relative change in the linear dimensions of (*1*) crazes and (*2*) unoriented areas between crazes in the direction of draw axis for PC specimens stretched in *n*-propanol. The dashed line refers to the PC glass transition temperature [43].

fibrillar material in shear bands will be ~40 m²/cm³ and the corresponding value of the surface energy will be 1.6–2.0 J/cm³. Note that the value of internal energy gained by a polymer, such as PS, PC, or PMMA, before reaching the yield point is 2–3 J/cm³ according to deformation calorimetry data [29–31]. The value of internal energy built up by the polymer at the first steps of deformation, as determined by the DSC technique, also lies within 2–3 J/cm³ [8]. Moreover, Li [51] managed to measure the excess internal energy of the shear-band material. It turned out that there is a simple means of isolating the shear-band-filling material in PS and measuring its stored energy by the DSC technique. Of course, this material in the pure form contains a considerably higher excess (by a factor of 2 to 3) of internal energy. This finding is another piece of evidence that the change in the internal energy of a polymer upon its deformation below the glass transition temperature may be due to the appearance of highly dispersed fibrillar material in shear bands and, hence, the emergence of excess interfaces in the polymer.

This result, despite of the roughness of estimation, allows the substantiated assumption that there is another factor, along with the aforementioned factors (changes in chain conformation, i.e., intramolecular energy due to *T–G* transitions; changes in the molecular packing and intermolecular interaction energy; distortions of bond angles and bonds; rupture of chemical bonds) responsible for the buildup of internal energy by a polymer at the first steps of its deformation. In addition to the other aforementioned possible physical causes of the change in the energy state during deformation, the excess internal energy may be associated

with the development of excess interfaces. Moreover, this contribution to the internal energy of a deformed polymer may be so high that it completely provides the experimentally measurable internal energy gained by the deformed polymer.

The proposed mechanism of buildup of internal energy does not conflict with numerous experimental data obtained by studying phenomena that accompany inelastic deformation of glassy polymers. In particular, with the joint use of IR spectroscopy and DSC techniques it was shown [8] that a change in size by annealing a polymer deformed in the glassy state strictly correlates with a change in its internal energy, as well as, which is very important, is accompanied by the recovery of intermolecular interactions disturbed by deformation. The observed effect is easy to explain in terms of the concepts advanced above. Indeed, the development of interfaces (shear bands with their highly dispersed inner structure) in a bulk polymer must be accompanied by the breaking of intermolecular bonds and, hence, a decrease in the intensity of intermolecular interactions. The reverse process (heat shrinkage of a deformed polymer) resulting in the recovery of the initial structure must be accompanied by the restoration of intermolecular bonds disrupted during the deformation of the polymer and, of course, by the recovery of the intermolecular interaction inherent in the initial polymer. Evidently, all internal interfaces characteristic of shear bands must also inevitably heal in this case.

The proposed mechanism is also supported by the data reported in [8], in which the low-temperature (annealing below T_g) recovery of the geometric dimensions of deformed polymer glasses is associated with large-scale β-molecular motion. According to the authors' interpretation, this type of molecular motion is the local manifestation of segmental motion at sites of increased free volume. This form of molecular motion differs from the principal α-relaxation process in the absence of cooperativity.

Beginning from the mid-1990s, wealth of studies have been performed concerning the specifics of molecular motion in thin (tens–hundreds of nanometers) films and surface layers of amorphous polymers [66–68]. It was shown that a dramatic depression in the glass transition temperature (by tens or hundreds of degrees) takes place in such thin layers. The reasons for this strong lowering of the glass transition temperature are, in particular, associated with the violation of the cooperativity of the vitrification process as a result of spatial constraints on the motion of polymer chains in the cases when the thickness of a polymer film or surface layer is comparable with the undisturbed size of macromolecules. As is seen, these results are in excellent agreement with the cited works devoted to revealing the mechanism of β-molecular motion in polymers. Moreover, it is this strong depression in the glass transition temperature in thin surface layers of amorphous polymers that makes it possible to self-consistently

explain the mechanism of the low-temperature recovery of deformed polymer glasses as well [55].

Naturally, the annealing of a polymer containing shear bands and, hence, excess internal energy, must be accompanied by an exothermic effect, since the formation of surface in a system is always thermodynamically unfavorable and the reverse process—merging interfaces—is always spontaneous. Probably, it is this exothermic effect that is observed in DSC thermograms during annealing of deformed glassy polymers. Figure 6 presents DSC data (as reported in [8]) for glassy PS deformed by compression followed by low-temperature (70°C) annealing for various periods of time. It is well seen that the exothermic peak (curves 1–3) gradually decreases during low-temperature annealing and disappears at all (curve 4–7) at long annealing times, thus indicating the healing of interfaces in the structure of shear bands. The appearance of the endothermic peak in the glass transition region of the bulk polymer during annealing (curves 5–7) is due to the physical aging of glassy polymers and probably refers to the part of the polymer that is located between shear bands. It is noteworthy that the low-temperature shrinking of the polymer takes place simultaneously with the relaxation of the exothermic DSC peak.

The effective healing (merging, coalescence) of interfaces is impossible unless the polymer occurs in the highly elastic (rubbery) state. In this case, the process of decreasing the surface area takes place at a high rate. An example of this process is the cyclic deformation of rubber. It is well known that this process may be accomplished with a very high rate; nonetheless, the rubber surface area increases in each tension cycle and decreases (heals) in each shrinking cycle.

For understanding the observed phenomena, it is important to take into account that the polymer glass transition temperature in thin surface layers not only strongly decreases [66–68] but also, which is very important, strongly extends its range towards the low-temperature side (below the corresponding glass temperature of the bulk polymer). Whereas the glass transition in the bulk polymer occurs in a relatively narrow temperature range [8], this transition in thin surface layers is strongly extended on the temperature scale.

The reasons behind this phenomenon are easy to explain by analogy with interpretation of the low-temperature recovery of crazed polymers. The development of interfaces upon deformation of glassy polymers is accompanied by the appearance in the bulk of the polymer of a material that has a reduced and "smeared" glass transition temperature. A part of this material has the glass transition temperature even lower than the experimental temperature; as a consequence, it relaxes immediately after unloading [24, 25]. Nonetheless, this part of strain can be fixed by deep cooling of deformed polymer, since it is not truly elastic. The slow heating of a deeply cooled deformed polymer leads to gradual devitrification of the oriented highly dispersed

material as its intrinsic local glass transition temperature is reached. As a result, the total gradual low-temperature shrinking, which is entropic in nature, takes place since the shear bands filled with highly dispersed oriented materials traverse the entire cross section of the polymer [55, 57–59]. The devitrification ensures not only the low-temperature shrinking of deformed polymer but also the gradual healing of the interfaces characteristic of the shear-band structure, which were produced in the first steps of deformation. As the glass transition temperature of the bulk polymer is attained, its general disorientation and the healing of all interfaces take place, thus resulting in the complete recovery of the initial structure and properties of the polymer [17].

The integrated consideration of structural rearrangements in a polymer in combination with data on the buildup of internal allows us to suggest the following picture of inelastic deformation and heat shrinkage. The deformation of a glassy polymer at the initial steps (before and at the yield point) actualizes a structure that is composed of two interrelated components, namely, the part of oriented polymer located in shear bands and the blocks of undeformed polymer that occur in between. As shown above, shear bands in polymers possess a highly dispersed fibrillar structure. Consequently, their development is actually the introduction of a considerable amount of interfaces into a polymer. This part of the deformed polymer may be called the surface component of its structure. The generation and development of interfaces in the structure of shear bands seems to be an important contribution to the buildup of internal energy by the polymer.

As we have noted above, the polymer occurring between shear bands is undeformed at the first steps and has nothing to differ in its structure or properties from the virgin unoriented polymer. The further inelastic deformation (the plateau region of stress–strain curves) leads to molecular orientation of polymer blocks occurring between shear bands. The orientation of this part of the polymer takes place without the formation of new interfaces; therefore, there is practically no buildup of internal energy in this deformation step. Let us call this part of oriented polymer the bulk component of its structure. It is noteworthy that the shear bands that appeared at the first steps of polymer deformation are incorporated into the polymer structure and retain their individuality and properties even after the complete transition of the polymer to the oriented state [58].

The annealing of the two-component system that is formed by the inelastic deformation of a glassy polymer is accompanied by the following structural rearrangements. The heating of the deformed polymer in a temperature range below its glass transition temperature results in the shrinking of the shear-band material (surface component), which has a reduced glass transition temperature over a wide temperature range (low-temperature contribution to thermally stimulated recovery). As a physical phenomenon, this part of heat

shrinkage of the deformed polymer is not only to due the entropy-driven contraction of the oriented material that fills shear bands and has a reduced glass temperature but also is accompanied by the healing of interfaces in the structure of shear bands. The interface healing process is characterized by an exothermic effect and the complete relaxation of accumulated internal energy.

The further heating of the polymer leads to the relaxation of the major part of oriented polymer (bulk component), which in essence does not differ from the shrinking of a bulk rubbery polymer and, therefore, occurs in its glass transition range (high-temperature contribution to thermally stimulated recovery).

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SPELL: 1. fibrill<u>iz</u>ation, 2. @, 3. pro<u>f</u>ilogram—ok?