# Reviews

## Structural aspects of deformation of amorphous polymers

***A. L. Volynskii★ and N. F. Bakeev***

*Department of Chemistry, M. V. Lomonosov Moscow State University,*
*1 Leninskie gory, 119899 Moscow, Russian Federation,*
*Fax: +7 (095) 939 0174. E-mail: volynskii@mail.ru*

Experimental and theoretical data on the inelastic deformation of amorphous glassy polymers were analyzed. The decisive role of direct structural methods in determination of the deformation mechanism of glassy polymers was established. A new mechanism of deformation and thermally stimulated recovery of strained glassy polymers was considered on the basis of structural data analysis.

**Key words:** amorphous glassy polymers, mechanical properties, thin films and surface layers, polymer crazing, inelastic deformation and thermally stimulated shrinkage, visualization of structural rearrangements.

### Introduction

The mechanism of deformation of glassy polymer has been the subject of comprehensive research for many years.[1,2] The interest in this problem is due to, at least, two circumstances. First, the deformation of glassy polymers has a number of features not quite understandable at present. One such feature is the difference in the inelastic behaviors of polymer glasses deformed below and above the yield point. Obviously, at the molecular level, the mechanism of inelastic deformation is the same at any stage of polymer deformation, namely, this is the orientation of polymer chains. The difference is in the fact that at the first stage (before the polymer yield point), the orientation takes place in narrow local areas, shear bands, that percolate through its bulk. After the yield point has been attained, the total transition of the polymer into the oriented state starts throughout the bulk. An especially intriguing item is the nature of the deformation reversibility of the oriented polymer glass during annealing at temperatures below the glass transition temperature.[3,4] Second, the extensive practical application of glassy polymers requires the most in-depth understanding of their mechanical behavior.

The purpose of this review is to analyze the modern views on the structure and the mechanism of inelastic deformation of amorphous glassy polymers. The attention is focused on the direct structural studies of the deformation mechanism of glassy polymers carried out in recent years. The results of these studies allow one to formulate new views on the mechanism of structural modifications that accompany inelastic deformation and thermally stimulated recovery of deformed glassy polymers.

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## Spatial nonuniformity of the plastic deformation of polymers

Amorphous polymers are structurally inhomogeneous solids with inhomogeneity dimensions of several to several tenths angstrom.[5–7] The structural inhomogeneity of an amorphous polymer has a fluctuative nonequilibrium nature, rather than a phase nature,[8,9] which creates substantial experimental difficulties in the studies of the structure and mechanism of modifications in amorphous polymers. The reason is that diffraction methods based on phase contrast of the samples (powder X-ray diffraction, electron-diffraction) are inapplicable. Repeated attempts[10,11] to use direct microscopic methods did not result in any universal model for the structure of amorphous polymers or the deformation mechanism that would take into account their structural inhomogeneity.

There exist at least three fundamental types of plastic deformation of solid polymers. In particular, shear yielding,[12] crazing,[13] and necking[14] processes exist under various conditions (in some cases, coexist). The three types of inelastic deformation have much in common, because they are based on the same structural modifications at the molecular level. One of the above types of plastic deformation of polymers (crazing) has a very important specific feature. The development of plastic deformation occurs in this case in narrow areas, crazes, containing microscopic voids. Due to the development of microvoids, the origination and development of crazes can be easily detected and studied in direct microscopic experiments.[15] Moreover, in these studies, structural modifications in the deformed polymer can be directly juxtaposed with its mechanical response. The multistage nature of crazing and its relationship with the mechanical response of the deformed polymer has been demonstrated using this method.[16]

The general pattern of inelastic deformation of a polymer by the classical crazing mechanism is shown in Fig. 1. In the first stages of polymer drawing before and about its yield point, a certain number of localized deformation areas (crazes) arise on its surface. The crazes grow along the direction perpendicular to the polymer drawing axis, while their width remains virtually constant and very small (fractions of a micron) (craze growth stage). This process goes on until crazes cross (percolate) the sample cross-section, which corresponds to the stretching curve reaching the plateau. After that, the next stage of polymer crazing, namely, craze broadening, starts. At this stage, the crazes that have percolated through the whole polymer cross-section grow along the stretching axis at a constant stress (the plateau region in the stretching curve). This is accompanied by the overall transformation of the polymer into the oriented (fibrillized) nanoporous state. These data allow one to conclude that the polymer is deformed in different ways before and after the yield point. Before the yield point, the narrow areas of the polymer occurring under plastic deformation percolate through its cross-section, while at higher deformations, these areas are broadened.

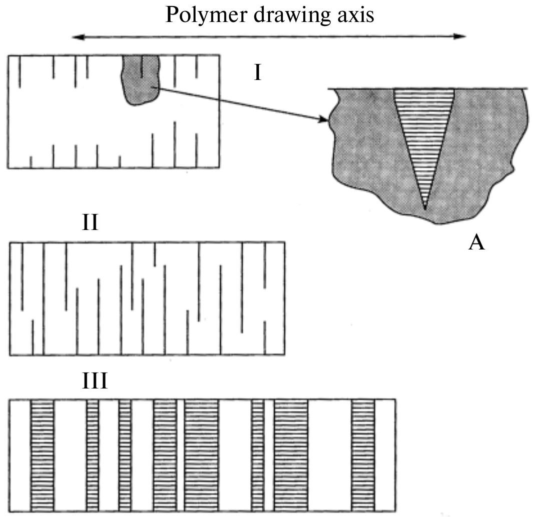

**Fig. 1.** Structural rearrangements of the polymer during deformation according to the classical crazing mechanism based on direct microscopic examination:[16] A is the craze vertex, I, II, III are the stages of initiation (I), growth (II), and broadening (III) of crazes.

Study of the structural modifications under conditions of shear plastic deformation is somewhat more difficult than the study of crazing due to the lack of microvoids in shear bands. Nevertheless, there are serious grounds to believe that the uniaxial stretching of the polymer by the shear plasticity mechanism involves similar structural modifications.[1,14] Apparently, the appearance of the neck, like the initiation of crazes, is due to the presence of defects or weak spots within or on the surface of the specimen. The shear flow of a material starts with the formation of the deformation sloping area (shear band). After this area has crossed the specimen cross-section, it changes the direction to that normal to the stretching axis and propagates within the specimen as a neck.

In the case of uniaxial compression, the yield point is also matched by a situation where a shear band appears at a certain point of the specimen and then propagates (percolates) through the whole cross-section. Subsequently, the stress decreases or remains constant. The compression flow of amorphous polymers, namely, polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), can be regarded as the shear yield accompanied by multiple development of shear bands. The shear bands can be readily seen in an optical microscope, which attests to the presence of clear-cut interfaces.[17–22].

Thus, plastic deformation of glassy polymers is accompanied by extensive structural modifications. The most important feature of these modifications is the appearance and development of real interfaces, irrespective of the deformation type. Under crazing conditions, a highly dispersed porous structure of the crazes is formed. Under shear plastic deformation conditions, shear bands appear.

## Molecular motion behavior in polymer thin films and surface layers

Since the inelastic deformation of a glassy polymer is nonuniform throughout the bulk and results in multiple interfaces, we would analyze the research into polymer structures and properties in thin interfacial layers. The studies carried out in recent years starting from the mid-1990s led to the discovery of a series of remarkable effects. The results of these studies were so unexpected and important that taking them into account would require revision of many views on the structure and properties of polymers, which seemed well established and final.

The first systematic research[23] dealing with high-precision measurement of the glass transition temperature ($T_g$) in thin films of a glassy polymer was published in 1994. The $T_g$ of thin PS films applied onto a hydrogen-passivated silicon substrate were determined by ellipsometric measurements. The film thickness was varied from 3000 to 100 Å. It was demonstrated that for a film thickness less than 400 Å, the $T_g$ value of the PS film starts to decrease sharply compared to $T_g$ of the block polymer. For a 100 Å-thick film, this decrease was 25 K, which was far beyond the error of ellipsometric determination of $T_g$. In this study, the molecular mass (MM) of PS varied from $120 \cdot 10^3$ to $2900 \cdot 10^3$, whereas the corresponding coil dimensions ($R_{ee}$ is the average distance between the ends of a non-perturbed macromolecule) ranged from 200 to 1000 Å. In all cases, the researchers[23] did not notice any dependence of $T_g$ on the MM. A large number of later publications have been devoted to this topic.[24—34] In particular, procedures for the preparation and study of properties of thin polymer films supported on solid substrates and or free thin films and the properties of thin surface layers of block polymers were developed.

Let us consider the properties of free thin films and surface layers of block polymers. In order to gain information on the properties of thin films non-perturbed by the substrate, procedures for the preparation of unsupported thin (hundreds of angstrom) films and procedures for measuring $T_g$. in these films have been developed.[35] A relevant example is provided by a publication[36] in which the Brillouin scattering and ellipsometry have been used to measure $T_g$ in two PS thin films with different MM as a function of film thickness. The results for free and $SiO_x$-supported films were compared. For free films, a sharp (>60 °C) decrease in $T_g$ starts from $h \approx R_{ee}$. For the same films supported on substrates, a decrease in $T_g$ was also observed but this was only 4 °C. This difference was attributed to the influence of the substrate.

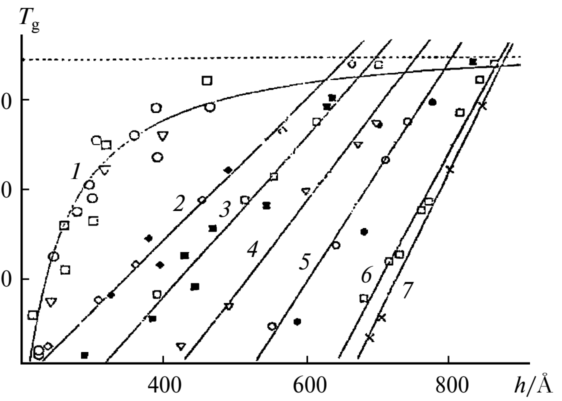

**Fig. 2.** Glass transition temperature of free PS films *vs.* film thickness: 116—347 (*1*), 541 (*2*), 691 (*3*), 1250 (*4*), 2077 (*5*), 6700 (*6*), 9000 k (*7*). The molecular mass of PS is indicated near the corresponding curves.[37] The dashed line shows the glass transition temperature of block PS.

Since most studies of free films have been carried out for PS, the experimental data obtained by different researchers can be generalized (Fig. 2).[37] It was found that the decrease in $T_g$ is much more pronounced in this case than for films on solid substrates. Moreover, the dependences of $T_g$ on thickness for PS were found to be different for samples with different MM. These dependences can be classified into two groups. At relatively low (see Fig. 2) MM values ($\leq 350 \cdot 10^3$), the variation of $T_g$ *vs.* film thickness is qualitatively similar to that obtained for supported PS films. In this case, $T_g$ starts to decrease gradually starting from film thicknesses of 50—70 nm and does not depend on the molecular mass of PS. However, for higher molecular masses, this influence does exist. For each MM, the dependence of $T_g$ on the film thickness becomes linear; in each case, there is some film thickness after which $T_g$ sharply decreases according to a linear law. The higher the polymer MM, the more pronounced the decrease in $T_g$ with a decrease in film thickness; the linear decrease in $T_g$ starts at smaller film thicknesses for higher MM.

Thus, in the case of free thin films, the glass transition temperature substantially decreases compared to that for the block polymer. This decrease is rather great and markedly depends on the polymer molecular mass.

This raises the question of whether similar processes occur in thin surface layers of block polymers? To answer this question, a number of studies dealing with the properties of the nanometer-thick surface layers of amorphous polymers have been carried out. These studies differ somewhat in procedural aspects from analogous studies of thin films. They are mainly based on the mechanical probing of the surface of block polymers. Procedures based on the atomic-force microscope principle proved to be most effective for this purpose.[26,38] The fact is that the mechanical response of the polymer surface depends substantially on its physical state. These procedures allow one not only to determine the local glass transition temperature but also to estimate the dynamic mechanical behavior of the polymer surface layer. On the basis of these data, it has been found[30,39] that in thin surface layers of PS and the PS—PMMA copolymer, the $T_g$ value is reduced by many tens of degrees. Recently, a new procedure for the study of the properties of a polymer surface has been developed;[40] this procedure actually combines the advantages of the probe microscopy and differential thermal analysis. This study made use of an atomic-force microscope with a thermal probe in order to carry out local thermoanalysis and to determine $T_g$ of a thin surface layer of a block polymer. Analysis of the atomic-force images thus obtained allowed the researchers[40] to conclude that the surface of a block polymer has a several nm-thick layer in which $T_g$ is sharply reduced.

Further perfection of the methods of surface probing of polymers allowed researchers to obtain new information on the structure and properties of the surface layers of block polymers. Indeed, a new procedure (new probe method to explore the dynamic mechanical properties of polymers near $T_g$) has been used to study[41] the surface properties of solid polymers by introducing nanoparticles (1—4 nm) of noble metals into their surface layer. During vacuum deposition, first, dispersed spherical metal particles with sizes depending on the polymer—metal pair and deposition conditions are formed on the surface.[42,43] Using X-ray photoelectron spectroscopy, it is possible to estimate the depth of penetration of these particles into the polymer surface layer.[44] For PS and PC, it has been shown that the surface layer has a reduced glass transition temperature compared to that of the block polymer. Presumably, the molecular motion near the surface is facilitated owing to the additional degrees of freedom.

Important results have been reported in a series of recent publications,[45—47] dealing with the diffusion of macromolecules through the interface below the glass transition temperature. The surfaces of polymers (PS and polyphenylene oxide (PPO)) were attached together and maintained in contacts for different periods of time at different temperatures, which were always below the glass transition temperature. It was found that both the contact between identical surfaces (PS—PS and PPO—PPO) and the heterophase contact (PS—PPO) give rise to adhesion. The strength of this adhesive contact is proportional to $t^{1/4}$, *i.e.*, it is controlled by diffusion. This result points unambiguously to a high segmental mobility in the polymer surfaces in the temperature range much lower than their bulk $T_g$.

Thus, the study of the molecular mobility and the properties of thin (nanometers or tens of nanometers) surface layers of block polymers has shown that intensive molecular motion is typical of these layers and thin films. This molecular motion is intensive to an extent that the surface layers of block polymers have substantially lower glass transition temperatures than the polymer bulk. Some researchers[28,45] believe that all glassy polymers are coated at room temperature by a very thin layer of the devitrified rubber-like material. Quite naturally, the efforts of many researchers have been aimed at determining the mechanism of this phenomenon. Nevertheless, no consensus view on the mechanism of this pronounced decrease in $T_g$ in thin surface layers has been elaborated as yet.

This problem could be solved, for example, by considering the specific features of polymer vitrification in a confined volume. In this case, the polymer phase is so small that realization of the equilibrium conformations of chains is hampered and the large-scale molecular motion changes. The glass transition is known[48,49] to be due to cooperative molecular motion which can occur only in the presence of a rather extended polymer phase. The results of a large number of studies can be interpreted in favor of the hypothesis that the decrease in $T_g$ is due to violation of the cooperative nature of the molecular motion upon polymer glass transition in thin films and surface layers.[50—53] Apart from the experimental studies cited above, this hypothesis is supported by a number of theoretical works. Using an interaction model, it has been shown theoretically[54] that a sharp decrease in $T_g$ takes place when the thickness of the free film becomes smaller than the distance between the ends of the nonperturbed chain. This fact may be responsible for the dependence of $T_g$ on the MM in thin polymer films. Presumably, free films with higher MM, first, induce the in-plane orientation of polymer chains when the distance between the ends of a nonperturbed film becomes comparable with the film thickness and, second, they decrease the cooperative length of the chain segments near the surface. As a consequence, the scale of the local segmental motion of molecular units decreases near the interface. The decrease in $T_g$ is attributed, in particular, to the decrease in the interaction parameter in the interaction model. The calculation of $T_g$ in terms of this model provides a good agreement with the experimental resulrs. The idea of possible existence of a "sliding" type of molecular motion of polymer chains in confined volumes, put forward in a publication[55] is a sort of this standpoint. According to calculations, in this case, too, the glass transition temperature should decrease when the geometric dimensions of the polymer phase become commensurable with the nonperturbed size of the macromolecules.

Equally popular is the viewpoint according to which the reduction of the glass transition temperature in the surface layers is due to segregation of the end groups of macromolecules in them.[29—32] The segregation concept of the end groups near the interface is based on the fact that, according to the Fox—Flory theory,[56] the chain ends act as a polymer plasticizer and thus decrease $T_g$. It is assumed that the higher concentration of the end groups in the polymer surface layers compared to that in the bulk results in a higher local content of the free space in them and thus decreases the glass transition temperature.

To conclude this section, we would like to cite a study[57] whose results can support both hypotheses. For elucidating the mechanism of decreasing $T_g$ in the surface layers and thin films of amorphous polymers, three polystyrene (PS) samples with different end groups were synthesized, in particular, (*1*) usual PS, (*2*) that with $\alpha,\omega$-PS$(NH_2)_2$, and (*3*) that with $\alpha,\omega$-PS$(COOH)_2$, as well as a large number of monodisperse fractions of each of the polymers. The nature of the end groups and the MM were varied in order to identify the effect of the end groups and the cooperative length of the structural element being vitrified on the decrease in $T_g$ near the surface. The $T_g$ values were determined by atomic force microscopy and scanning viscoelastic microscopy, which allows one to find the dynamic mechanical characteristics in the polymer surface layers. Using the photoelectron X-ray spectroscopy, the concentration of end groups near the surface was estimated. It was shown that a decrease in $T_g$ related to the change in MM can be traced both for the block and for the surface. A decrease in the surface $T_g$ compared to the block $T_g$ was observed over the whole MM range. The surface $T_g$ starts to decrease at lower molecular masses and decreases more sharply *vs.* MM than the block value. An exception is PS with $(COOH)_2$ end groups, which does not show a dependence of the decrease in $T_g$ on MM, although $T_g$ on the surface is still lower than in the bulk. Using the temperature—time superposition principle, the effective activation energy of $\alpha$-relaxation ($\Delta H$) was determined. It was shown that in all cases, the activation energy of the $\alpha$-transition in the surface layer equals 230±10 kJ mol$^{-1}$, whereas this value for the block polymer ranges from 360 to 880 kJ mol$^{-1}$, according to different estimates.[58] The results of this study indicate that the above factors can both contribute to the decrease in $T_g$ on the polymer surface.

## Structural and mechanical properties of polymers with a thin solid coating

The information considered above indicates that, first, the structural rearrangements that ensure the inelastic deformation of solid polymers are accompanied by development of phase interfaces, and, second, a polymer existing in thin surface layers has specific properties sharply differing from those of a block polymer. For adequate understanding of the structural features of the deformed polymer, direct microscopic data are required. Direct investigations of the structures of amorphous polymers present a serious problem, as they have no phase contrast and, therefore, the conventional structural methods such as powder X-ray diffraction, electron diffraction, and microscopy are inapplicable.

Recent years have seen vigorous development of studies into the mechanical behavior of polymer films with a thin solid coating deposited on the surface.[59,60] The deformation of coated films results in a unique type of surface structurization bearing important information on the deformation mechanisms of both the thin coating and the substrate polymer. Owing to the latter circumstance, study of the structural rearrangements of these films can be used as a versatile direct microscopic procedure for investigation of the deformation mechanisms of solid polymers.

Now we consider the key structure-mechanical properties of polymer films with a thin hard coating, below referred to as a "hard coating on a pliable substrate". The electronic photomicrographs of three such objects are shown in Fig. 3. It can be seen that deformation of sys-

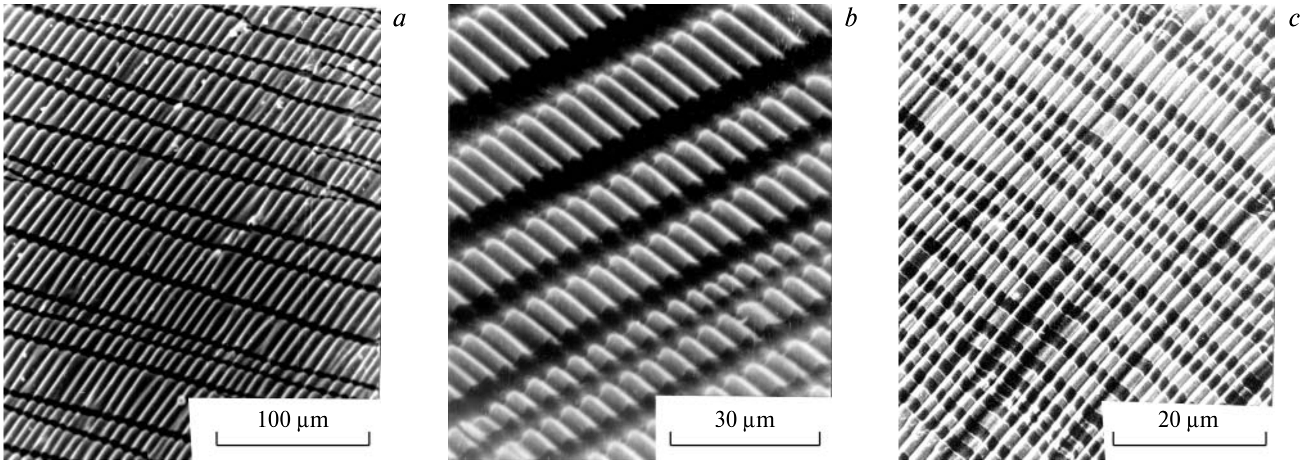

**Fig. 3.** Scanning electron micrographs of the films of natural rubber with a thin (10 nm) gold coating after stretching by 50% at room temperature (*a*); polyvinyl chloride with a thin (10 nm) platinum coating (*b*), and PETP with a thin (15 nm) platinum coating after stretching by 100% at 90 °C (*c*).

tems of this type is accompanied by at least, two general phenomena: cracking of the coating to form numerous islands (cracks grow at right angle to the stretching axis of the substrate polymer) and appearance of a microrelief. Amazing is the regular pattern of the microrelief and its strict orientation relative to the stretching axis of the substrate. The hollows and hills of the arising microrelief are always oriented strictly along (parallel to) the stretching axis.

Detailed investigation of these phenomena has shown that they are general and do not depend on the nature of the substrate or the coating materials. As substrate polymers, polyethylene terephthalate (PETP), PS, PC, polyvinyl chloride, polyethylene, polypropylene, and various rubbers were used. The coatings used included gold, platinum, copper, aluminum, silver, lead, silicon dioxide, carbon, and even a rigid-chain polymer, nitrocellulose. In all cases, during deformation of systems of this type, repeated regular cracking of the coating took place to give a regular microrelief.

It was shown that these phenomena occur when the following conditions are met: (i) substantial difference between the moduli of elasticity of the coating and the substrate (several decimal points), (ii) negligibly small thickness of the coating compared to the thickness of the substrate.[61—63]

For understanding of the mechanism of appearance of regular structures of the given type, it is significant that the polymer film subjected to uniaxial stretching experiences simultaneously two kinds of deformation. The elongation along one direction is accompanied by contraction in the perpendicular direction. Therefore, the solid coating on the film surface also experiences two kinds of deformation: compression and stretching. This fact allows both phenomena, that is, the formation of a regular microrelief and the regular fragmentation of the coating to be considered separately.

It is the coating compression that is responsible for the appearance of the regular microrelief. The coating is an anisodiametric solid that undergoes uniaxial compression on the surface of the stretched polymer film. The phenomena that accompany uniaxial compression of anisodiametric solids were first considered by Euler more than 200 years ago. He demonstrated that during uniaxial compression of an anisodiametric solid (fiber, film, membrane), after a critical load is reached, the solid loses stability and assumes a half-wave shape (Fig. 4, *a*, *b*). If an anisodiametric solid, in particular, a thin hard coating, is firmly attached to a pliable substrate (base), the pattern of the loss of stability by this coating dramatically changes. When the critical compressing strength has been attained, the solid is unable to assume the half-wave shape, because a deviation from the straight shape would give rise to a restoring force from the substrate proportional to the magnitude of deviation. Due to interaction between the applied external force and the arising internal resistance from the substrate, the coating would be inevitably folded like a folding rule, thus acquiring a sinusoidal shape with the wave period $\lambda$ (see Fig. 4, *c*, *d*).[61—63]

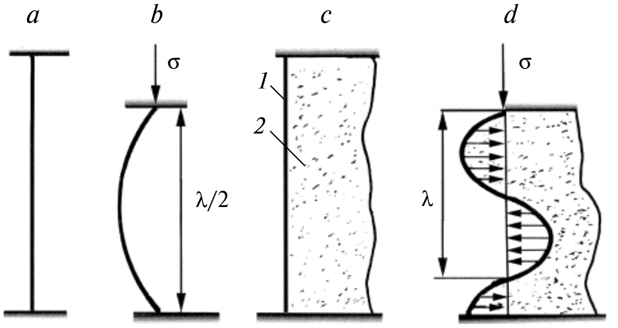

**Fig. 4.** Scheme of the loss of stability of an anisodiametric solid on uniaxial compression in the free state (Euler loss of stability) (*a*, *b*) and on a pliable substrate (*c*, *d*): (*1*) coating, (*2*) substrate.

The relief period is determined by the following facts. The work of deformation for compression of an anisodiametric solid (in this case, the coating) increases with an increase in the number of bends (*i.e.*, with a decrease in the relief period). However, the pliable but rather long substrate attached to the coating induces modifications of this process. It is evident that the greater the relief period, all other factors being the same, the greater the relief amplitude. An increase in the relief amplitude implies detachment of a part of the polymer "attached" to the substrate to a relatively large distance from its initially smooth surface. This substrate deformation requires a substantial effort, *i.e.*, a definite work is to be performed. In other words, an increase in the period of the arising relief, which is "favorable" for the coating, is absolutely "unfavorable" for the pliable polymer substrate. The real relief period is found from the minimization condition of the general balance of forces (stresses) in the coating and the substrate.[61—63]

The regular fragmentation of the rigid shell is also related to specific feature of the transfer of mechanical stress from the pliable substrate to the solid coating through the interface. The pattern of regular fragmentation of the coating depends, in particular, on the mechanism of substrate deformation. It is well known that polymer films can be deformed in, at least, two ways: either uniformly (like a piece of rubber) or nonuniformly (inelastic deformation of the polymer to give a neck or a craze). In the latter case, the fragment of the initial nondeformed polymer and a fragment of the deformed polymer that has passed into the oriented state coexist continuously during deformation (see Fig. 1). Although in both cases, the fragmentation of the solid coating occurs regularly, this regularity is attained in different ways.

In the case of uniform deformation of the polymer substrate, the regular fragmentation of the coating is not attained immediately.[64] During the early stages of stretching, the dimensions of the coating fragments are not identical. This is due to the fact that in early destruction stages (when the elongation of the polymer substrate is small), the crucial contribution to the coating fragmentation is made by surface microdefects typical of any real solid, which initiate the destruction of the coating at the sites where they are accumulated. Defects of this type are randomly (chaotically) arranged in the coating, which is responsible for the irregular, random destruction. However, this early broad size distribution of coating fragments is followed by a rather interesting and unique process, namely, destruction of each of the fragments. After the random disintegration of the coating into fragments, the substrate stretching continues and, therefore, each fragment formed remains under load (Fig. 5). The stress in each fragment is distributed nonuniformly. It is zero on the fragment ends, while as a fragment of the coating moves away from the end, the stress grows and reaches a maximum exactly at the center. During further stretching of the substrate, the stress in each fragment increases and, finally, it reaches the ultimate stress limit exactly at the center of the fragment. These processes induce a remarkable destruction of the coating through division into two equal parts. The "division" can be observed in direct microscopic experiments; it continues as long as the weak pliable substrate can transmit a stress exceeding the coating strength to coating fragments (Fig. 6). In view of the foregoing, the fragment dimensions become equal and a system with a rather narrow size distribution appears on the substrate surface.

The coating splits even more regularly upon nonuniform deformation of the substrate polymer.[65] This results in an extremely narrow size distribution of the coating fragments (Fig. 7). Actually, the structure formed is composed of very thin ribbons of the coating virtually identical in size, parallel to each other, and extending from one end of the sample being deformed to the other. The reason for the spontaneous formation of this unique structure is that the set of characteristic defects of the coating does not participate in the fragmentation. During nonuniform deformation, a fragment of the initial nondeformed polymer continuously coexists with a fragment of the deformed polymer that has passed to the oriented state (so-called neck). This means that two parts of the coating also coexist, namely, the one split into fragments on the deformed part of the polymer and the intact part that coats the nondeformed area of the polymer. All events associated with the coating fragmentation take place in a narrow moving area located between the oriented and nonoriented parts of the deformed polymer. This area always includes the edge of the fractured coating the stress

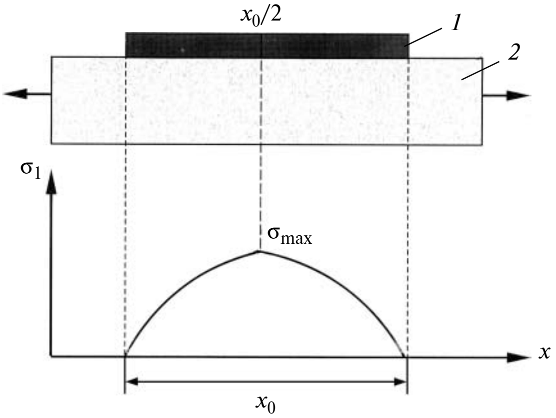

**Fig. 5.** Scheme of fragmentation of the hard coating on uniaxial affinity stretching of the substrate polymer: (*1*) coating, (*2*) substrate, $x_0$ is the size of a coating fragment, $\sigma_1$ is the deformation stress in the coating.

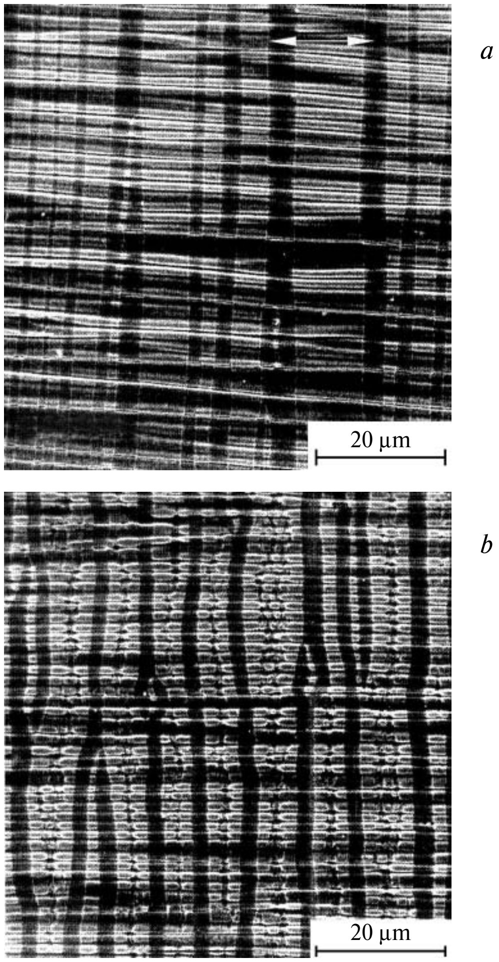

**Fig. 6.** Scanning electron micrographs of a PETP sample with a thin (15 nm) platinum coating after stretching by 50% at 90 °C (*a*) and the same sample after stretching by additional 50% at a higher stress (*b*).

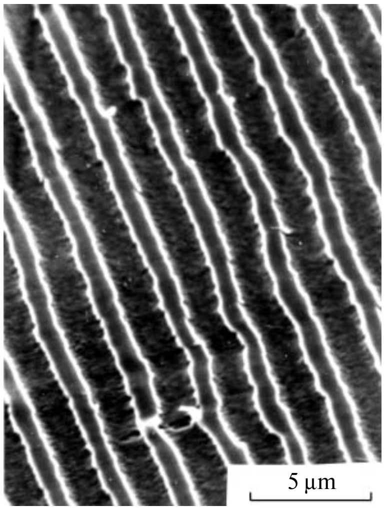

**Fig. 7.** Scanning electron micrographs of the surface of a PETP sample with thin (15 nm) platinum coating after stretching by the classical crazing mechanism.

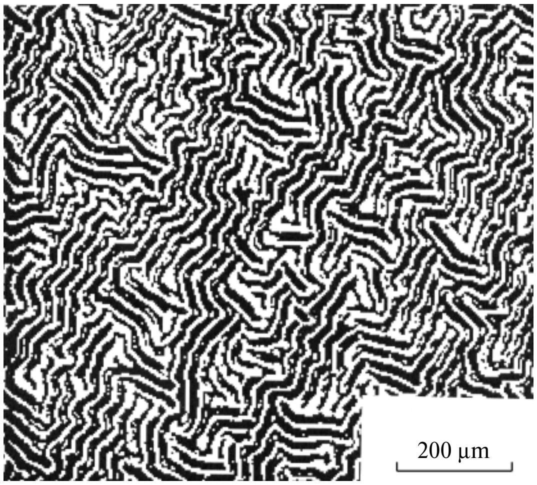

**Fig. 8.** Optical micrograph of an PDMS sample with a thin (50 nm) gold coating applied on the surface at 110 °C.[66] The photograph was taken after cooling the sample to room temperature.

in which is evidently equal to zero. On moving away from the edge, the stress in the coating grows and rapidly reaches the ultimate stress limit. This is the instant the every next ribbon of the coating is torn off. The presence of microdefects does not influence the fragmentation of the coating, because the surface of the polymer that has not passed to the oriented state is almost not deformed (value of elastic deformation does not exceed several percent). The ribbons are successively torn off from the coating as the material approaches the ultimate stress limit and, as a consequence, the widths of all fractured fragments are nearly equal. It follows from the presented data that study of the structure-mechanical behavior of polymers with a thin hard coating provides important information on the deformation mechanism of the substrate polymer.

Equally important information concerning the deformation of the polymer substrate can also be gained from other types of deformation. In particular, in-plane compression of the coating has been implemented.[66—68] To this end, a polydimethylsiloxane (PDMS) film heated to 50—250 °C was coated with a thin hard coating either by vacuum deposition (gold) or by oxidation of the surface layer of PDMS in an oxygen plasma (oxidized hard PDMS layer). In both cases, cooling of the PDMS film to room temperature accompanied by its thermal shrinkage resulted in a wonderful regular microrelief appearing on the polymer surface (Fig. 8). The mechanism of formation of regular folds is related to the loss of stability of the thin coating on compression on the pliable substrate. It was found that the wave length (length of the fold) $\lambda$ of the regular microrelief depends on the properties of the substrate and the coating materials.

The loss of stability by the hard coating on the polymer substrate under in-plane compression can be induced much more easily when polymer films with an in-plane orientation are used as the substrates. In a series of publications,[69—71] 10—100 nm thick hard coatings (gold, platinum, copper, stainless steel, carbon, *etc.*) were applied onto the surface of biaxially oriented polymer films (PETP, PP). The subsequent annealing of these films gives rise to in-plane shrinkage and microreliefs similar to those presented above (Fig. 9). An advantage of this method is that the compression deformation is much greater than in other experimental techniques, because the shrinkage of in-plane oriented films reaches ≥30% (the thermal shrinkage of PDMS does not exceed 2—3%).

Upon the the annealing and the concomitant in-plane shrinkage of the PETP film, the coating really loses stability and acquires a strange, spectacular microrelief (see Fig. 9). This relief covers uniformly the whole sample surface, which is indicative of uniform (affinity) compression of the polymer during annealing.

Thus, the deformation of "hard coating on a pliable base" allows one to gain important information on the deformation of the substrate polymer. In particular, fragmentation patterns of the coating for substrate polymers occurring in the glassy and rubber-like state are different in principle.

## Mechanism of inelastic deformation and thermally stimulated shrinkage of oriented glassy polymers

The above results indicate that the decrease in the glass transition temperature in thin films and surface layers of amorphous polymers is their fundamental property. This feature of amorphous polymers cannot but reflect on

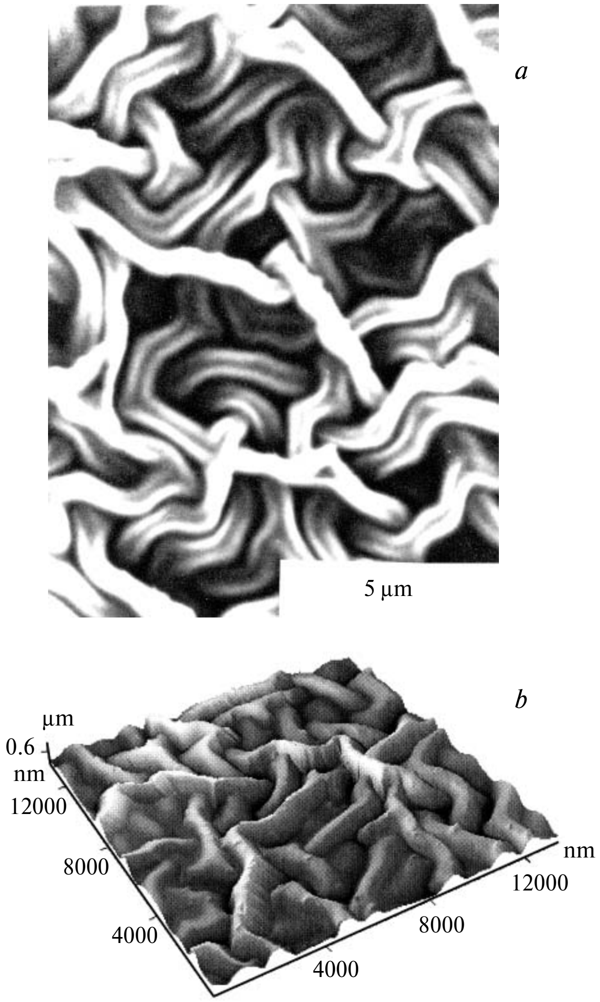

**Fig. 9.** Scanning electron micrograph of a PETP sample with a thin (15 nm) gold coating deformed above the glass transition temperature under uniaxial compression after the in-plane shrinkage by 25% during annealing (*a*) and three-dimensional reconstruction of the atomic force image of the same sample (*b*).

their macroscopic properties in the temperature range below the glass transition temperature in those cases where the polymer contains interfaces. Now we consider in more detail the most general properties of amorphous polymers having a clear-cut interface.

### *Crazing*

A general method for creating clear-cut interfaces in polymers is crazing.[72] As noted above, crazing is a specific type of inelastic deformation of solid polymers, which is accompanied by the development of a fibrillar porous structure, which imparts a high level of interfaces to the deformed polymer. Therefore, polymers deformed by the crazing mechanism become nonspecific porous adsorbents.[73–75] In addition, crazed polymers were found to exhibit a number of properties unusual for the glassy state. It was found that crazed polymers show large reversible deformations[76,77] and exhibit rather peculiar physicochemical[78] and mechanical behavior.[79] It is the high level of interface that is responsible for the unique properties of crazed polymers.

There are numerous indications that the properties of crazed polymers differ crucially from the properties of conventional oriented polymers.[80] This fact was first noted by Kambour and Kopp.[81] They found that crazed PC has a lower modulus of elasticity and a higher reversible deformation than the initial polymer. They attributed the unusual mechanical behavior of the crazed PC resorting to the model of a craze as an open-porous structure[82] and arrived at the conclusion that the molecular mobility in the craze is much higher than in the block due to the proximity to the surface. The high molecular mobility of the polymer in the craze structure is also indicated by the publication[83] demonstrating that annealing of crazed PS below $T_g$ results in not only closure of crazes but also in polymer monolithization, *i.e.*, healing of the interfaces. This implies the abnormally high molecular mobility in the craze fibrils.

In another publication,[84] crazes were initiated in PS thin films, their dimensions were recorded, and the distances between the fibrils and fibril diameters were measured by electron diffraction in a transmission electron microscope. The distances between the fibrils and fibril diameters increased during aging at room temperature. These changes were accompanied by coalescence of fibrils, and 750 h later, it was impossible to distinguish separate fibrils. It is clear that this process requires a high mobility of molecular chains.

The possibility of large-scale low-temperature molecular motion in a crazed polymer has been detected in a study[85] dealing with the molecular mobility in crazed and block PS and brominated PS carried out by temperature stimulated depolarization current. For highly crazed samples, the dielectric signal is markedly facilitated at temperatures almost 100 °C below their glass transition temperature. This facilitation is less pronounced for crazed samples annealed 10—20 °C below the glass transition temperature, which is indicative of partial healing (coalescence) of the phase interfaces in the low-temperature region. The annealing of crazed samples above the glass transition temperature results in complete healing of the structure.

The unusual thermomechanical behavior of crazed samples is worthy of special note.[86] Figure 10 shows the curves of size recovery during the annealing of PC samples stretched at room temperature in air with formation of a neck (*1*) and by the classical crazing mechanism (*2*) and a PMMA sample deformed by the classical crazing mechanism (*3*) to give a neck at 100 °C. It can be seen that PC deformed with the formation of a neck shows a moderate shrinkage (~12%) at temperatures below glass transition temperature; the shrinkage mechanism is considered

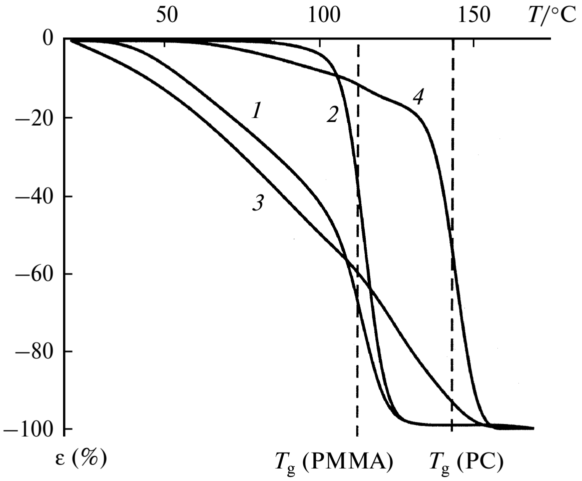

**Fig. 10.** Temperature dependence of the recovery of the dimensions of PMMA (*1*, *2*) and PC (*3*, *4*) deformed under uniaxial stretching conditions: (*1*, *3*) samples deformed in *n*-propanol by the classical crazing mechanism; (*2*, *4*) samples stretched in air (PMMA at 100 °C, PC at room temperature). The vertical dashed lines mark the glass transition temperature.

below. The recovery of the dimensions of this sample, as was to be expected, takes place around the glass transition. The shrinkage of the crazed sample occurs almost completely (by 95%) below the glass transition temperature. In the case of PMMA, the shrinkage of the crazed sample also occurs almost entirely in the temperature range below the glass transition, whereas the sample stretched by the shear yield mechanism at 100 °C, restores its dimensions almost completely at the glass transition temperature of the polymer. Note that the molecular motion responsible for the low-temperature recovery of crazed polymers shows itself in the temperature range more than 100 °C below the glass transition temperature of the block polymer.

Direct microscopic data indicate that the highly disperse material of crazes is responsible for the unusual thermomechanical behavior of the crazed polymer.[87] The dependences of the relative variation of the linear dimensions of crazes and the gaps between them on the annealing temperature obtained in direct microscopic examination are presented in Fig. 11. It can be seen that closure of the edges of individual crazes takes place almost entirely below the glass transition temperature of the PC. However, the nonoriented fragments of the initial polymer located between the crazes not only show no shrinkage but even grow somewhat due to thermal expansion. Similar results have been obtained for the annealing of crazed PMMA samples.[88]

The unusual thermomechanical properties of crazed polymers can be attributed to the decrease in the glass transition temperature in the highly dispersed oriented material of crazes, which is fully in line with the experimental data considered in the preceding sections. Estimates[85] show that fibrils 10 nm in diameter contain at most 10 chains. From this it follows that all molecules in the craze fibrils occur actually in the surface layer. Thus, the low-temperature shrinkage of crazed glassy polymers is due to the entropy shrinkage of fibrils that connect the craze edges as their local glass transition temperature is attained. Note that although the authors of the publications cited above have no up-to-date data on the molecular mobility in thin films and surface layers at their disposal, they have connected the discovered phenomena to the specific properties of the polymer near the free surface.

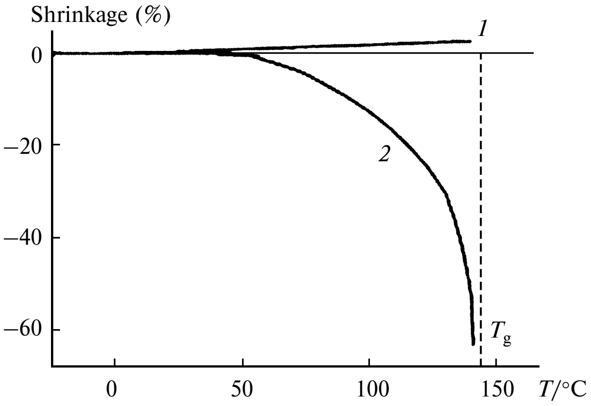

**Fig. 11.** Temperature dependence of the relative change in the linear dimensions ε of crazes (*1*) and nonoriented sections between them (*2*) toward the drawing axis for PC samples stretched in the AAS. The vertical dashed line shows the glass transition temperature of PC.

### *Shear flow*

One more type of plastic deformation of glassy polymers is shear flow (forced elastic deformation). This type of deformation has been studied much more comprehensively than crazing due to its practical significance. The forced elastic deformation underlies a versatile technique, namely, orientational drawing of polymers, which provides optimization of the mechanical properties of fibers and films.

Nevertheless, there still exist experimental facts that cannot be interpreted unambiguously. For many years, researchers have repeatedly noted specific properties of amorphous polymers in the temperature range knowingly below their glass transition temperature that are not quite clear yet. Back in the mid-20th century, some new type of molecular motion was detected[1] within the polymer glassy state at low deformations (below the yield point); this was called the elastic aftereffect deformation. Despite the fact that this type of molecular motion exists far below the glass transition temperature, the author suggested[1] that there is probably no sharp boundary between the forced elastic deformation and elastic aftereffect deformation mechanisms.

During the subsequent years, researchers have repeatedly noted a rather intensive, apparently a large-scale molecular motion in polymers in the temperature range corresponding to the glassy state, *i.e.*, in the range where this type of molecular motion is frozen according to the existing views. The molecular motion of this sort can be clearly detected, for example, in the measurement of internal stresses during annealing of a deformed polymer with fixed dimensions[89] below the glass transition temperature.

The large-scale molecular motion in deformed glassy polymers shows itself most readily and vividly in a study of strain relaxation during low-temperature annealing. It has already been noted (see Fig. 10) that PC subjected to cold drawing shows partial shrinkage in the temperature range below the glass transition temperature. This type of thermomechanical behavior is general, being inherent in almost any amorphous polymer. A typical example of this behavior is shown in Fig. 12,[90] in which the curve for uniaxial compression of PMMA is considered together with the relative contributions of the low-temperature (below glass transition) and high-temperature (in the region of glass transition) relaxation processes to the thermal shrinkage. In the context of this review, it is significant to note the following fundamental result (see Fig. 12): the low-temperature component of shrinkage is related to the deformation component that occurs below the yield point. On deformation above the yield point, inelastic strain is accumulated, which relaxes during annealing in the region of glass transition temperature of the block polymer.

For the understanding of the mechanism of the above-noted abnormal features in the mechanical behavior of glassy polymers, the crucial factor, in our opinion, is to identify the basic distinctions between the deformation patterns before and after the yield point. At the first glance, the uniform, elastic, and reversible deformation (so-called Hooke´s region in the stretching curve) takes place before the yield point. However, the polymer deformation in this region has some specific features that preclude regarding it as truly elastic and uniform. This deformation can be fixed by deep cooling of the polymer after uniaxial deformation.[90,91] Before the yield point has been attained, the polymer deformation becomes nonuniform throughout the volume and shear bands appear in the polymer.[92,93] The formation and growth of the shear bands in polymers have been studied in detail by a number of methods; in particular, it has been shown[94,95] that the shear bands, similarly to crazes, contain oriented fibrillized polymer, as indicated by the results of direct microscopic examination.

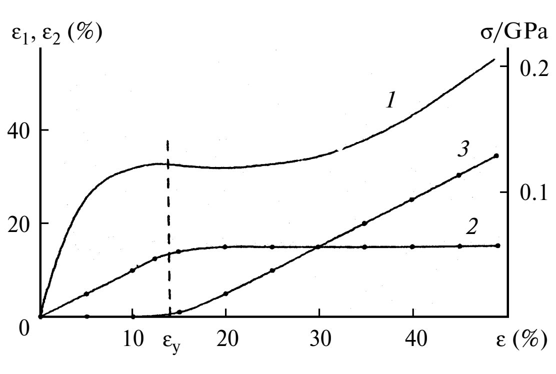

**Fig. 12.** Curve of the uniaxial compression of PMMA at room temperature (*1*), low-temperature (*2*) and high-temperature (*3*) contributions to the thermally stimulated shrinkage for the annealing of samples subjected to uniaxial compression below glass transition temperature.[90]

An adequate understanding of the abnormal features in the mechanical and thermomechanical behavior of glassy polymers requires, in our opinion, taking into account this fundamental difference in the deformation mechanisms of polymers before and after the yield point. Resorting to recent experimental data concerning the structure and the properties of surface layers of amorphous polymers provides a new interpretation for the abnormal mechanical and thermomechanical features of polymer glasses.

## *Mechanism of low-temperature recovery of deformed polymer glasses*

The mechanism of low-temperature shrinkage of polymer glasses deformed below the glass transition temperature has not relied on direct microscopic data until recently. This accounts for the lack of consensus of opinion on the mechanism of low-temperature shrinkage glassy polymers during annealing. Some researchers[96,97] attribute the specific features of the deformation of polymer glasses to their structural inhomogeneity at the microscopic level. In other studies, inelastic deformation of a polymer glass is interpreted as the formation[98,99] and decay[99] of microscopic shear transformations. In other publications,[100,101] the polymer plasticity below the glass transition is attributed to the β-molecular motion. The studies[102,103] in which the plastic deformation of a solid polymer is described using the free volume concept are also noteworthy.

Recently,[104] a direct microscopic procedure for visualization of the structural rearrangements that accompany the thermally stimulated shrinkage, including the low-temperature one, of deformed polymers has been developed. The essence of this procedure is as follows. A thin metallic coating is applied onto the surface of the deformed polymer. The subsequent annealing and shrinkage give rise to a microrelief in the coating, which provides important information on the structural rearrangements that accompany the deformation of the substrate polymer. The structural rearrangements detected in de-

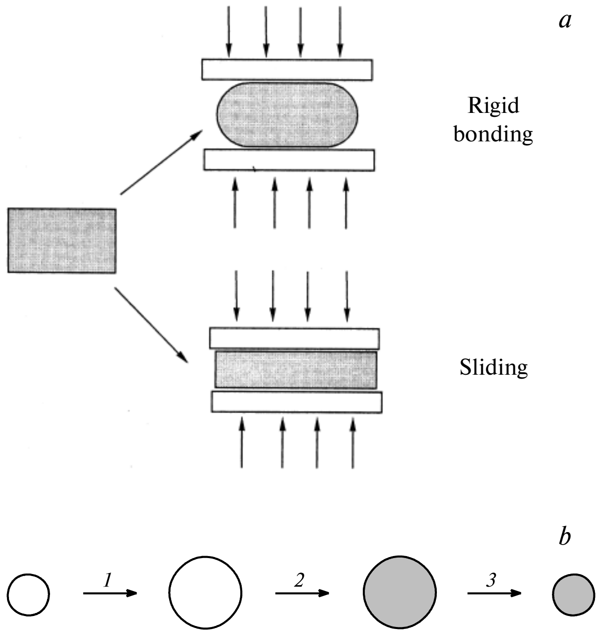

**Fig. 13.** Different variants of uniaxial compression (*a*) and sample preparation block diagram for direct microscopic examination (*b*): (*1*) deformation, (*2*) coating application, (*3*) annealing (shrinkage).

formed polymers using this procedure have been considered above in more detail.

In recent works,[93,105] this procedure has been used to study the mechanism of the low-temperature recovery of polymer glasses. In this connection, it is necessary to touch upon some procedural aspects. A polymer sample has been subjected to uniaxial compression under conditions of rigid bonding of the polymer to the compressing surface[3,4,96,97,99] (Fig. 13, *a*). In this case, the uniaxial compression affords a barrel-shaped sample. The thermally stimulated recovery of the dimensions of these samples has been studied by measuring the height of the sample during annealing. The same Figure sketches the mode of uniaxial compression of the polymer that is free to slide relative to the compressing surfaces. In this case, the sample being deformed is not only reduced in height due to the increase in the surface area being in contact with the compressing surfaces. The diameter of this sample also changes. The experimental procedure is shown in Fig. 13, *b*.

Even the first experiments using this procedure revealed the basic differences between the shrinkage mechanisms of polymers deformed above and below the glass transition temperature. The shrinkage of the polymer with a thin coating deformed above the glass transition temperature gives rise to a regular and highly spectacular microrelief distributed over the whole sample surface (see Fig. 9). The mechanism of formation of this microrelief has been described above in detail.

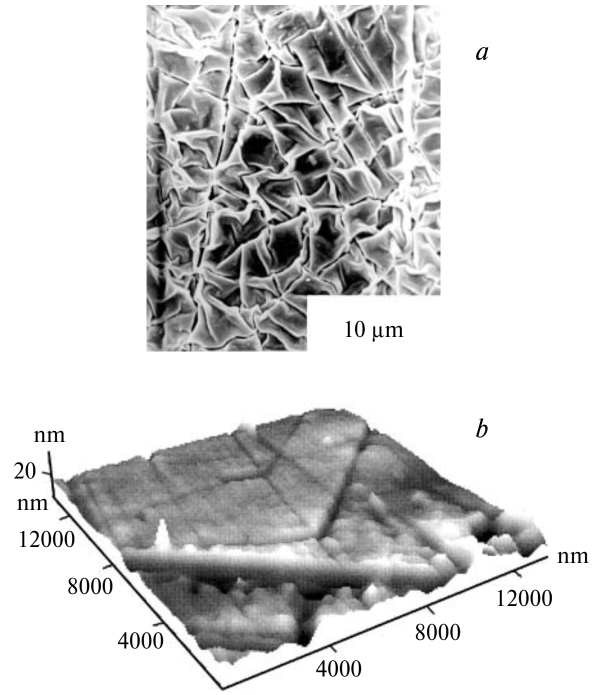

**Fig. 14.** Scanning electron micrograph of a PETP sample deformed at room temperature and undergoing in-plane shrinkage by 16% during annealing (*a*) and 3D reconstruction of the atomic-force image for the same sample (*b*). Frame size 10×10 μm. Prior to the annealing, a thin (10 nm) platinum coating was applied onto the sample surface.

Now we consider the response of the metallic coating to the in-plane shrinkage of PETP deformed below the glass transition temperature. On annealing even at 50 °C, *i.e.*, 25 °C below the glass transition temperature (Fig. 14, *a*), shrinkage is accompanied by structural rearrangements in the surface layer that differ basically from those observed for shrinkage of a polymer deformed above the glass transition temperature (*cf.* Figs. 9 and 14). It can be easily seen that at this annealing temperature, the sample surface becomes covered with straight bands, which cross it from edge to edge and also cross one another at different angles. The band widths are unequal, the width distribution being rather broad. The data from atomic force microscopy (see Fig. 14, *b*) show that the bands are valleys of different width. Since the bands cross the whole sample surface under examination, one can suggest that they run through the whole cross-section of the deformed polymer. The wider the bands, the deeper they penetrate into the polymer surface, and *vice versa*.

In a recent publication,[105] new, fairly important features of the thermally stimulated shrinkage of amorphous polymers subjected to inelastic deformation under uniaxial compression have been identified using the above-described procedure. It was shown that the deformation of a glassy polymer can be conventionally divided into two phases. The first phase (below the yield point) involves transition of the polymer into very thin surface layers located in the shear bands and separated by the blocks of the initial, non-deformed polymer. At the second phase (after the yield point has been reached), the total bulk transition of the polymer into the oriented state starts. Conversely, during the annealing of deformed polymers, first, when the annealing temperature is below the glass transition temperature, shrinkage of the polymer starts in the shear bands and, subsequently, the total shrinkage of the oriented polymer takes place around the glass transition temperature. Figure 14 illustrates the foregoing in relation to the deformation and shrinkage of PETP.

Now we consider the mechanism of plastic deformation and the subsequent low-temperature recovery of the geometric dimensions of deformed glassy polymers. Let us compare the data presented in Figs. 9 and 14. According to the experimental conditions, in both cases (above and below the glass transition temperature), surface area of the polymer increases upon in-plane stretching. The increase in the surface area is inevitably accompanied by substance ergress from the polymer bulk to the surface. The results obtained confirmed the well-known views stating that above glass transition temperature, this process is uniform and involves the whole surface in the same way as during deformation of a liquid. The specific nature of the polymer shows itself as the in-plane orientation, which accompanies the process and is obviously responsible for the subsequent thermal shrinkage observed in experiments.

In the reverse shrinkage process, the recovery of the former surface takes place uniformly; as a result, the applied coating is also uniformly compressed over the whole surface area. The affinity of the deformation of rubber-like polymers is among the key conditions of the statistical theory of high elasticity. This accounts for the formation of the uniform relief (see Fig. 9) described in detail in previous publications.[69—71].

During the in-plane deformation of the same polymer below $T_g$, the gain in the surface area occurs in a different way. This process is concentrated in discrete inelastic deformation areas, *viz*., shear bands, which contain the oriented material. This process occurs *via* spreading and subsequent broadening of the shear bands similarly to the processes involved in crazing.[72] As a consequence, the first stages of deformation yield a polymeric material composed of nonoriented blocks separated by narrow areas (shear bands or crazes), which contain the highly oriented polymer and are separated from the blocks by well-formed interfaces.

The reverse thermal shrinkage process is again non-uniform, because the oriented polymer localized in the shear bands is responsible for the reversibility of the deformation at annealing temperatures below $T_g$. The experimental data obtained by the new microscopic procedure (see Ref. 93 and Fig. 14) show that the polymer shrinkage occurs, first of all, in the shear bands, as indicated by coating drawing-in into the polymer in the shear areas.

As noted above, numerous experimental data indicate that in the interfaces of glassy polymers, the glass transition temperature is sharply reduced and the $\alpha$-relaxation process widely extends along the temperature scale. This implies that the polymer containing local areas (shear bands, crazes) filled by the highly dispersed oriented material restores its dimensions during annealing following the successive devitrification of the accumulated plastic deformation areas (crazes or shears). This process should occur at temperatures much lower than the glass transition temperature of the block nonoriented polymer. It is significant that the number of these accumulated plastic deformation areas is relatively small, and depends on the experimental conditions.[62] Their number is incommensurable with the number of microheterogeneities typical of the structure of amorphous polymers.[3—7] This implies that the appearance and development of these plastic deformation areas is not related to the inner structural inhomogeneity. This small number of crazes or shear bands is probably due to some random structure imperfections (defects and stress raisers) inherent in a real polymer and differing in the potential risk of initiation of plastic deformation areas.

## Conclusion

In conclusion we would like to emphasize the exceptional significance of the structural studies for elucidation of the mechanism of deformation of solid polymers. The advent of direct microscopic methods for visualization of the structural rearrangements of the deformed polymer made it possible to compose the general picture of the deformation of solid polymers based on direct microscopic examination. Analysis of the results obtained in these studies leads to the conclusion that the polymer deformation below the glass transition temperature gives rise to specific areas containing the oriented polymer and having clear-cut interfaces. Both in the case of crazing and in the development of shear bands, these areas run through the polymer bulk and are thus responsible for properties generally typical of this oriented highly dispersed material. The main factor responsible for the low-temperature recovery of the annealed oriented polymers is the decrease in the glass transition temperature taking place in their surface layers. The successive devitrification of the oriented material that fills the accumulated deformation areas initiates the entropy force responsible for the observed low-temperature recovery of the deformed glassy polymers.

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