

Visualization of Structural Rearrangements During Annealing of Solvent-Crazed Isotactic Polypropylene¹

A. L. Volynskii, T. E. Grokhovskaya, A. I. Kulebyakina, A. V. Bol'shakova, and N. F. Bakeev

Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia

e-mail: volynskii@mail.ru

Received January 24, 2008;

Revised Manuscript Received September 3, 2008

Abstract—Structural rearrangements taking place upon the annealing of solvent-crazed isotactic PP are studied by the direct microscopic method. Independently of the type of its crystalline structure, solvent-crazed PP undergoes shrinkage in a wide temperature interval, starting even from room temperature and up to its melting temperature. This shrinkage is a result of the structural processes in crazes and proceeds via shutting down of the walls of individual crazes. This low-temperature shrinkage of solvent-crazed PP is assumed to have an entropy nature. This process involves the contraction of extended polymer chains and their transition into thermodynamically favorable conformations. This contraction is allowed because, upon annealing, the entropy contracting force increases. As a result, the crystalline framework of oriented PP melts down (amorphization), extended chains appear contracted, stored stresses relax, and subsequent recrystallization in the unstressed state takes place.

DOI: 10.1134/S0965545X09040051

INTRODUCTION

The deformation mechanism in solid polymers is a challenging task of modern materials science. However, progress in this direction is limited by the absence of any direct experimental methods for studying the evolution of structural rearrangements in the course of deformation. In recent years, a new microscopic procedure has been proposed [1–4]; the use of this procedure makes it possible to gain direct information on the above structural rearrangements and offers new knowledge concerning the deformation mechanism of amorphous polymers at temperatures below [5] and the above glass transition temperature [6]. In particular, annealing of PET samples oriented above the glass transition temperature was accompanied by both shrinkage and elongation along the direction of preliminary tensile drawing, the so-called phenomenon of spontaneous self-elongation [6, 7]. In this case, after annealing, the resultant length of the sample is smaller as compared with its initial length, but the use of the above microscopic procedure allows a direct and vivid visualization of the spontaneous self-elongation of PET under the above conditions [1–4].

In our recent works, we have used this microscopic procedure to study structural rearrangements in the course of deformation and annealing of amorphous glassy polymers after solvent crazing or, in other words, after their tensile drawing in the presence of adsorptionally active liquids environments [8–10].

Deformation and shrinkage of the oriented amorphous polymers were accompanied by features unknown earlier. Therefore, one can reasonably expect that the proposed direct microscopic procedure [1–4] can also be efficiently used for the visualization and characterization of structural rearrangements during the deformation and shrinkage of semi-crystalline polymers.

The objective of this work is the use of the proposed microscopic procedure [1–4] for the visualization of structural rearrangements in solvent-crazed isotactic PP upon its annealing.

EXPERIMENTAL

In this work, we used commercial unoriented films of isotactic PP with a thickness of 150 μm . We studied the samples of initial PP and annealed PP (APP) after its annealing at 140°C for 3 h. Specimens with a gage size of 6 \times 20 mm were cut from the initial film and stretched in ethanol at room temperature by the selected tensile strains on an Instron-1122 universal tensile machine; the strain rate was 5 mm/min. After the tensile drawing, the samples with their fixed dimensions were dried and then released from the clamps. Surface of the stretched samples was decorated with a thin platinum layer (10 nm) by the plasma ionic deposition on an Eiko IB-3 standard sputtering instrument. The deformed samples were sandwiched between two glasses and annealed in a thermostated chamber at a given temperature for 1 h. The morphology of the deformed samples was studied on a Hitachi

¹ This work was supported by the Russian Foundation for Basic Research, project nos. 05-03-32538 and 06-03-08025-ofi).

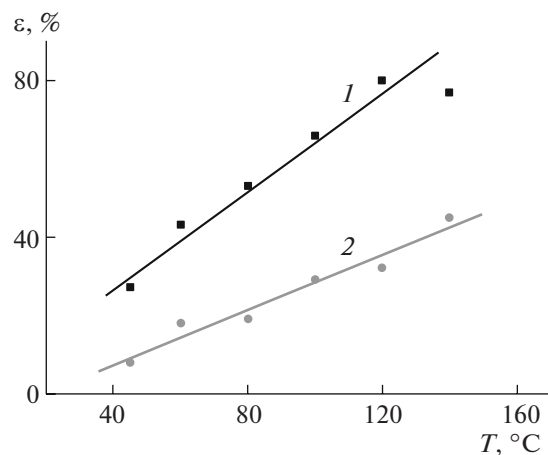


Fig. 1. Temperature dependence of the relative shrinkage of the solvent-crazed PP samples after their tensile drawing in ethanol by 100%: (1) PP annealed at 140°C and (2) initial PP.

S-520 scanning electron microscope. For SEM observations, the samples were fractured along the direction of their preliminary tensile drawing at a liquid nitrogen temperature. The scenario of the isothermic annealing of solvent-crazed PP was the following: the sample was fixed by the clamps of an Instron-1122 tensile machine and placed into the heating chamber; then, the temperature was gradually increased from 20 to 150°C, and all stress changes were recorded.

Note that the solvent-crazed samples based on the annealed PP and initial PP were prepared in somewhat different ways. The point is that, after its release from the clamps of the tensile machine, the initial PP retains its dimensions. However, after its release from the clamps, the annealed PP immediately undergoes marked shrinkage even at room temperature. In this case, PP was annealed once the sample contracted down to its constant dimensions at room temperature. Hence, the samples were stretched by 200%, dried under isometric conditions, and released from the clamps. The residual strain was 100%, and this value corresponds to the tensile strain of the solvent-crazed samples based on initial PP.

RESULTS AND DISCUSSION

Prior to the analysis of the experimental evidence on our structural studies, let us consider some structural mechanical attributes of PP. In contrast to amorphous polymers, PP is able to undergo both modes of solvent crazing and the mode of solvent crazing depends on the type of crystalline structure of the initial polymer [11]. As was shown in [12–14], isotactic PP with its highly disordered smectic crystalline structure (initial PP) undergoes deformation in the presence of adsorptionally active liquid environments (AALE) via classical solvent crazing. Annealing of iso-

tactic PP increases its degree of crystallinity and assists its gradual transition into the monoclinic crystalline modification [15]. The above structural rearrangements of PP entail concomitant changes in the mechanism of its deformation in AALE. Annealed PP [12–14] is characterized by its relatively high degree of crystallinity and experiences so-called delocalized solvent crazing [11].

The mechanism of deformation of PP in AALE is still unclear. A new visualization procedure and direct microscopic observations on the thermally stimulated shrinkage of the deformed amorphous polymers [1–4] made it possible to advance certain justified speculations concerning the deformation mechanism. In this work, this approach was used to study the deformation mechanism of isotactic PP. In this context, the characterization of its thermomechanical behavior provides important information on the deformation of a polymer because, as in all other cases, inelastic deformation of PP in AALE results in its molecular orientation. Annealing of oriented polymers is accompanied by changes in their geometrical dimensions, which is a necessary condition for efficient use of the proposed microscopic procedure [1–4].

Let us consider some specific features of the solvent-crazed PP samples. Figure 1 presents the temperature dependence illustrating changes in the linear dimensions of the solvent-crazed PP samples after their tensile drawing in AALE (ethanol) by 100% and drying with fixed dimensions. The thermomechanical behavior of the solvent-crazed PP samples is different from that of the solvent-crazed amorphous polymers. First, both for initial PP and annealed PP, thermally stimulated shrinkage commences virtually at room temperature and increases linearly within the entire temperature interval. Second, the thermomechanical behavior of the solvent-crazed polymer is strongly controlled by its initial crystalline structure. Third, in contrast to solvent-crazed amorphous polymers [7], PP is unable to attain complete strain recovery even at high annealing temperatures.

Let us consider the direct microscopic data for the initial PP after its tensile drawing in AALE via classical solvent crazing. Figure 2 shows SEM images of the initial PP after its tensile drawing in AALE (ethanol) by 100% and annealing at 120°C. For the initial PP, it is seen that its tensile drawing in AALE results in nucleation of the regions of plastically oriented material with porous structure, so-called crazes (Fig. 2, regions A, C). At the selected tensile strain (100%), crazes propagate throughout the whole cross section of the sample. As follows from Fig. 2, both crazes and alternating regions of the unoriented polymer (region B) have a smooth surface relief. On the surface of each craze, craze fibrils are seen to merge and form a monolithic film, which isolates their inner space. The above structural attributes are also typical of crazes in glassy amorphous polymers [16].

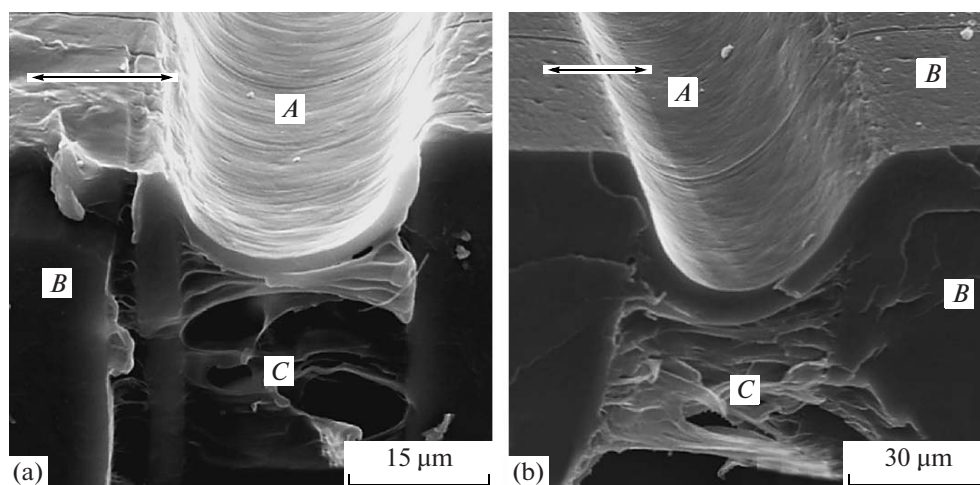


Fig. 2. SEM images of the solvent-crazed sample based on initial PP (a) after its tensile drawing in ethanol by 100% and (b) after postannealing 120°C. Hereinafter, the direction of tensile drawing (contraction) is shown by arrows. Region *A* is the craze surface, region *B* corresponds to the undeformed bulk polymer, and region *C* is the fractured surface of the craze.

It is also seen that postannealing of the initial solvent-crazed PP at 120°C entails no critical changes in the craze structure (cf. Figs. 2a and 2b), even though Fig. 1 shows that this process is accompanied by marked changes in the geometrical dimensions of the sample (shrinkage is higher than 30%). This behavior is likely explained by the fact that trivial microscopic observations do not allow us to reveal or visualize any structural rearrangements taking place in the polymer sample during its thermally stimulated shrinkage.

Hence, one can expect that the deposition of a thin metallic coating onto the polymer sample before its annealing (this decoration serves as the basis for the proposed microscopic visualization procedure) [1–4] will make it possible to visualize the structural rearrangements taking place in the solvent-crazed samples based on the initial PP upon shrinkage. To this end, all further microscopic observations of the solvent-crazed samples based on initial PP have been performed by using the above technique of sample preparation.

Let us consider in detail the SEM data for the initial PP after its tensile drawing via classical solvent crazing and annealing in a free state at different temperatures. Figure 3 presents SEM images of the initial PP after its tensile drawing in AALE by 100% and annealing at 45°C (by 120°C below the melting temperature of PP). As a result of annealing, the surface of the solvent-crazed PP acquires a specific surface micropattern. The basic pattern elements are the folds located in crazes in the direction perpendicular to the axis of preliminary tensile drawing (Fig. 3a, region *A*). Even though the length of these folds is small, they span along the entire craze axis: in the craze center, their height increases (in Fig. 3b, bright white regions) and, near craze walls, their height is small. This result indicates that, upon the thermally stimulated shrinkage of initial PP (Fig. 1, curve 2), craze walls approach

each other because development of folds on the surface of the metal-coated polymers results from compression on the surface of the supporting polymer. One can also conclude that the polymer material between crazes is not involved in the shrinkage because its surface preserves its smooth relief at all postannealing temperatures.

The proposed procedure also makes it possible to conclude that, in crazes, low-temperature shrinkage of the solvent-crazed initial PP is not homogeneous. As was shown in [17], the higher the nucleated folds in the coating, the higher the degree of the compressive strain of the supporting polymer. At the center of the craze, shrinkage seems higher than that near the craze walls, and this conclusion is proved by the different thicknesses and heights of folds formed on the polymer surface upon annealing. This result allows us to conclude that the draw ratio of the polymer changes along the craze width: at the center, the draw ratio is higher than that near the craze walls.

To demonstrate that the shrinkage takes place not only on the polymer surface but also in the polymer bulk, the proposed scenario of the sample preparation was slightly changed. The test sample was brittle-fractured before its post annealing; then, both the surface of the solvent-crazed sample and its fractured surface were decorated with a metallic coating; only after that, the sample was annealed. Figure 3c shows the corresponding SEM image. The folds oriented perpendicular to the direction of the preliminary tensile drawing are seen to be nucleated not only on the surface layer of crazes but also in their bulk (Fig. 3c, region *B*). This observation proves the earlier assumption that shrinkage is provided exclusively by the craze material and takes place over the entire volume of crazes.

Figure 4 presents the SEM images of the sample based on the initial PP after its tensile drawing by

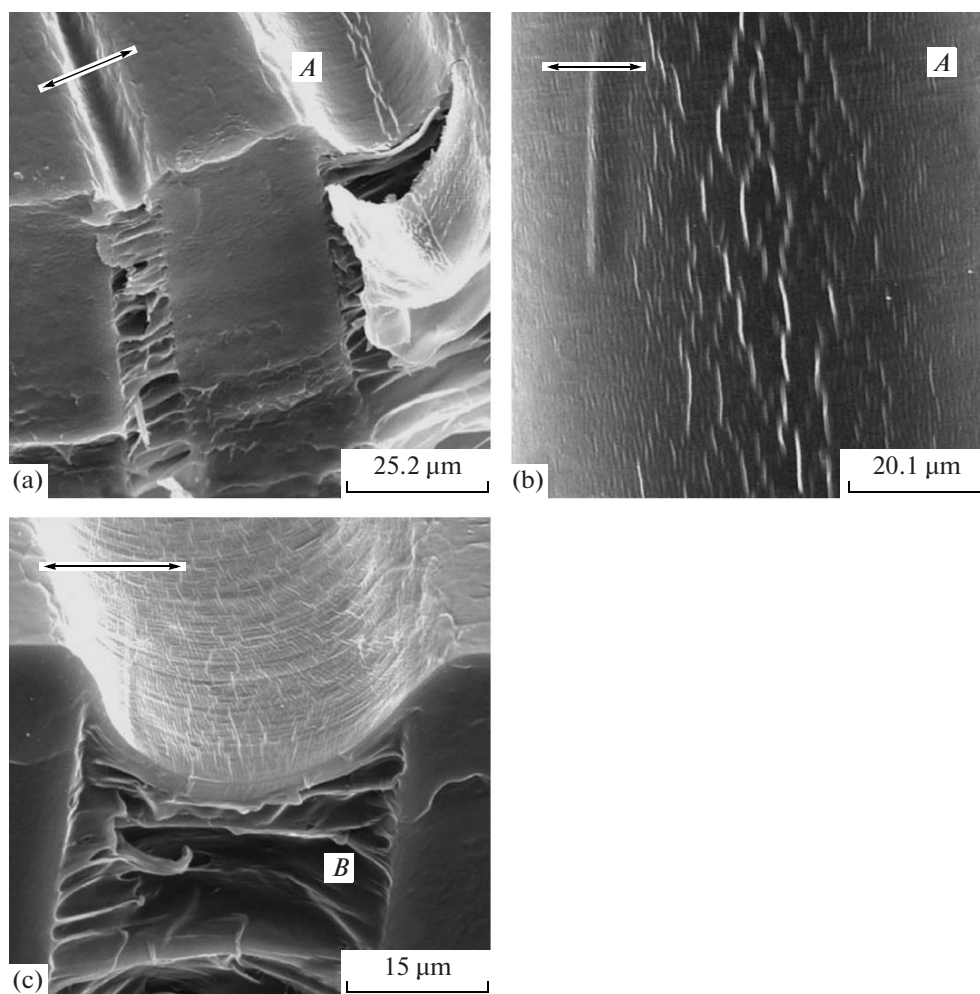


Fig. 3. SEM images of the solvent-crazed sample based on the initial PP after its annealing at 45°C and (a, b) deposition of a thin (10 nm) platinum coating and (c) after the deposition of a thin coating onto the fractured surface of the sample prior to annealing. Region *A* is the craze surface with folds; region *B* is the fractured surface of the craze.

100% in AALE and annealing at 60 and 80°C. The corresponding SEM images show that the whole surface of crazes is covered by well-pronounced folds oriented along the craze axis. However, comparing Figs. 3a, 4a, and 4c, one can observe that, with increasing annealing temperature, the number of high folds increases. This tendency is probably related to increased shrinkage of the samples, and this assumption agrees with the temperature dependence of shrinkage for the solvent-crazed samples based on the initial PP (Fig. 1). Note that, upon annealing and temperature-induced shrinkage, the fibrillar structure of crazes appears to be distorted: the craze fibrils tend to merge and form large aggregates.

Annealing at 100°C results in the further evolution of the formed surface micropattern (Fig. 5). First, high folds located along the craze axis appear to occupy the entire surface of crazes, and their density increases (Fig. 5a). Still, they coexist with smaller folds. Second, one can observe the nucleated cracks in the coating,

which are oriented perpendicular to the craze axis and, hence, to folds (Fig. 5b). The emergence of cracks in the coating indicates the development of discontinuities, which are directed perpendicular to the tensile drawing direction. This shows that the shrinkage of the surface layer formed by the merged craze fibrils is accompanied by a certain widening in the perpendicular direction. Note that the structural rearrangements in the craze surface layer at this scale can hardly be identified by any other method. As follows from Fig. 5a (region *A*), the shrinkage at room temperature is accompanied by a marked increase in the diameter of craze fibrils and by an increase in the thickness of the craze surface layer.

Figure 6 presents the SEM images of the samples based on the initial PP after their tensile drawing in AALE by 100% and annealing at 120 and 140°C. Annealing at higher temperatures is seen to result in the development of cracks in the coating, which tend to widen with increasing annealing temperature.

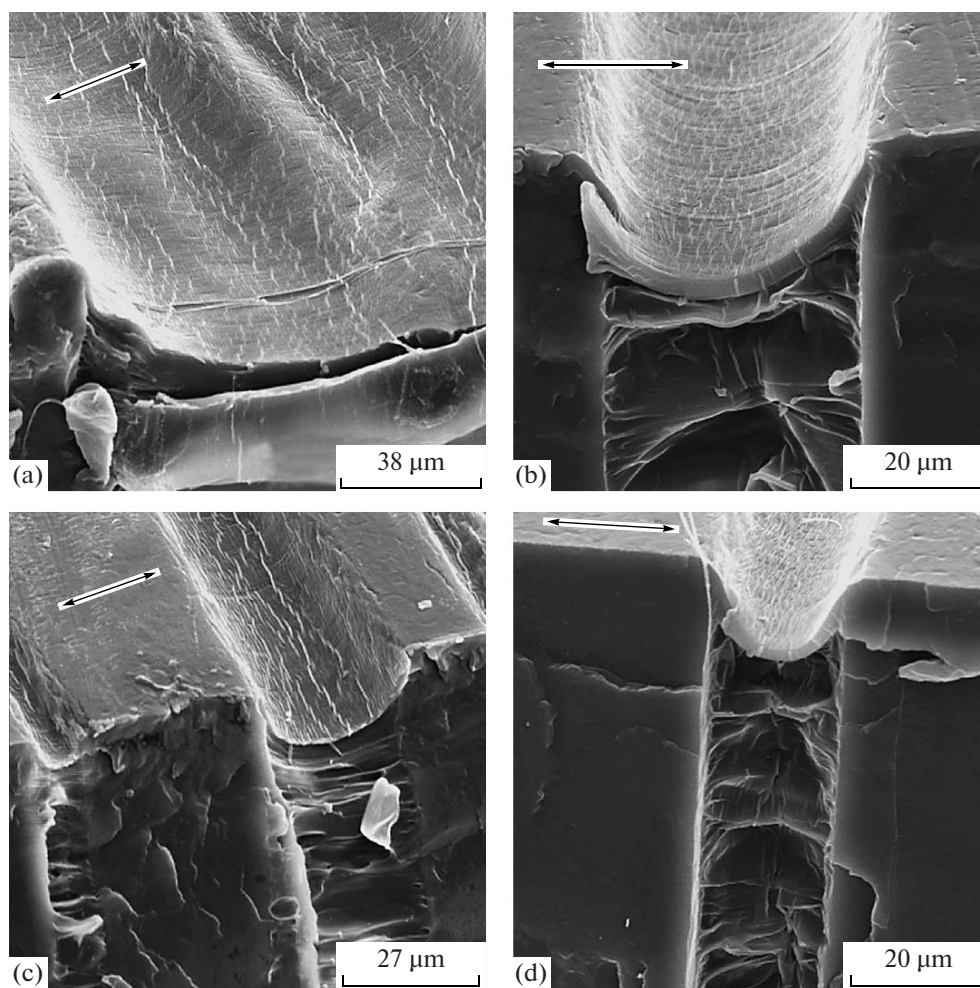


Fig. 4. SEM images of the solvent-crazed samples based on the initial PP after their annealing at (a, b) 60 and (c, d) 80°C: (a, c) the samples are decorated with a thin (10 nm) platinum coating and (b, d) the fractured surface of the samples is decorated with a platinum coating prior to annealing.

On the one hand, this fact suggests that, upon shrinkage, the sample tends to recover its initial dimensions (Fig. 1). On the other hand, the craze widens in the direction perpendicular to the direction of tensile drawing. Preliminary deposition of the metallic coating onto the side surface of the solvent-crazed sample makes it possible to reveal that, with increasing annealing temperature, the fibrillar material in the volume of crazes appears to be “folded,” and no fibrillar structure can be distinguished (Figs. 6b and 6d, region *A*). Hence, the direct microscopic observations allow us to conclude that the low-temperature shrinkage of the solvent-crazed sample based on the initial PP proceeds via the closure of craze walls and the craze fibrils become shorter and thicker. However, completeness of the craze structure is not achieved.

Let us consider the structural rearrangements in the course of the thermally stimulated shrinkage of the solvent-crazed samples based on the annealed PP. Note that the mechanical behavior of the annealed PP is significantly different from that of the initial PP.

After its tensile drawing in AALE, drying, and release from the clamps of the tensile machine, the solvent-crazed samples based on the initial PP retain their geometrical dimensions. Their corresponding SEM images after the postannealing are presented in Figs. 1–6. At the same time, when the annealed PP with fixed dimensions is dried in the clamps, the dried material exhibits no stability and cannot retain its geometrical dimensions. After its release from the clamps, the sample exhibits a marked shrinkage at room temperature without any postannealing. In this case, the shrinkage is high and can achieve 50% with respect to the initial tensile strain of the solvent-crazed samples based on the annealed PP. With allowance for this, the samples of the annealed PP were stretched by 200% in AALE, dried with fixed dimensions, and released from the clamps of the tensile machine. After this procedure, at room temperature, the sample shrinks by 50% with respect to the initial tensile strain of the solvent-crazed samples. As a result, this sample appears to be deformed by 100%, and this tensile strain is equal to

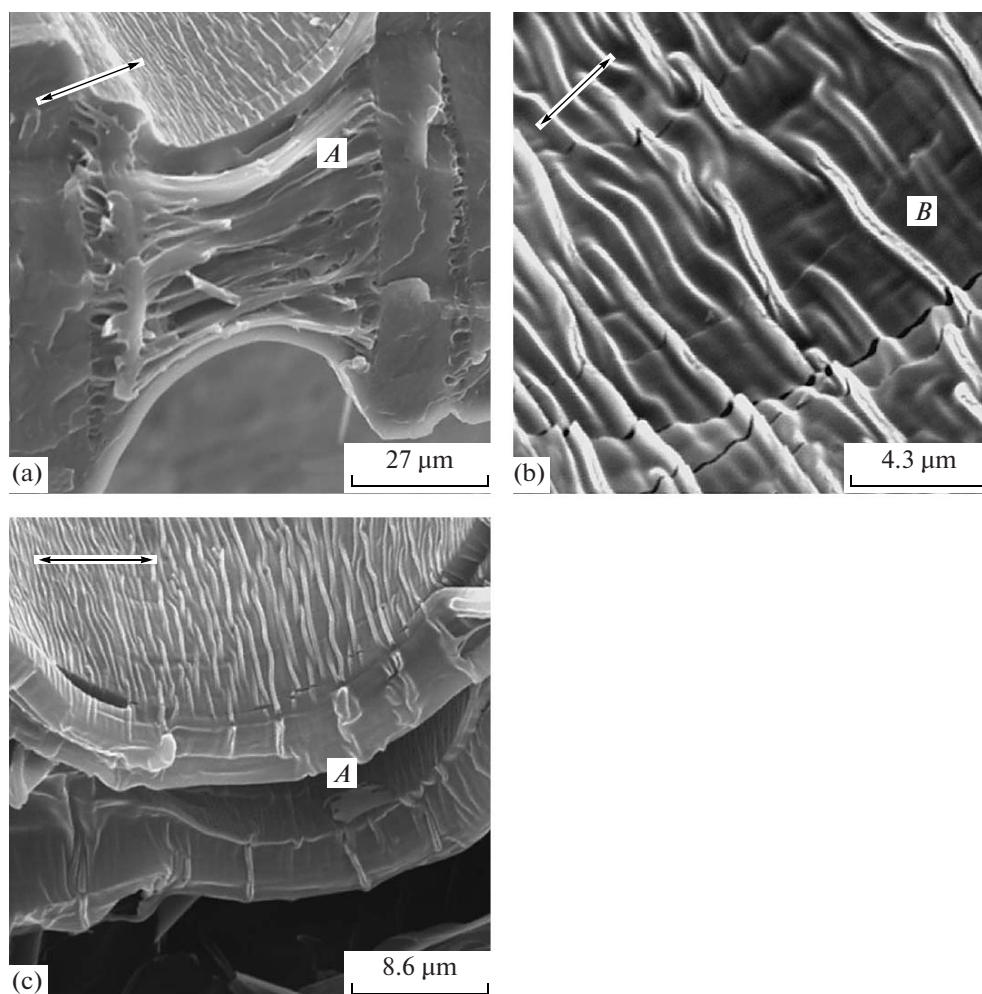


Fig. 5. SEM images of the solvent-crazed samples based on the initial PP (a, b) after their annealing at 100°C and deposition of a thin (10 nm) platinum coating and (C) after the deposition of the coating onto the fractured surface prior to annealing. Region *A* is the fractured surface of the craze, region *B* is the craze surface.

that of the solvent-crazed samples based on the initial PP. This material was subjected to postannealing, and its behavior is illustrated by the thermomechanical curve shown in Fig. 1.

Let us first characterize the shrinkage of the annealed PP at room temperature immediately after tensile drawing in AALE, drying, and release from the clamps of the tensile machine. The phenomenon of high stain recovery for the solvent-crazed samples based on the annealed PP immediately after their drying and release from the clamps was observed for the first time, and the mechanism behind this phenomenon is still unclear. The proposed microscopic procedure makes it possible to visualize the structural rearrangements in the course of the reversible strain recovery. In this case, the sample of the annealed PP was stretched by 200% in ethanol, dried with fixed dimensions, and then its surface was decorated with a thin metallic (platinum) layer, and the sample was released from the clamps. As was mentioned above, this sample

shrinks down by 50% with respect to its initial tensile strain. Figure 7 shows that this shrinkage is accompanied by development of the microrelief on the polymer surface and its structural elements are folds oriented perpendicular to the direction of tensile drawing. The above folds uniformly cover the entire surface of the polymer sample after its shrinkage, and this pattern attests that the tensile strain is uniformly distributed over the entire volume. In the coating, no cracks are observed, because the shrinkage proceeds without any widening of the sample in the direction perpendicular to the direction of tensile drawing.

Let us consider the processes taking place in the course of the thermally stimulated shrinkage of the solvent-crazed samples based on the annealed PP. Figure 8 presents the SEM images for the annealed PP after its tensile drawing in ethanol and for the same sample but after its annealing at 120°C. This indicates that the conventional microscopic observations do not allow us to reveal any specific structural features nei-

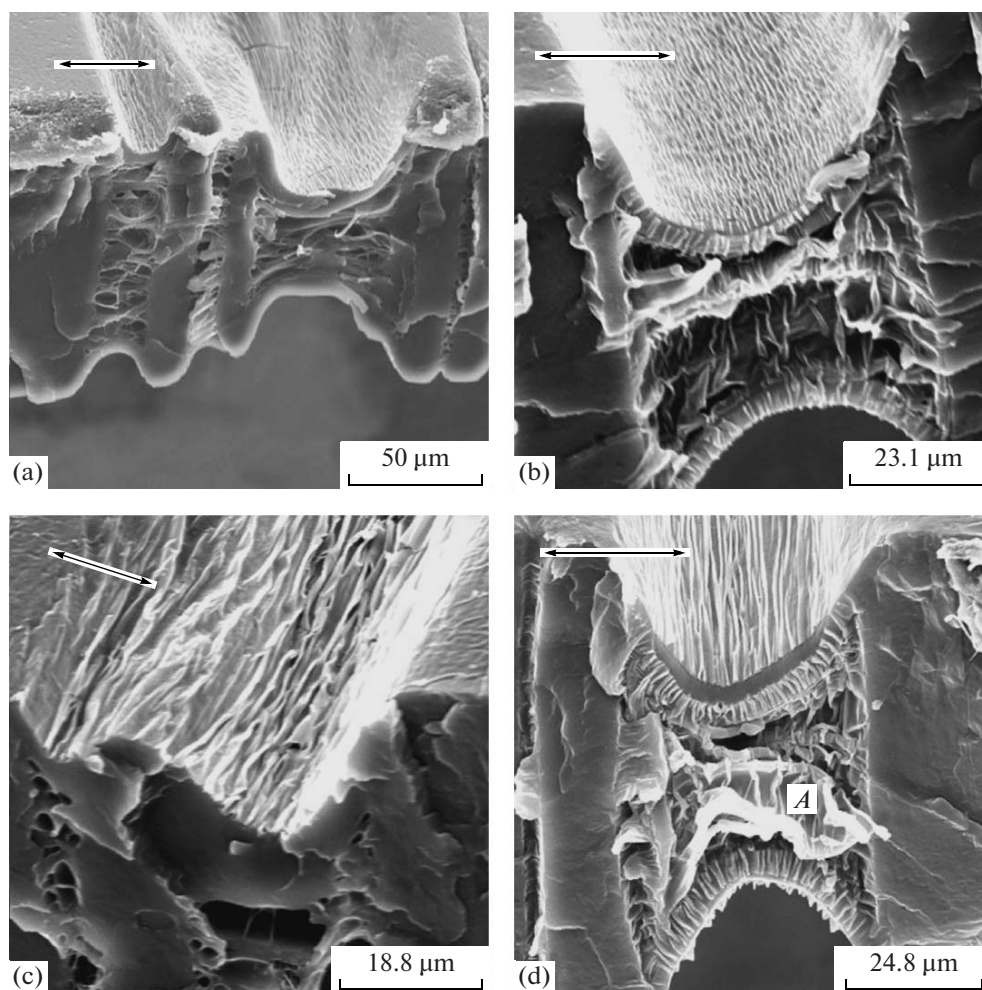


Fig. 6. SEM images of the solvent-crazed samples based on the initial PP after their annealing at (a, b) 120 and (c, d) 140°C: (a, c) the samples are decorated with a thin (10 nm) platinum coating and (b, d) fractured surface of the samples is decorated with the coating prior to annealing. Region *A* is the fractured surface of the craze.

ther for the solvent-crazed sample based on the annealed PP nor for the same sample (Fig. 8a) but after its postannealing (Fig. 8b). Surface of the sample and its fractured side surface are seen to be flat and do not show any characteristic details.

To reveal the fine structural details in the PP samples after delocalized solvent crazing, a similar visualization procedure was used. As in our previous experiments, the samples of the annealed PP were stretched in AALE and released from the clamps. Then, the samples were fractured in liquid nitrogen, and the fractured surface was decorated with a thin platinum coating. The obtained samples were annealed at different temperatures. This postannealing is accompanied by shrinkage, and its level depends on the annealing temperature (Fig. 1). After this treatment, the samples were examined on a scanning electron microscope.

Figure 9 presents the SEM images of the above PP samples after their postannealing at 120 and 140°C. First, let us mention that the sample has the folded

surface pattern, which uniformly covers the entire surface of the sample (region *A*), as well as the fractured surface (region *B*). Moreover, one can observe multiple cracking, and the formed cracks are also uniformly distributed over the sample. This attests that, in contrast to the initial PP, deformation of the annealed PP is homogeneous [11], and this feature translates into its shrinkage. This process is accompanied by an increase of the linear dimensions of the sample in the direction perpendicular to the direction of tensile drawing, and this conclusion is proved by the orientation of the cracks growing in the coating. This pattern has an obvious similarity with the surface relief patterns observed for the affine shrinkage of amorphous polymers after their tensile drawing at temperatures above glass transition temperature [18]. The proposed visualization procedure does not allow us to reveal the structural details of the delocalized solvent crazing since, in this case, typical pore dimensions are too small. However, our observations prove that the strain is delocalized over the entire volume of the polymer

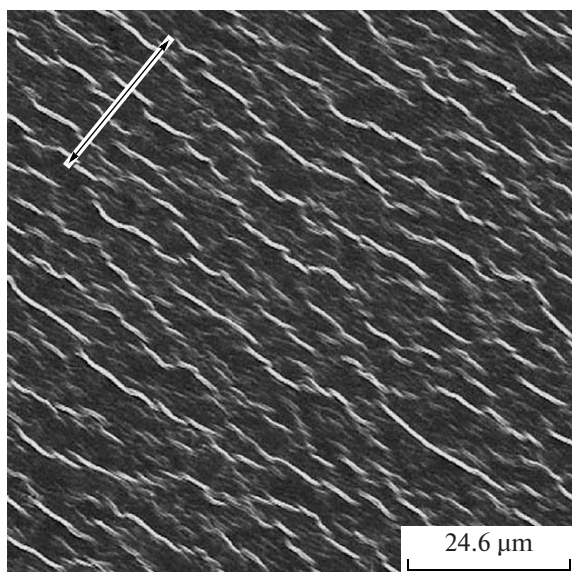


Fig. 7. SEM images of the solvent-crazed samples based on the annealed PP after tensile drawing in AALE by 200% and drying under isometric conditions. Prior to being set free, the surface of the samples was decorated with a thin platinum coating (shrinkage comes to 50% with respect to the initial tensile strain).

sample, and this behavior is known to be typical of this mode of solvent crazing; the principal features of this process have been discussed above [11].

Even though the direct microscopic observations made it possible to refine many details of the thermally stimulated shrinkage of the solvent-crazed PP, the following problems remain unclear. What is the nature behind the low-temperature shrinkage of the solvent-crazed samples based on the initial and annealed PP? Why, as compared with the initial sample, are all the

attributes of shrinkage better pronounced for the annealed PP?

As was shown in [19, 20], deformation of an amorphous polymer controls the character of its thermally stimulated shrinkage. When the polymer undergoes homogeneous deformation, for example, at temperatures above the glass transition temperature, the subsequent thermally stimulated shrinkage also shows its homogeneous (affine) character. When deformation of a polymer is inhomogeneous and proceeds, for example, via the development of shear bands, its thermally stimulated shrinkage is also inhomogeneous and proceeds via the relaxation of the oriented material in the shear bands bridging the blocks of the unoriented polymer [19, 20]. If this observation is universal, the mechanism of deformation of a semicrystalline polymer can provide important information on the mechanism of its thermally stimulated shrinkage.

Modern speculations on the mechanism of high strains in semicrystalline polymers are based on the concept of recrystallization [21, 22]. In its general case, this mechanism can be represented as follows. Under the action of the applied stress, the melting (amorphization) temperature of the polymer crystalline lattice decreases. As this temperature depression achieves the temperature at which deformation takes place, the polymer melts down. Then, recrystallization commences, and this process is accompanied by the formation of a fibrillar structure, which is oriented along the direction of tensile drawing and, hence, stable to the action of the tensile stress. As a result, a neck with an oriented crystalline structure and stable dimensions is formed.

Therefore, in the mechanism of structural rearrangements upon the deformation of a semicrystalline polymer, the key role is played by the mechanical stress. For the solvent-crazed PP, its shrinkage also

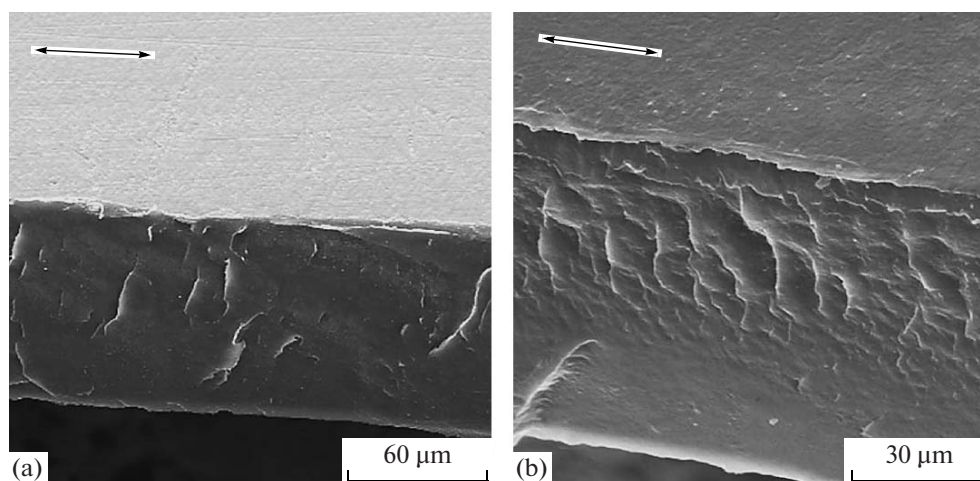


Fig. 8. SEM images of the solvent-crazed samples based on the annealed PP (a) after its tensile drawing in ethanol by 100% and (b) annealing at 120°C.

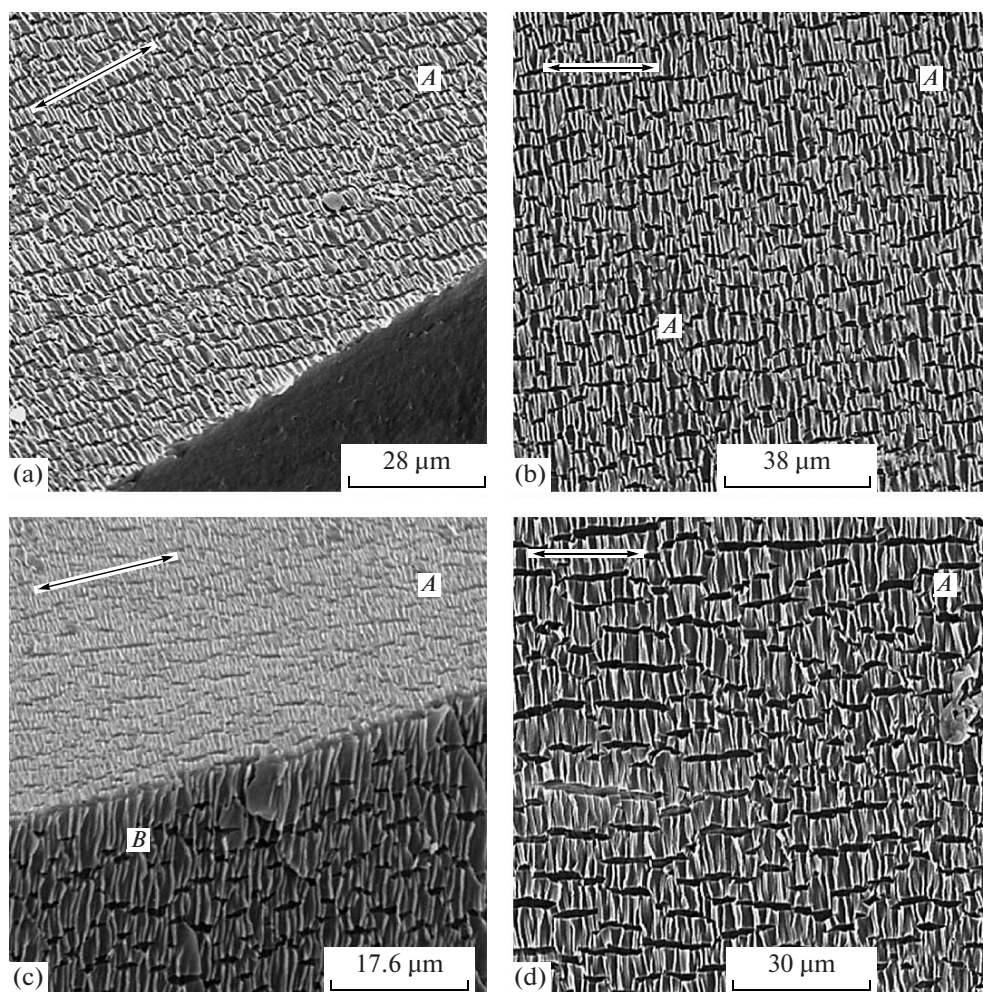


Fig. 9. SEM images of the solvent-crazed samples based on the annealed PP after their postannealing at (a, b, c) 120 and (d) 140°C: (a, b, d) the samples were decorated with a thin (10 nm) platinum coating and (C) the fractured surface of the sample was decorated with a metallic coating. Region *A* is the surface of the sample, and region *B* is the fractured surface.

results from the development of internal stresses. Figure 10 presents the data on the isothermic heating of the solvent-crazed samples based on preannealed (curve 1) and initial PP (curve 2). As follows from Fig. 10, with increasing temperature, the stress in the solvent-crazed samples starts to increase virtually at room temperature. This increase in stress is observed in both cases at temperatures below $\sim 100^\circ\text{C}$; then, stress decreases with increasing temperature nearly to the melting temperature of PP. This temperature dependence of stress with its maximum is explained by the two oppositely directed processes. An increase in stress likely is related to an increase in the entropy force in the oriented polymer chains, and a decrease in stress comes from the depression in yield stress with increasing temperature [23].

This seems to be very important, because it makes it possible to reveal the nature of the above phenomenon. Indeed, with increasing temperature, an increase in stress in a solid with fixed dimensions is possible

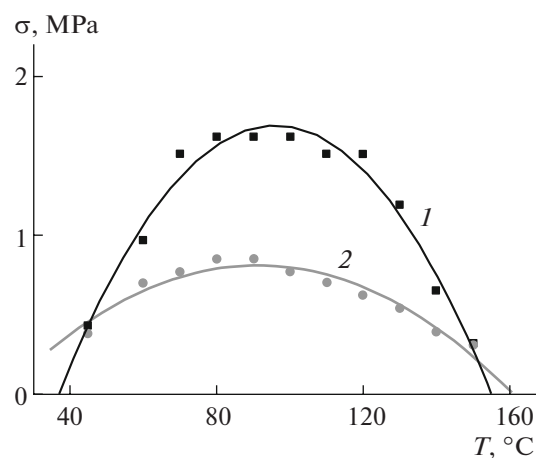


Fig. 10. Curves illustrating isometric annealing of the solvent-crazed samples based on (1) preannealed PP and (2) initial PP after their tensile drawing in AALE by 100%.

only for oriented polymers with the chain structure of macromolecules at temperatures above the glass transition temperature [24]. Therefore, the observed low-temperature shrinkage has an entropy nature. However, at room temperature, PP exists $\sim 140^\circ\text{C}$ below its melting temperature; hence, it seems unclear how, under such conditions, the molecular motion responsible for the low-temperature shrinkage of the solvent-crazed PP proceeds.

Let us remind the reader that recrystallization of the initial unoriented material is crucial for the tensile drawing of a semicrystalline polymer via necking. This process is associated with tensile stress and related temperature. For this reason, the oriented polymer in the neck “remembers” its temperature of tensile drawing and annealing. The necked material becomes unstable, and shrinkage takes place only when the polymer is heated above the temperature of tensile drawing or subsequent annealing [23].

Noteworthy is that the stress-induced melting (amorphization) by itself is insufficient to provide the recrystallization of a semicrystalline polymer during its tensile drawing. The development of the crystalline phase with its long-range ordering requires sufficient amounts of material. At the same time, in the course of the tensile drawing of a semicrystalline polymer in AALE (via crazing), the stress-induced amorphization is also coupled to the dispersion of polymer into the aggregates of oriented macromolecules with dimensions of 5–10 nm. Under the above conditions, the stress-induced amorphization of a polymer is insufficient to provide its efficient recrystallization because the polymer is dispersed into spatially separated aggregates of macromolecules containing ~ 10 oriented macromolecules [25]. With the allowance for the fact that, after its stress-induced amorphization, the polymer exists in its rubbery state (above glass transition temperature), it acquires the ability for high reversible strains [24]. Removal of the adsorptionally active solvents from the volume of crazes, when shrinkage of the solvent-crazed sample is prevented, is accompanied by the coagulation (coalescence) of the fibrillar aggregates of macromolecules and by an increase in their dimensions [16]. Obviously, this coarsening of the oriented polymer phase is also accompanied by a partial recrystallization of the fibrillar material, and polymer, on the whole, acquires its aggregative stability. However, due to the high level of the interfacial surface, this system exists in a state of static equilibrium when the entropy contraction force of the amorphized oriented polymer is equilibrated by the strength of the framework of the recrystallized polymer.

This material is subjected to annealing in its free-standing state. Once temperature is increased, the entropy contraction force of the amorphized polymer immediately starts to grow in full accordance with the statistical theory of the rubbery state [24]. This stress decreases the melting temperature of the crystalline framework down to room temperature, and the poly-

mer melts down (amorphization). The amorphized polymer undergoes relaxation (contraction) and recrystallization in its less stressed (less oriented) state. This process is similar to the above phenomenon of recrystallization, which takes place during the cold tensile drawing of the polymer [21, 22]. The difference is that this proceeds in the opposite direction and results not from the action of the applied external force but from the entropy-driven internal stress. As the annealing temperature of the solvent-crazed polymer is increased, the contraction force increases (Fig. 10); as a result, more “high-melting” regions of the solvent-crazed polymer appear to be involved in the recrystallization and the resultant shrinkage increases. The overall stress continues to grow until the crystalline framework is able to resist the contraction force of the amorphized oriented chains of the crystalline polymer. However, with increasing temperature, this resistance inevitably decreases and the stress in the sample goes down until the polymer appears to be in its fully unstressed recrystallized state.

The difference in the thermomechanical behavior of the initial and annealed PPs is the following. Classical solvent crazing (initial PP) is accompanied by the nucleation and growth of individual crazes, in which craze fibrils bridging their opposite walls can acquire a marked length (tens of microns). Since the diameter of craze fibrils is tens of nanometers [16], they are flexible and mobile aggregates of macromolecules able to merge into bundles of bigger dimensions. As a result of this coagulation, the size of the bundles significantly increases and this process is accompanied by their partial recrystallization into an oriented crystalline lattice. In the solvent-crazed PP, this lattice provides its aggregative stability; hence, upon the removal of AALE from the polymer structure, the sample retains its dimensions.

Deformation of the annealed PP in the presence of AALE proceeds via delocalized solvent crazing [11]. This implies that all intercrystallite amorphous regions are simultaneously involved in stretching. Obviously, provided all other conditions are the same, the length of fibrillar aggregates linking the neighboring crystallites is appreciably lower than that upon classical solvent crazing. As a result, their ability for coagulation and formation of a continuous phase appears to be fully suppressed. Hence, their ability for recrystallization is prohibited, and a marked fraction of the intercrystallite material preserves its amorphous state upon the removal of AALE from the volume of crazes. Therefore, the “dry” solvent-crazed sample based on the annealed PP undergoes significant marked shrinkage. This behavior seems evident because, at room temperature, amorphous PP exists in the rubbery state well above its glass transition temperature. Upon further tensile drawing, all processes related to the shrinkage (Figs. 1 and 10) are better pronounced in the solvent-crazed sample based on the annealed PP, as compared with the case of initial PP, because, upon

delocalized solvent crazing, the resulting specific surface is higher and, hence, all recrystallization processes are prohibited.

Hence, in this work, low-temperature shrinkage of the solvent-crazed PP has been discovered for the first time, and we have shown that this process has an entropy nature. This shrinkage results from contraction of the extended polymer chains and their transition to more thermodynamically favorable contracted conformations. This contraction is possible because, in the course of annealing, the entropy-driven contraction force increases. This force leads to the melting (amorphization) of the crystalline lattice of the oriented PP; as a result, the extended chains shrink, the stored stresses relax, and their further recrystallization in the unstressed state takes place.

ACKNOWLEDGEMENTS

We would like to thank V.I. Gerasimov for fruitful discussions.

REFERENCES

1. A. L. Volynskii, T. E. Grokhovskaya, A. S. Keчек'yan, et al., Dokl. Akad. Nauk **374**, 644 (2000).
2. A. L. Volynskii, A. S. Keчек'yan, T. E. Grokhovskaya, et al., Polymer Science, Ser. A **44**, 374 (2002) [Vysokomol. Soedin., Ser. A **44**, 615 (2002)].
3. A. L. Volynskii, T. E. Grokhovskaya, A. S. Keчек'yan, and N. F. Bakeev, Polymer Science, Ser. A **45**, (2003) [Vysokomol. Soedin., Ser. A **45**, 449 (2003)].
4. A. L. Volynskii, T. E. Grokhovskaya, V. V. Lyulevich, et al., Polymer Science, Ser. A **46**, (2004) [Vysokomol. Soedin., Ser. A **46**, 247 (2004)].
5. A. L. Volynskii, T. E. Grokhovskaya, A. I. Kulebyakina, et al., Polymer Science, Ser. A **48**, (2006) [Vysokomol. Soedin., Ser. A **48**, 823 (2006)].
6. A. L. Volynskii, T. E. Grokhovskaya, O. V. Lebedeva, and N. F. Bakeev, Polymer Science, Ser. A **48**, (2006) [Vysokomol. Soedin., Ser. A **48**, 834 (2006)].
7. A. L. Volynskii, T. E. Grokhovskaya, and N. F. Bakeev, Dokl. Akad. Nauk **400**, 487 (2005).
8. A. L. Volynskii, T. E. Grokhovskaya, A. I. Kulebyakina, et al., Polymer Science, Ser. A **49**, 816 (2007) [Vysokomol. Soedin., Ser. A **49**, 1946 (2007)].
9. A. L. Volynskii, T. E. Grokhovskaya, A. I. Kulebyakina, et al., Polymer Science, Ser. A **49**, 1198 (2007) [Vysokomol. Soedin., Ser. A **49**, 1224 (2007)].
10. A. L. Volynskii, A. I. Kulebyakina, D. A. Panchuk, et al., Polymer Science, Ser. A **49**, 1265 (2007) [Vysokomol. Soedin., Ser. A **49**, 2063 (2007)].
11. A. L. Volynskii, O. V. Arzhakova, L. M. Yarysheva, and N. F. Bakeev, Polymer Science, Ser. B **42**, 70 (2000) [Vysokomol. Soedin., Ser. B **42**, 549 (2000)].
12. E. A. Shmatok, O. V. Kozlova, L. M. Yarysheva, et al., Dokl. Akad. Nauk SSSR **302**, 1428 (1988).
13. E. A. Shmatok, O. V. Arzhakova, L. M. Yarysheva, et al., Vysokomol. Soedin., Ser. B **32**, 577 (1990).
14. E. A. Shmatok, S. V. Kalinina, O. V. Arzhakova, et al., Vysokomol. Soedin., Ser. A **32**, 1282 (1990).
15. J. Grembowicz, S. F. Lau, and B. Wunderlich, J. Polym. Sci., Polym. Symp., No. 71, 19 (1984).
16. A. L. Volynskii and N. F. Bakeev, *Solvent Crazing of Polymers* (Elsevier, Amsterdam, 1995), p. 248.
17. S. L. Bazhenov and V. V. Lyulevich, Khe Tszyanpin, et al., Polymer Science, Ser. A **43**, (2001) [Vysokomol. Soedin., Ser. A **43**, 996, 2001)].
18. A. L. Volynskii, T. E. Grokhovskaya, O. V. Lebedeva, and N. F. Bakeev, Polymer Science, Ser. A **48**, (2006) [Vysokomol. Soedin., Ser. A **48**, 834 (2006)].
19. A. L. Volynskii, A. S. Keчек'yan, T. E. Grokhovskaya, et al., Polymer Science, Ser. A **44**, (2002) [Vysokomol. Soedin., Ser. A **44**, 615 (2002)].
20. A. L. Volynskii, T. E. Grokhovskaya, A. S. Keчек'yan, and N. F. Bakeev, Polymer Science, Ser. A **45**, (2003) [Vysokomol. Soedin., Ser. A **45**, 449 (2003)].
21. V. A. Kargin and G. L. Slonimskii, *Short Essays on Physical Chemistry of Polymers* (Khimiya, Moscow, 1967) [in Russian].
22. V. I. Gerasimov, Doctoral Dissertation in Chemistry (Moscow, 1980).
23. V. I. Gerasimov, V. D. Zanegin, V. D. Smirnov, and M. V. Ivanov, Vysokomol. Soedin., Ser. A **21**, 1615 (1979).
24. L. Treloar, *The Physics of Rubber Elasticity* (Oxford Univ. Press, Oxford, 1949; Mir, Moscow, 1975).
25. A. S. M. Yang and E. J. Kramer, J. Polym. Sci., Part A **23**, 1353 (1985).