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Temperature-Induced Relaxation in Deformed Polymer Glasses

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Temperature-induced relaxation of polymer glasses after their plastic deformation involves recovery of residual deformation and relaxation of inner energy stored by polymer during deformation. In general case, this process is realized in two temperature regions: at temperatures below polymer glass transition point and in temperature region of glass transition. Complex behavior of temperature-induced relaxation is considered in terms of specific features of elementary relaxation transitions and conformational changes in the deformed polymer as well as according to the speculations concerning supermolecular organization of polymer glasses. Principal approaches to the description of this phenomenon based on the examination of literature data are outlined. The importance of the research activities focused on temperature-induced relaxation of the deformed polymers is related to the development of modern theories of plastic deformation of glassy polymers.

Keywords: Polymer glasses; relaxation; plastic deformation; structure

INTRODUCTION

Temperature-induced relaxation of plastically deformed polymer glasses has been a subject of many investigations [1–17]. In general case, temperature-induced relaxation involves recovery of residual deformation and relaxation of inner energy stored by polymer during its plastic deformation. This relaxation is realized in two well-pronounced temperature regions: at temperatures below polymer glass transition temperature T_g (i) and in temperature region of glass transition (ii). The existence of two relaxation modes allows one to suggest the existence of the corresponding modes of plastic deformation of glassy

polymers. In connection with this, investigations focused on relaxation behavior of the deformed polymer glasses [1, 5, 7, 10, 17] provided a basis for the development of speculations concerning the mechanism of plastic deformation in glassy polymers.

Practical aspects of this problem seem to be quite evident. Deformation and relaxation behavior of polymer glasses are directly related to the development of advanced construction materials with improved properties, which are characterized by combination of high rigidity and low brittleness. On the other hand, processing of polymer glasses into final articles is usually accompanied by polymer plastic deformation. Hence, shape stability and stability of properties of final articles appear to be intimately related to relaxation of this deformation in polymer under operating temperatures. In connection with this, the problems related to temperature-induced relaxation are of great practical importance for improvement in thermal stability of polymer materials based on polymer glasses [6].

At the present time, there is a vast of experimental evidence concerning temperature-induced recovery of residual deformation and relaxation of inner energy in the deformed polymer glasses. However, in many cases, experimental results obtained by different authors were in conflict with each other. This conflicting evidence suggests the necessity of a thorough examination of all available literature data concerning the experimental results as well as mechanisms of temperature-induced relaxation in deformed polymer glasses.

1. Experimental Evidence Concerning Temperature-Induced Relaxation in Deformed Polymer Glasses

Temperature-induced relaxation of residual deformation ε_{res} of plastically deformed polymer was studied for various polymer glasses [1–17]: initial and cross-linked PMMA [2–6], PS [7, 10], copolymers of styrene with methacrylic acid [1], PC [7, 10], amorphous PET [7, 10, 13], polysulfone [7], and cross-linked epoxy-amine polymers [7–16]. In [2–4], the test samples were uniaxially compressed at deformation temperatures T_{def} from 293K to polymer glass transition temperature T_g . After than, they were cooled by liquid nitrogen in a stressed state. Temperature-induced recovery of ε_{res} was estimated by measuring the changes in height of the free-standing samples at heating

with constant heating rate starting with 213K. In [7–16], the samples were deformed under uniaxial and hydrostatic compression and under creep condition at T_{def} . Temperature-induced relaxation of ϵ_{res} was also studied by measuring the changes in linear dimensions of the deformed samples at constant heating rate.

Despite a variety of polymers and regimes of plastic deformation, all regularities of temperature-induced relaxation of ϵ_{res} show general character.

In general case, recovery of geometrical sizes of plastically deformed polymer glasses takes place in two well-defined temperature regions and involves two components: low-temperature component ϵ_1 and high-temperature component ϵ_2 (Fig. 1). Let us note that high-temperature component of relaxation ϵ_2 is realized in rather narrow temperature region related to polymer glass transition, whereas low-temperature component ϵ_1 is associated with a wide temperature interval at temperatures below T_g . Minimal temperature, at which the appearance of low-temperature relaxation was revealed, is equal to 103K [7].

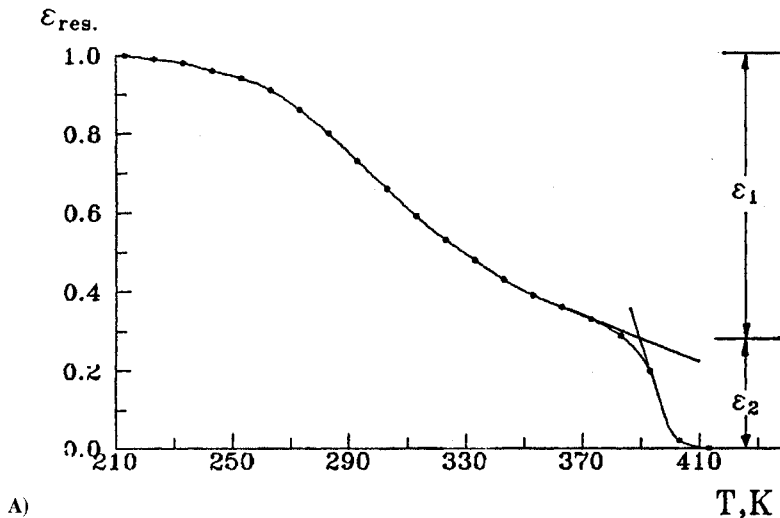


FIGURE 1 Temperature dependences of relative residual deformation ϵ_{res} of PMMA ($T_{\text{def}} = 293$ K, $\epsilon = 20\%$, uniaxial compression) [2] (A) and rate of recovery of residual deformation ϵ_{res} of epoxy-amine polymer ($T_{\text{def}} = 188$ K, $\epsilon = 25\%$, uniaxial compression under creep conditions) [10] (B).

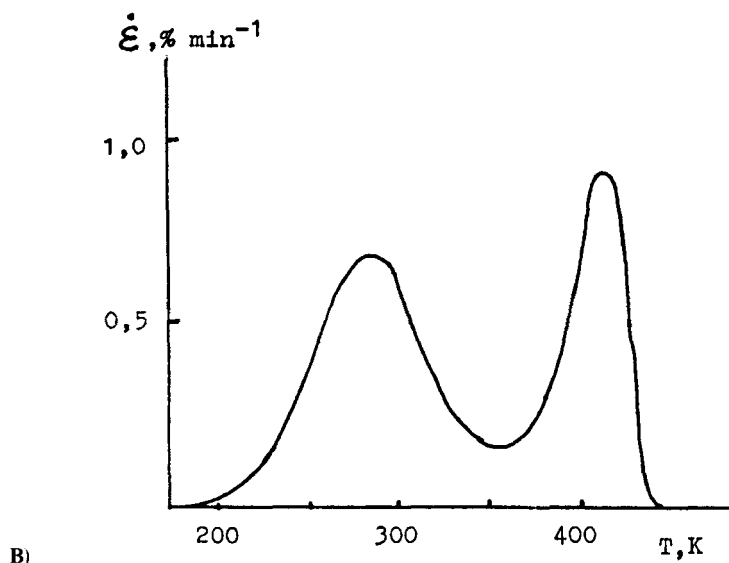


FIGURE 1 (Continued).

Each temperature below T_g is associated with a certain recovery of ϵ_{res} , and the whole temperature dependence of ϵ_1 shows a well-pronounced smooth character (Fig. 1a).

The ratio between the low-temperature and high-temperature components of recovery of ϵ_{res} was studied as a function of strain [2, 5]. For the compressed samples with rather low strains complete recovery of ϵ_{res} takes place at temperatures below T_g (Fig. 2, curves 1, 2). On the contrary, complete recovery of ϵ_{res} of the samples with high strains is observed on heating to T_g (Fig. 2, curves 3–5). However, in this case low-temperature component is also involved.

Figure 3 shows the dependences of low-temperature ϵ_1 and high-temperature ϵ_2 components on strain as well as the corresponding stress-strain diagram of uniaxial compression of PMMA. As follows from Figure 3, in the case of the samples with strains below yield point ϵ_y , recovery of ϵ_{res} proceeds via low-temperature mode ϵ_1 . At the strain corresponding to ϵ_y , component ϵ_1 is maximal, and further increase in compression strain is associated with the appearance and growth in component ϵ_2 at constant ϵ_1 .

As evidenced by DSC studies of deformed polymer glasses [1, 7, 10, 17, 18], on heating the samples of deformed polymer, a well-

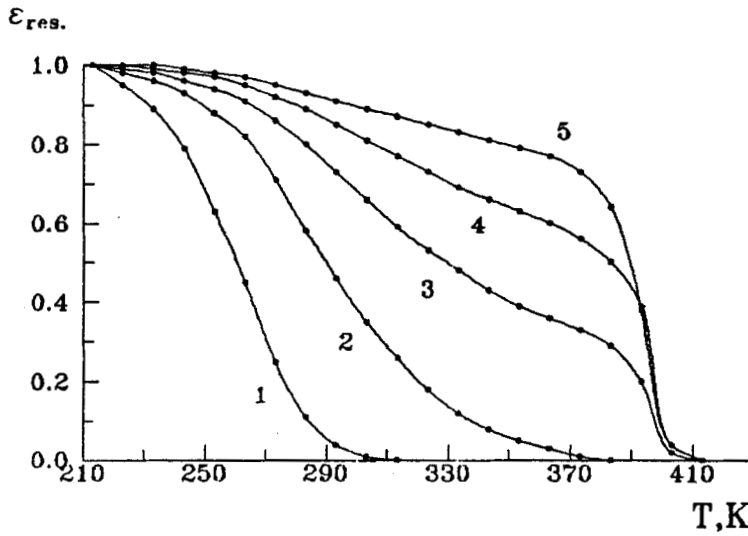


FIGURE 2 Recovery of residual deformation ϵ_{res} of PMMA samples with strains 10 (1), 14 (2), 20 (3), 30 (4), and 50% (5). ($T_{def} = 293$ K, uniaxial compression) [2, 5].

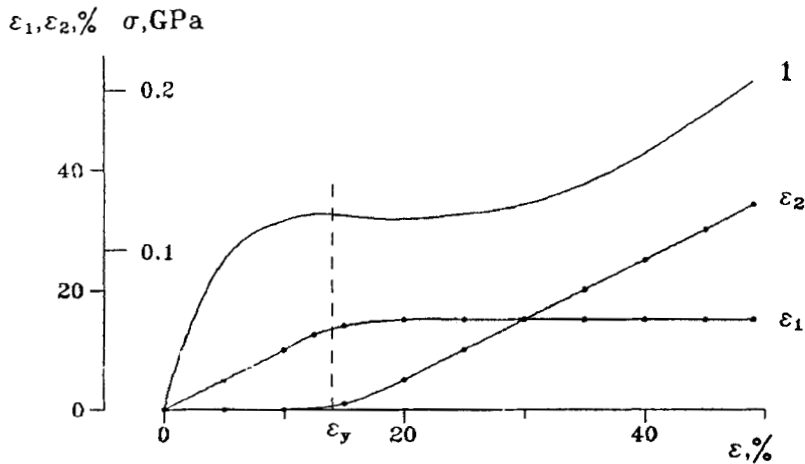


FIGURE 3 Stress-strain curve corresponding to uniaxial compression of PMMA samples at 293 K (curve 1) and low-temperature ϵ_1 and high-temperature ϵ_2 components of temperature-induced recovery of residual deformation versus strain ϵ [2, 5].

pronounced exothermic effect is observed, in contrast to initial undeformed sample (Fig. 4). The corresponding area of the exothermic peak in DSC curves provides a quantitative characterization of excess enthalpy ΔH_{exo} of the deformed polymer.

Examination of thermodynamic parameters of polymer deformation (work for deformation W , deformation heat Q_{def} , and variations in inner energy of the deformed polymer ΔU_{def}) in cyclic loading regime [8–10] showed that unloaded sample is characterized by stored inner energy ΔU_{st} . The values of ΔH_{exo} estimated from the DSC curves for the deformed samples are quite similar to the values of ΔU_{st} as obtained by deformational calorimetry [9,11] and measurements of heats of dissolution of deformed samples [11].

Hence, excess enthalpy may be related to inner energy stored in the deformed and unloaded samples. In connection with this, hereinafter, we will make no difference between these two parameters, and relaxation of enthalpy on heating of deformed samples will be treated as relaxation of inner energy.

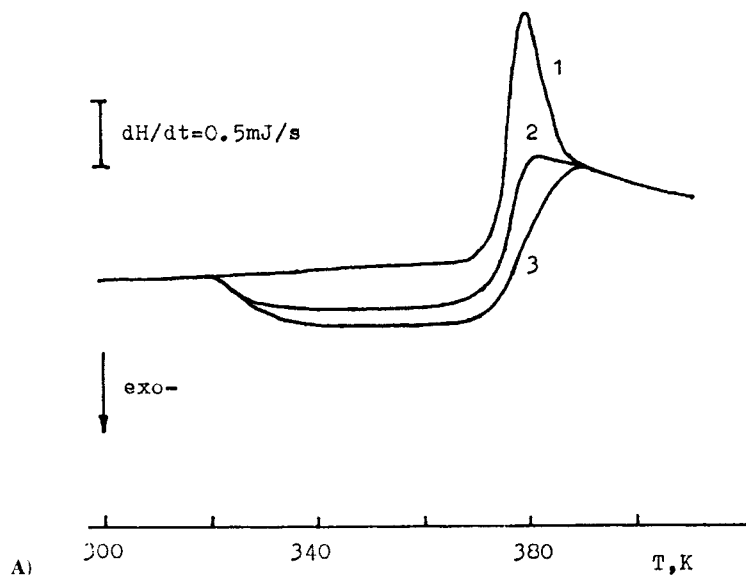


FIGURE 4 DSC curves of virgin PS (1) and PS uniaxially compressed to strains 20 (2) and 40% (3) (A); and virgin PVC (1) and PVC uniaxially drawn (2) and compressed (3) to strain 40% (B) [1].

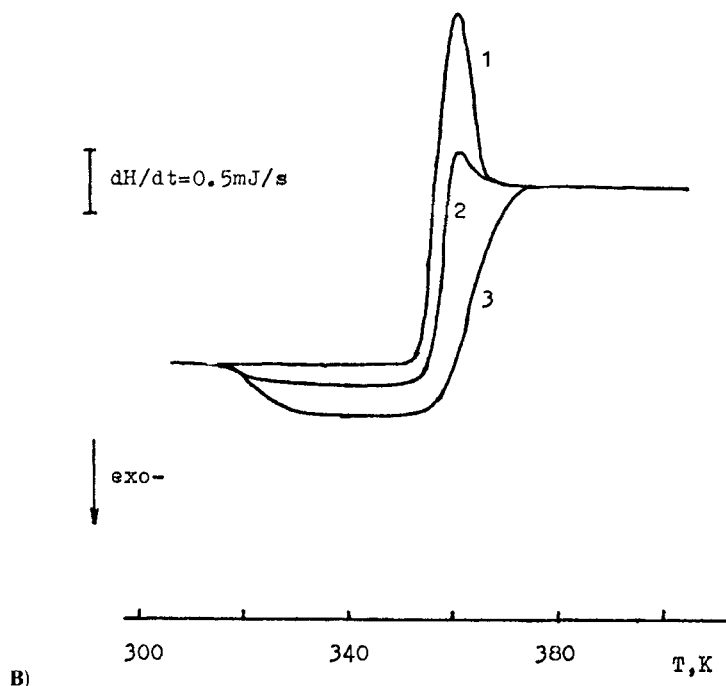


FIGURE 4 (Continued).

Figure 5 shows the resolution of work for polymer deformation W into deformation heat Q_{def} and stored inner energy ΔU_{st} as estimated by deformational calorimetry [7, 10]. Let us emphasize that, at all stages of deformation studied, a marked fraction of W is stored in polymer as ΔU_{st} . This feature is characteristic of plastic deformation of glassy polymers. In the case of an ideal plasticity, work for deformation is completely transformed to Q_{def} . The behavior of most of plastic materials (primarily, crystalline metals) is close to the above pattern and changes in inner energy induced by plastic deformation are only few percent of W . For polymers, the corresponding value is estimated to be as high as ten percent.

Comparison between Figures 3 and 5 suggests a formalized correlation of strain dependences of low-temperature component ε_1 of relaxation of residual deformation and stored inner energy ΔU_{st} . As was shown in [10, 12], almost all inner energy ΔU_{st} is related to low-temperature component ε_1 and relaxation of ΔU_{st} is observed at

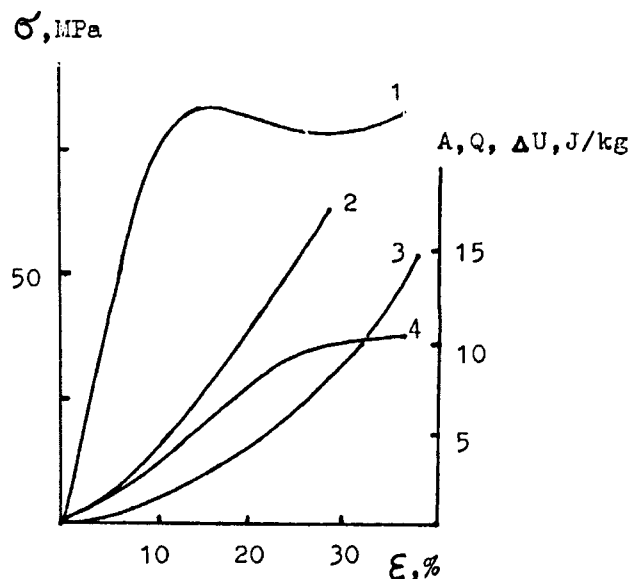


FIGURE 5 Stress-strain curve corresponding to uniaxial compression of PS at 303 K (1) and mechanical work for deformation W (2), heat of deformation Q (3), and inner energy ΔU (4) as a function of strain ε [10].

temperatures below T_g . However, this result appears to be in conflict with the speculations presented in [1,18], according to which temperature-induced relaxation of stored inner energy shows a two-stage character, and complete relaxation of ΔU_{st} takes place at temperatures corresponding to temperature region of glass transition (Fig. 6, curve 1). In connection with this, there is no evident correlation between the energy stored in polymer during its plastic deformation and low-temperature component ε_1 of relaxation of ε_{res} . Nevertheless, storage of inner energy in polymer is always associated with the appearance of residual deformation.

2. Modern Approaches to Description of Temperature-Induced Relaxation in Deformed Polymer Glasses

Hence, temperature-induced relaxation of plastically deformed polymer glasses involves two events. The first is related to recovery of residual deformation, which is associated with two well-defined tem-

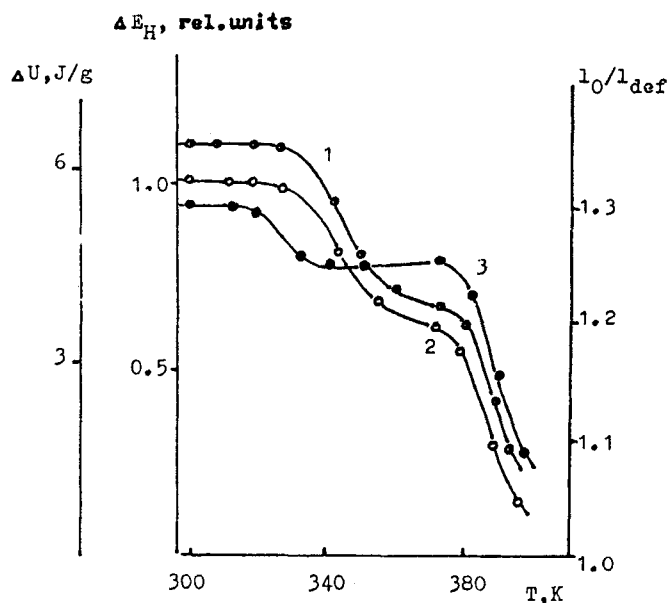


FIGURE 6 Temperature dependences of relaxation of stored inner energy ΔU_{st} (1), recovery of hydrogen bonds ΔE_H (2), and recovery of linear dimensions l_0/l_{def} (3) of copolymer of styrene with 16 mol.% of methacrylic acid ($T_{def} = 293$ K, $\epsilon = 30\%$, uniaxial compression) [1, 8].

perature regions, whereas the second is provided by relaxation of stored inner energy ΔU_{st} , which is also characterized by a two-stage character [1]. To gain a deeper insight into the mechanism of temperature-induced relaxation of the deformed polymer glasses, let us discuss the nature of these phenomena and correlation between them. Let us start our discussion with possible reasons of changes in inner energy during deformation of glassy polymers.

In general case, storage of inner energy during polymer deformation may be related to the two following reasons [1, 19]:

1. *Conformational (intramolecular) changes*

Plastic deformation of polymers, similar to rubbery deformation, is accompanied by a lowering in conformational entropy, and changes in intramolecular conformational energy. In contrast to rubbery deformation, plastic deformation of polymer glasses at temperatures below

T_g is not associated with a complete recovery of energy intramolecular balance on polymer unloading. The reason is related to the frozen-in segmental mobility at temperatures below T_g .

For polymer chains with different conformational energy, i.e., with hindered inner rotation, the changes in intramolecular energy are dictated by transition from one conformational state to another ones. The tendency of changes in energy state of the deformed polymer (increase or decrease in inner energy) are controlled by the sign of temperature coefficient of unperturbed dimensions of macromolecule $d \ln \langle r^2 \rangle_0 / dT$, where $\langle r^2 \rangle_0$ is a mean distance between the ends of free-standing polymer chain.

Positive values of $d \ln \langle r^2 \rangle_0 / dT$ are characteristic of polymers, in which more extended conformational sequences possess higher energy. As a result of plastic (or rubberlike elastic) deformation or with increasing temperature, the fractional content of such sequences increases, and inner energy of deformed polymer also increases.

In the case of polymers, in which extended conformations are characterized by lower conformational energies and $d \ln \langle r^2 \rangle_0 / dT < 0$, polymer deformation is associated with a decrease in inner energy.

Hence, in general case, polymer deformation may be accompanied either by increase or decrease in inner energy. In connection with this, transformation of energy conformational state during polymer deformation may hardly be considered as a universal factor responsible for an increase in inner energy of the deformed polymer.

2. Development of inner stresses

In deformed polymers, a certain fraction of work for deformation is associated with the development of inner stresses in polymers. Relaxation of these inner stresses should be accompanied by scattering of the stored energy. The nature of strain-induced inner stresses will be discussed in more detail.

3. Development of new surfaces

In general case, deformation of polymer bodies is accompanied by the development of a new surface as a result of microcracking and crazing as well as polymer fibrillation. However, this factor may be ignored taking into account small contributions from the above processes to the changes in energy state of the deformed polymer.

4. *Disruption of chemical bonds*

Disruption of chemical bonds in polymers under their deformation is recognized by the appearance of free radicals in the material [20]. However, the number of disruption events is rather small, and the number of macromolecules involved does not exceed 10^{18} g^{-1} . The energy providing the formation of free radicals and energetics of concomitant mechanochemical processes are negligibly small, and this factor may be ignored.

5. *Changes in volume of deformed polymer*

With increasing temperature from room temperature to glass transition temperature, direct measurements of changes in volume of PS samples after their uniaxial compression showed no marked changes in volume within an accuracy of $\Delta V/V = 10^{-4}$ [14, 21]. In this case, during heating, a marked release of the stored inner energy is observed. This evidence suggests that storage and release of inner energy for deformed glassy polymers may take place at small volume changes.

Hence, the above speculations concerning the possible sources providing changes in energy during polymer deformation allow us to conclude that the development of inner stresses and their storage in unloaded samples, subsequent relaxation of which is characterized by exothermic character, is of primary importance.

According to the theory developed by Oleinik *et al.* [7, 10, 17], storage of inner energy in deformed glassy polymers is related to the fact that, under the action of external stresses, elementary local shear bands (plastic shear transformations) appear in polymer. Plastic shear transformations (PSTs) are nonconformational shear structures, each of which is characterized by local shear strain $\varepsilon_{\text{PST}}^{\text{loc}}$ and is surrounded by field of elastic stresses. Local shear strains and field of elastic stresses corresponding to PSTs may exist only in polymer glasses because of their high viscosity and they are not allowed in rubbery state because of fast relaxation.

Accumulation of PSTs in glassy polymer proceeds at rather early stages of deformation, and as concentration of PSTs increases, inner energy of the deformed polymer also increases. At strains of about 25–30%, stationary stage of deformation of glassy polymer is realized,

and this stage is characterized by constant high level of stored inner energy (Fig. 5, curve 4). This evidence is assumed to be controlled by equilibrium between nucleation and degradation of PSTs. Degradation of PSTs is associated with their transition into new chain conformations and severe conformational gauche-trans rearrangements. This process is accompanied by the appearance of extended coils enriched with nonequilibrium conformational sequences. Finally, local inner energy of PST disappears, but local strain remains preserved. Let us note that evolution of PSTs was invoked in [7, 10] to rationalize an increase in mechanical loss as well as an increase in enthalpies of activation of relaxation processes in deformed polymer glasses, as compared with initial samples.

Low-temperature relaxation of deformed polymer glasses at temperatures below T_g is provided by recovery of stored PSTs associated with their transition to initial state. In this case, both local inner energy and local shear strain of each PST disappear. This process is assumed [7] to have nothing in common with conformational changes in polymer chains. Speculations concerning nonconformational nature of low-temperature relaxation via recovery of PSTs are supported by direct spectral observations [13]. According to [13], relaxation processes in polymer glasses at temperatures below T_g do not involve conformational trans-gauche transitions¹. High-temperature relaxation of residual deformation in the region of polymer glass transition is controlled by entropy recovery of nonequilibrium conformations of macromolecular coils via segmental mobility. Just within temperature region of glass transition, dramatic conformational rearrangements accompanied by the trans-gauche transitions were observed [13].

The problems concerning the scale of molecular motions responsible for development and relaxation of PSTs arise. According to [7], structural rearrangements in PSTs, which are able to relax at temperatures below polymer T_g , should be of small-scale order. As follows

¹ We would like to clarify this point. Within certain limits, conformational changes in polymer chain due to segmental mobility (transition from excited extended coil to equilibrium state) may be provided by torsional oscillations of groups of atoms around equilibrium state without any trans-gauche transitions within monomer unit [22]. In connection with this, we believe that the absence of trans-gauche transitions in temperature region associated with low-temperature relaxation does not provide an unequivocal evidence concerning nonconformational nature of this relaxation mode.

from experimental observations, the onset of low-temperature relaxation of ϵ_{res} was revealed at 103 K. This allows one to conclude that, at such temperatures, structural rearrangements involved in low-temperature mode of relaxation cannot be associated with large-scale (for example, segmental) motions in macromolecular chains [7]².

In [15, 16], activation volumes corresponding to the development and relaxation of PSTs were estimated from sensitivity of these processes to shear stresses and external hydrostatic pressure. In the case of epoxide polymer, at temperatures from 293 to 363 K, activation volume estimated from sensitivity of appearance and relaxation of PSTs to shear stress component was found to be equal to 0.25–0.4 nm³. The corresponding values estimated from sensitivity of relaxation of PSTs to hydrostatic pressure component were 0.055 and 0.1 nm³ for epoxy polymer and polycarbonate, respectively. The above values for activation volume of relaxation of PSTs correlate well with the corresponding values for the γ - and β -relaxation modes. This evidence allows one to conclude that low-temperature relaxation via recovery of PSTs is dictated by small-scale molecular motions. Let us note that activation volume for high-temperature component of recovery of residual deformation is close to that of the α -relaxation.

The speculations concerning the small-scale character of structural rearrangements associated with low-temperature component of temperature-induced relaxation of ϵ_{res} do not provide any explanation of a smooth character of temperature dependences of this mode of relaxation. Relaxation of PSTs should be sensitive to the appearance of γ - and β -relaxation modes on polymer heating, the activation volumes of which are comparable to the corresponding characteristics of relaxation of PSTs. In temperature region associated with the above relaxation modes, one should anticipate a sharp increase in recovery of ϵ_{res} . However, experimental curves show no marked contributions from any relaxation modes in recovery of ϵ_{res} in glassy state (Fig. 1a). The existence of a wide temperature region associated with relaxation of ΔU_{st} and smooth character of low-temperature component of recovery

²We think that recovery of ϵ_{res} at such low temperatures does not provide an unequivocal evidence in favor of small-scale molecular motions responsible for low-temperature mode of relaxation. This problem will be discussed in more detail later.

of ε_{res} is treated from the viewpoint of a wide distribution of activation energies of relaxation of each PST [7].

Let us also note that the theory of temperature-induced relaxation of the deformed polymer glasses based on speculations concerning PSTs has been developed for defect but uniform polymer medium with no account for specific structural features of glassy polymer.

During recent decades, the problems related to structure of amorphous glasses are being widely discussed in literature. Let us mention some of them.

As demonstrated by electron microscopy [23–30], electron diffraction [29, 31], positron annihilation [32], light scattering measurements [33], small-angle X-ray scattering [27], and wide-angle X-ray scattering [31], polymer glasses are characterized by structural inhomogeneity related to the existence of heterogeneous ordered regions with higher packing density (domains, clusters) with dimensions up to several nanometers. These domains are joined with each other by numerous tie chains, which constitute the regions with lower packing density and ordering. Evidently, an individual macromolecule appears to be involved in several domains and interdomain regions, and this factor is responsible for cooperative character of structure of glassy polymers.

Experimental evidence obtained provided a fundamental basis for the development of various structural models of glassy polymers. The difference between the models advanced is related to the type of principal morphological structural unit: fibril [4], domain [34, 35], globule [36–38], and cluster [39, 40]. However, at the present time, a certain lack of convincing experimental evidence does not allow one to decide in favor of this or that particular model. Hence, in this work, our speculations will be based only on unequivocal conclusion concerning structural inhomogeneity of glassy polymer, which is associated with the existence of local structural regions with different packing density and ordering of macromolecules or their fragments. This approach allows a plausible description of specific effect of plasticizing agents on molecular mobility in polymers [41, 42], dual-mode sorption of gases by glassy polymers [43–45], development of the irreversibly bound form of low-molecular-mass compounds in polymers [46–48]. The speculations concerning structural inhomogeneity are also invoked to rationalize mechanical properties of polymer glasses [23, 28, 43]. Let

us mention some works [42, 49, 50, 51], in which specific dual transitions observed in temperature region of glass transition were treated in terms of structural regions with different packing density. In this case, low-temperature transition is attributed to the appearance of segmental mobility in loosely packed regions, whereas high-temperature transition is related to segmental mobility in densely packed domains. According to [51], for various polymers, the temperature regions associated with these transitions may be shifted by dozens of degrees.

To a certain extent, structural approach providing description of temperature-induced relaxation in the deformed polymer glasses was outlined in [1]. As a principal reason accounting for an increase in inner energy during deformation of glassy polymer, changes in energy of intermolecular interaction were considered. Comparing the data obtained by DSC and IR spectroscopy [18] allowed one to advance some ideas concerning the nature of changes in energetic state of glassy polymers under deformation. PS and copolymers of styrene with methacrylic acid (from 2 to 33 mol%) were studied. Let us note that the above copolymers are characterized not only by universal Van-der-Waals intermolecular interaction but also by a specific mode of intermolecular interaction, which is controlled by double and ordinary hydrogen bonds between carboxyl groups in methacrylic acid. The energies of these bonds are 38 and 19 kJ/mol, respectively.

In addition to calorimetric studies providing estimation of ΔU_{st} , IR spectroscopy was used to determine.

- parameter of universal intermolecular interaction related to interaction between benzene rings;
- energy parameter of specific intermolecular interaction associated with hydrogen bonds between carboxyl groups of methacrylic acid;
- parameter of intramolecular energy with respect to the ratio between absorption bands of gauche- and trans-isomers.

In the cases of PS, an increase in inner energy during deformation was shown to be accompanied by a decrease in intensity of universal intermolecular interaction. Contribution from intramolecular energy to changes in polymer energy state was so small that ΔU_{st} was considered as measure of energy changes in intermolecular interaction.

In the case of deformation of copolymers of styrene with methacrylic acid, changes in universal intermolecular interaction was

rather small, and an increase in inner energy during deformation was primarily associated with disruption of intermolecular hydrogen bonds [52–54]. As evidence by DSC scans, exothermic effect for deformed copolymers is controlled by recovery of hydrogen bonds with heating.

As follows from Figure 6, the temperature dependences of relaxation of ΔU_{st} (curve 1) and recovery of hydrogen bonds (curve 2) show parallel profiles. Temperature dependence of recovery of linear dimensions of deformed samples (curve 3) demonstrates the similar behavior. All above processes proceed in two stages. The first stage is associated with the β -transition, whereas the second one is observed within temperature interval of polymer glass transition.

Hence, storage of inner energy in glassy polymers during their deformation is related to violation of intermolecular specific interactions [1]. (This conclusion correlated well with the speculations presented in [55]. According to [55], storage of inner stresses during the deformation of glassy polymer is primarily related to changes in intersegmental distances.) With increasing temperature, exothermic effect is attributed to the recovery of the disrupted intermolecular bonds. Let us note that low-temperature mode of relaxation of stored inner energy and recovery of residual deformation is directly related to the β -transition in polymer glasses [1]. To provide a more detailed description of the mechanism of relaxation of the deformed polymer glasses, let us consider correlation between the α - and β -transitions.

Speculations concerning the mechanism of the β -relaxation in glassy polymers and its correlation with the α -relaxation were advanced in [1] and based on DSC measurements on activation parameters of the β -transition in glassy polymers [56–58] reinforced with NMR data obtained for the loaded oriented polymer [59], long-wave IR spectroscopy [60–65] as well as with theoretical and spectral examination of the dynamics of hydrogen bonds [52, 53]. As was proposed, the principal structural kinetic unit responsible for both β - and α -transitions in glassy polymers is statistic (thermodynamic) segment. The mechanism of the β -transition involves quasi-independent and localized motion of statistic segment associated with the overcome of intermolecular barriers and with participation of the transgauche transition in more loosely packed regions. The relaxation α -transition is accomplished via large-scale cooperative motions of the contacting neighboring segments in a whole volume of a polymer

body. Hence, an event associated with the α -transition is nothing more but a cooperation of several events of the β -relaxation.

From this standpoint, the onset of structural relaxation of polymer glasses, which involves enthalpy relaxation and recovery of ϵ_{res} , corresponds to the temperature region associated with the β -relaxation (Fig. 6). Just at these temperatures, more loosely packed regions are involved in segmental mobility. A complete enthalpy relaxation and a complete recovery of ϵ_{res} of the deformed polymer glasses takes place at the temperature corresponding to the relaxation α -transition via segmental mobility in a whole polymer sample.

However, the data on recovery of ϵ_{res} in the deformed glassy polymers [1, 18] (Fig. 6, curve 3) appears to be in conflict with the corresponding data obtained in [2–4, 7]. As was mentioned earlier, recovery of ϵ_{res} of the deformed polymer glasses was observed starting with 213K [2–4] and 103K [7]. This does not allow one to correlate the onset of recovery of ϵ_{res} with the onset of relaxation β -transition. Furthermore, the temperature dependence of ϵ_1 appears to be insensitive to the appearance of the β -relaxation (Fig. 1a). However, let us emphasize that, according to [1], low-temperature component ϵ_1 of recovery of residual deformation is attributed to the appearance of segmental mobility in structural regions with lower packing density.

In our opinion, the speculation concerning structural inhomogeneity in polymer glasses should have logical development. Two structural sublevels with higher and lower packing density as recognized by modern structural and physicochemical studies are limiting cases in structural organization of glassy polymer. We believe that there is a continuous spectrum of intermediate states (structural sublevels) with different packing density and ordering. Within this standpoint, the temperature dependence of recovery of ϵ_{res} for the deformed polymer glasses was examined [5, 6].

Each of these structural sublevels is associated with its own relaxation time and activation energy of segmental mobility. A continuous spectrum of packing density and local ordering within the sublevels of structural inhomogeneity of polymer glasses is responsible for a continuous spectrum of activation energies and relaxation times of segmental mobility in polymer glasses. Hence, at each temperature below T_g local segmental mobility within certain sublevels is allowed. As temperature increases, segmental mobility in structural sublevels with

higher packing density comes into play, and, finally, at T_g all polymer sample appears to be involved in segmental motion.

In the case of the deformed polymer glasses, with increasing temperature, the appearance of segmental mobility in structural sublevels with higher packing density is accompanied by a gradual recovery of plastic deformation within this particular sublevels. A gradual appearance of segmental mobility in structural levels with higher packing density allows one to rationalize a smooth character of temperature dependence of ε_1 (Fig. 1a) as well as to explain the fact that each temperature is associated with a certain value of recovery of ε_{res} . A complete recovery of plastic deformation is accomplished at T_g , when the segments in densely packed structural regions (domains) are involved in segmental mobility (Fig. 1a, component ε_2). Hence, molecular mechanism for low-temperature relaxation is similar to that of high-temperature mode and involves transition of excited chain conformations to initial equilibrium state via segmental mobility in local structural sublevels in polymer glasses. Let us now consider the validity of this approach.

At the present time, the existence of structural sublevels with different packing densities in polymer glasses has been unequivocally proved by modern experimental methods [23–33], and the dimensions of free volume in loosely packed regions are comparable to activation-volume of segments. This reasoning suggests a possible realization of segmental mobility in local structural sublevels at temperature below polymer glass transition point. (Direct observations indicating realization of segmental mobility in structural sublevels with lower packing density for polymer glassy state were reported in [1, 42, 49, 51]).

Additional factors assisting segmental mobility in local structural regions in glassy polymer are the following. First, asymmetry of the field of intermolecular interaction provided by free volume is associated with a decrease in activation energy of segmental mobility [66]. Second, a certain decrease in activation energy of segmental mobility may be also related to the existence of inner stresses in polymer stored during polymer processing or polymer deformation [2, 4]. Deformation of glassy polymer is accompanied by severe structural rearrangements and/or displacements in cooperative system of supermolecular (or supersegmental) structural elements. As a result, the development of inner (most likely, elastic) stresses is observed. Highly cooperative

nature of structural organization in glassy polymers may be invoked to rationalize higher level of inner energy stored during polymer deformation, as compared with low-molecular-mass glassy and crystalline materials.

Hence, the advanced mechanism [5,6] for temperature-induced relaxation in the deformed polymer glasses, which is based on speculation concerning a step-by-step appearance (with increasing temperature) of segmental mobility in structural sublevels with different packing density, seems to be quite plausible with respect to experimental evidence on structure, mechanical properties, and specific features of relaxation in polymer glasses. The only point, which lacks direct experimental support, is related to a continuous spectrum of packing density in polymer glasses. However, this assumption seems to be a further development of modern speculations concerning structural inhomogeneity in glassy polymers.

Finally, we would like to mention that the description of two-stage character of recovery of residual deformation via a gradual appearance of segmental mobility in structural regions with different packing density allows one to approach the problems of plastic deformation of polymer glasses from a somewhat different standpoint [5,6]. At early stages (at $\varepsilon < \varepsilon_y$), plastic deformation is associated with a step-by-step mechanical activation of segments in polymer regions with lower packing density. This fraction of residual deformation is able to relax at temperatures below polymer glass transition temperature due to thermally activated segmental mobility within the above structural sublevels (low-temperature component ε_1). As strain increases, the segments within more densely packed polymer regions appear to be involved in mechanical activation. Relaxation of this fraction of ε_{res} is allowed only in the temperature region corresponding to glass transition (high-temperature component ε_2) and is realized via thermal activation of segments within the whole volume of polymer samples.

The above reasoning may serve as an extra argument in discussion concerning the interplay between diffusion (molecular kinetic) [67–69] and solid crystallike [70–72] theories for plastic deformation of polymer glasses. The first approach is related to mechanically activated liquidlike rearrangement in chain segments, which are similar to those in rubbers. Within the second approach, plastic deformation of polymer glasses is dictated by evolution of small-scale local shears, which

are similar to defects in crystals. By analogy with deformation behavior of crystals (for example [73,74]), which is characterized by a well-pronounced transition from dislocation mechanism to diffusion mechanism at $T_{\text{def}} \geq 0.6-0.7 T_m$, in [75], similar transition of polymer plastic deformation to diffusion mechanism was observed at temperatures above a certain temperature T_1 . In [7,10,17], plastic deformation of glassy polymer at temperatures below T_g is considered in terms of the mechanism of a solid body, and the threshold temperature associated with the transition from solid-body mechanism to diffusion mechanism is provided by glass transition temperature. Speculations concerning structural inhomogeneity in polymer glasses, which accounts for a gradual involvement of polymer segments within local structural regions into stress-activated liquidlike rearrangements, allow one to advance a plausible description of plastic deformation in glassy polymers, which is based on universal molecular kinetic fundamentals without any appeal to crystallike theories concerning deformation of solid bodies.

CONCLUSION

Temperature-induced relaxation in plastically deformed polymer glasses is accompanied by recovery of residual deformation in two well-pronounced temperature intervals at temperatures below T_g and in the temperature interval of polymer glass transition as well as by relaxation of the stored inner energy. At the present time, the mechanism of temperature-induced relaxation of the deformed polymer glasses is treated in terms of two alternative approaches.

The first approach [7,10,17] is based on speculations concerning independent recovery of elementary local shear bands (plastic shear transformations) at temperatures below polymer glass transition temperature and entropy recovery of nonequilibrium conformations of macromolecular coils via realization of segmental mobility in polymer at temperatures corresponding to polymer glass transition.

An alternative approach involves the speculations concerning structural inhomogeneity in polymer glasses, that is, the existence of local structural regions with different packing density and ordering [1,2,4-6]. According to this approach, the recovery of residual deformation at

temperatures below T_g is rationalized in terms of a gradual involvement of structural regions with lower packing density into segmental mobility [5,6]. A complete relaxation of plastically deformed polymer glasses is accomplished at temperatures associated with polymer glass transition via realization of segmental mobility in a whole polymer sample.

Even though at the present time there is no one universal theory accounting for temperature-induced relaxation in deformed polymer glasses, the importance of research in this field of polymer physics is indisputable. A sophisticated pattern of relaxation in plastically deformed glassy polymers is a macroscopic manifestation of a set of physical processes, which are responsible for and/or accompany plastic deformation of this case of polymer materials. In this work, we discussed some approaches to the description of deformation and relaxation behavior of polymer glasses in terms of solid-body [7,10,17] and diffusion theories [1,5,6]. In our opinion, these approaches are not conflicting but complementary with respect to each other. Evidently, in the case of polymer glasses, which take intermediate position between liquids and true solid bodies, one should reasonably anticipate a superposition of solid-body and liquidlike diffusion mechanisms of plastic deformation and relaxation. This intriguing problem is still unclear and generates much interest from the viewpoint of the development of a mechanics of this class of polymers.

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