# Estimation of Structural and Energy Parameters of Solvent Crazing in Polymers[1]

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Received October 5, 2000;
Revised Manuscript Received January 9, 2001

**Abstract**—The procedure for the preparation of polymer samples which allows the application of the Eyring–Lazurkin approach for the analysis of the structural and energy parameters of polymer solvent crazing was worked out. Changes in the activation energy of the process were shown to be responsible for the effect of surface-active liquid media on the mechanical response of polymer with the activation volume remaining almost unchanged.

## INTRODUCTION

Plastic inelastic deformation of solid polymers may be achieved by, at least three ways. Under various conditions, either shear banding, necking, or crazing is developed [1]. Notwithstanding the fact that the above modes of plastic deformation of solid polymers are well known, and characterized and present an evident practical importance, many fundamental aspects of the above phenomena are still unclear. Therefore, presently, not only a clear understanding concerning the principal difference between the above modes of inelastic deformation of solid polymers and the reasons responsible for their coexistence is missing but even various criteria for nucleation of a certain mode of deformation are still debating [1].

Thus, there is a necessity to perform a correct quantitative estimation of the structural and energy parameters for various modes of inelastic deformation of solid polymers in order to assess the fundamental reasons for their similar and different features. At the present time, such parameters are estimated within the framework of a single avowed approach. This approach as advanced by Lazurkin and Eyring [2, 3] allows one to determine the two key parameters such as activation energy and activation volume via the analysis of the temperature–time dependences of mechanical characteristics of polymers

$$\sigma_y/T = U_0/(\gamma T) + R/\gamma \ln(v/A), \qquad (1)$$

where $\sigma_y$ is the stress providing inelastic deformation (usually, yield stress), $v$ is the strain rate; $U_0$ is the activation energy of the process, $\gamma$ is the activation volume, $A$ is the empirical constant, $R$ is the universal gas constant, and $T$ is the absolute temperature.

Analysis of the inelastic deformation of solid polymers through eq. (1) provides important information concerning the fundamental features of this process. The necessary condition for applying eq. (1) is the linear dependence of stress of inelastic deformation of polymer on the strain rate. For the deformation of polymers in air, this linear dependence holds in a wide range of variations in strain rates, and this trend allows a reliable estimation of $U_0$ and $\gamma$ [4]. If polymers are deformed in the presence of active liquid media when an efficient development of crazing is observed, a linear dependence of stress on the logarithm of strain rate is violated [5, 6]. As a result, analysis of structural and energy parameters of this mode of inelastic deformation of solid polymers through eq. (1) is unfeasible.

In this work, an attempt was made to advance an original methodical procedure which makes it possible to apply Eq. (1) for the experimental estimation of structural and energy parameters of solvent crazing. The effect of the nature of liquid media and the structure of initial polymers on the specific features of solvent crazing in PET was also studied.

## EXPERIMENTAL

In this work, we used the films of amorphous unoriented PET with a thickness of 100 μm. The crystallized PET samples were prepared by annealing of amorphous samples at 140°C for 2 h. For the deformation of polymers in air and in the presence of adsorptionally active environments, the corresponding stress–strain diagrams were recorded on an Instron-4301 universal tensile machine. As active environments in which deformation of PET was carried out, several organic solvents wetting polymers were selected. To perform a

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comparative estimation of the intensity of interaction between polymer and liquid medium, the swelling of amorphous PET in the selected solvents at 60°C was studied. This temperature was chosen because it is close to the glass transition temperature of PET (75°C), and this allows one to reduce dramatically the time required for the attainment of sorptional equilibrium. Once equilibrium degree of swelling was achieved, the swollen samples were characterized by DSC on a Mettler thermal analyzer at a heating rate of 20 K/min, and the corresponding glass transition temperatures of the above systems were obtained.

This evidence permits one to classify the selected liquid media into the two groups: the solvents which do not swell polymer to any marked extent and thus do not reduce its glass transition temperature such as saturated hydrocarbons (*n*-hexane, *n*-heptane, *n*-hexadecane), ethylene glycol, low-concentrated solutions of aliphatic alcohols and the solvents which induce a marked swelling of PET and reduce its glass transition temperature. For example, the glass transition temperature of amorphous PET samples swollen to equilibrium in ethanol, *n*-propanol, *n*-butanol, $CCl_4$, and in 20% MEK solution in ethanol is equal to 43, 47, 50, 35, and 25°C, respectively. It seems important to note that all selected liquid media do not swell the crystallized PET (the degree of swelling is less than 1%, independently of the nature of liquid medium).

## RESULTS AND DISCUSSION

Let us consider the principal reasons responsible for the nonlinear dependence of yield stress or stress at post-yield region on the logarithm of strain rate for the deformation of polymer in liquid medium. First of all, let us remind that, under such conditions, inelastic deformation is spatially localized not at a single site (at the boundary between neck and the initial undeformed polymer) as is observed upon the deformation of polymer in air. Upon crazing, the transition of polymer to oriented state proceeds simultaneously at multiple zones, crazes [7]. The number of the nucleated crazes is controlled by the surface activity of liquid medium [8], loading rate or, to be more correct, by the level of stress maintaining the deformation of polymer [9], as well as by the geometric features of the sample [10]. Let us note that, under the conditions of constant strain rate, stress in the sample of deformed polymer changes in rather a complex way. First, one may observe the so-called Hookean region of the stress–strain curve which is followed by the yield point or the point of forced elasticity; then, one may observe the post-yield region of stationary deformation (craze thickening region). As a result, the stage of craze nucleation shows a rather complex character which is dramatically controlled by stress. Depending on the loading rate or, in other words, the stress level in polymer, the number of the nucleated

crazes may vary from several hundreds (thousands) per mm of length [10] to 1 per whole sample [11].

The second stage of crazing referred to as the craze tip advance is not less complicated [12]. The rate of craze tip advance is controlled by the above factors and also by the viscosity of the selected solvent [5].

In turn, the number of the nucleated and widening crazes also defines the stress level in the deformed polymer. This phenomenon is referred to as the factor of multiplicity of localized plastic deformation sites [13]. The meaning of this phenomenon is the following. Generally speaking, instead of strain rate, Eq. (1) should involve the rate of polymer transition to the oriented state, that is, the rate of orientational transformation of polymer. The strain rate may be used only when this value is proportional to the rate of polymer transformation. It is this situation that takes place upon the deformation of polymer in air and the development of a single deformation zone where polymer transformation to oriented state is localized (region at the boundary between neck and unoriented part of the polymer sample). In this case, for example, as the strain rate is increased, the rate of polymer transformation to oriented state is increased. For solvent crazing, the whole situation is essentially different. The polymer transition to oriented state takes place at one time at multiple zones referred to as crazes. This implies that, at a fixed strain rate, the rate of polymer transition to oriented state should be *n* times lower than the corresponding rate of traditional necking, provided *n* zones of polymer transition to oriented state (*n* crazes) are nucleated. Evidently, such a complicated character of the dependence of the number of the nucleated crazes on various conditions of polymer deformation should exert a quite complex effect on stress. There is a small wonder that, under such conditions, a linear dependence of stress on the logarithm of strain rate is violated.

The character of stress–strain rate dependence is also controlled by such an important factor as the ability of a solvent to penetrate effectively and in sufficient amounts to the active deformation sites in polymer. As was shown in [5], the viscosity of the solvent used has a strong effect on stress in the deformed polymer and may be the reason for deviation from the linear dependence of stress on the logarithm of strain rate.

Hence, to obtain the linear dependence of stress on strain rate suitable for the analysis through Eq. (1), one should eliminate the effect of, at least, two above-mentioned factors such as the factor of the multiplicity of localized plastic deformation sites and the kinetic factor responsible for a well-timed and sufficient delivery of an active solvent to the sites of orientational transformation of polymer.

To eliminate the first factor, the following procedure was applied. The PET sample was stretched in the presence of *n*-propanol at a strain rate of 50 mm/min to a tensile strain of 25%. As was repeatedly shown earlier [7],

the deformation of PET under such conditions proceeds exclusively via the nucleation and growth of crazes. Then, the tensile drawing was ceased, and the sample was allowed to stay with fixed dimensions in the presence of *n*-propanol for 15 min. Upon keeping the sample under such conditions, one may observe a dramatic stress drop which corresponds to the propagation of all stress-nucleated crazes through the cross section of the sample. Then, the samples were released from the clamps of tensile machine and dried in a vacuum drier for 2–4 h. Upon evaporation of the active solvent, the edges of the grown crazes come close and, as a result of shrinkage, the samples almost recover their initial dimensions [14]. This procedure allows preparation of the solvent-crazed samples of PET which contain no active solvent but have, according to the microscopic data, about 20 crazes per mm of gage length which grown through the whole cross section. A similar procedure was performed for the crystallized PET. In the latter case, the number of the grown crazes is equal to ~100 per mm.

Actually, the above procedure enables one to prepare samples which, upon the repeated stretching, should not experience the first two stages of solvent crazing, that is, the stages of craze nucleation and craze tip advance. These stages are known to be exceptionally complex and sensitive to many external factors; as a result, upon the deformation of polymer in the presence of liquid medium, the linear dependence of stress on the logarithm of strain rate is violated. When the first two stages are prevented, the whole situation is markedly simplified and the application of mechanical stress directly leads to the development of the final stage of solvent crazing, that is, the stage of craze thickening [15].

To prevent the second kinetic factor limiting an efficient delivery of the sufficient amounts of a solvent to the active deformation sites of a polymer, one should estimate the rate of solvent delivery to the craze boundary where the orientational transformation of polymer takes place. This estimation may be performed by calculation under the assumption that the driving force responsible for the rate of solvent penetration through the porous structure of craze ($dZ/dt$) is given by capillary pressure ($P_c$) [16]:

$$dZ/dt = -(\rho^2/8\eta)P_c/Z, \qquad (2)$$

where $\rho$ is the radius of a capillary (pore radius), $Z$ is the distance from a meniscus to the surface of a liquid which, in the case studied, is equal to 50 μm and this is the maximum distance which the liquid should pass to achieve the site of orientational transformation of polymer (from surface to the half-thickness of the film), and $\eta$ is the viscosity of a liquid. Taking into account that $P_c = 2\sigma\cos\theta/\rho$ (where $\sigma$ is the surface tension of solvent

and $\cos\theta$ is the contact angle), we arrive at

$$dZ/dt = \rho\sigma\cos\theta/4\eta Z. \qquad (3)$$

Formula (3) allows one to estimate the rate of the penetration of a wetting liquid ($\cos\theta = 1$) through a system of capillaries in the structure of a craze. As was shown in [17], the pore size in crazes formed upon the deformation of PET in the presence of liquid media is equal to 3–4 nm. Taking into consideration this value and the above assumptions, the rate of penetration of a wetting liquid through the system of microscopic pores of a given size appears to be not less than 20 mm/min. According to direct microscopic observations, the rate of the propagation of craze boundary is only equal to ~0.2 mm/min even when the strain rate is 100 mm/min. Therefore, the values of strain rates selected for the repeated tensile drawing PET make it possible to prevent the kinetic hindrances taking place upon the penetration of active liquid to the sites of orientational transformation of polymer. One may expect that the above procedure will allow one to exclude factors responsible for the nonlinear character of the dependence of stress on the logarithm of strain rate and, thus, will enable to apply eq. (1) for the experimental estimation of the structural and energy parameters of the solvent crazing of PET.

The samples prepared via the above procedure were tested in the presence of various solvents and in air. Figure 1 presents the typical results of this study. For both amorphous (Fig. 1a) and crystallized PET (Fig. 1b), the repeated strain–stress curves show a quite characteristic profile. In both cases, the stress–strain diagrams corresponding to the repeated stretching show the two yield points.

A similar behavior was observed in [18, 19] where the appearance of the two yield points was explained as follows. Upon shrinkage taking place after the first stretching cycle, a highly disperse material in the craze volume coagulates via the folding of individual craze fibrils and the development of interfibrillar and intrafibrillar coagulation junctions. The repeated stretching of such system proceeds so that, at the early stage, it shows an elastic character until the stress corresponding to the strength of the as-formed coagulation network is achieved.

This moment is associated with the first yield point. Naturally, the more active is the solvent used, the lower the stress corresponding to the onset of the fracture of the coagulation network. Evidently, the maximum stress is observed for the deformation of the polymer in air which is known to be mostly unfavorable sorptional medium (Fig. 1, curves *3*). A further deformation (after the first yield point) proceeds via the unfolding of craze fibrils which have coagulated upon the removal of the adsorptionally active liquid. As was shown by the direct microscopic observations [18], this process is accompanied by the opening and widening of crazes which were formed upon the first stretching cycle and coagu-
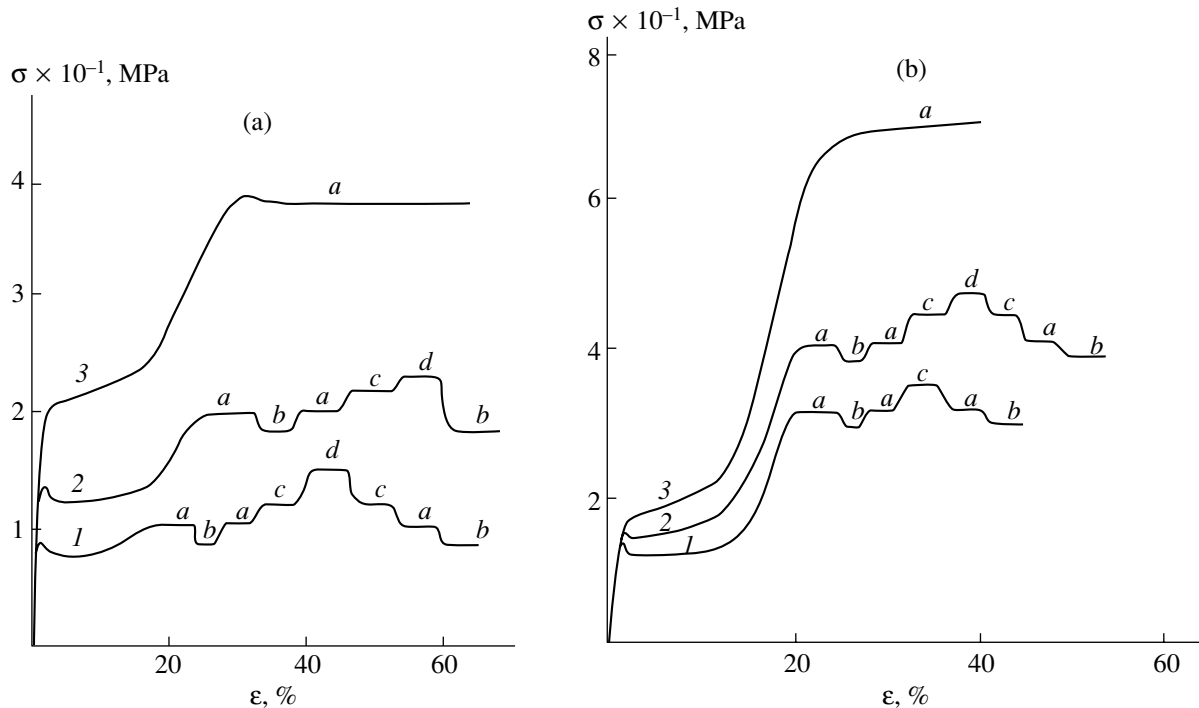
**Fig. 1.** Stress–strain curves for the repeated tensile drawing of (a) amorphous and (b) crystallized PET in (*1*) ethanol, (*2*) *n*-hexane, and (*3*) in air. Regions *a–d* stand for the fragments of the stress–strain curves corresponding to abrupt changes in strain rates: 1, 0.1, 10, and 50 mm/min, respectively.

lated upon the removal of the active solvent from crazes. Evidently, the higher the activity of the surrounding medium, the lower the stress in the repeated stretching cycle (Fig. 1), and vice versa. The above-mentioned process proceeds until all craze fibrils in the craze volume are extended; after this, the process of the orientational transformation of the polymer recommences. When the repeated tensile drawing is carried out in the presence of a liquid medium, the process of craze widening also recommences. When deformation of polymer takes place in air, one may observe necking [18]. The onset of the widening of the formed crazes or the onset of necking is related to the appearance of the second yield point in the corresponding stress—strain diagrams of the repeated stretching.

It is important to note that changes in the strain rates of the repeated stretching lead to the reversible changes in the stress in the sample. As follows from Fig. 1, with increasing or decreasing the strain rate, the same stress level is attained. This result unequivocally suggests that, upon the repeated tensile drawing, no additional crazes are formed, and the whole process proceeds via the widening of the as-formed crazes. It is also evident that the active liquid experiences no kinetic hindrances upon its delivery to the zone of the active deformation of polymer. Finally, one may conclude that we managed to eliminate the effects of both factors on the deformation of PET in the presence of liquid medium: the factor of the multiplicity of the sites of localized plastic deformation and the kinetic factor.

Figures 2a and 2b present the values of the second yield point plotted against the logarithm of strain rate for the deformation of amorphous and semicrystalline PET in the presence of various liquid media and in air. Let us note that the above dependences are linear in a wide range of variations in strain rates. This fact implies that the objective of the present work has been achieved, and eq. (1) may be used for the experimental estimation of the structural and energy parameters of solvent crazing of PET. In the case of amorphous PET, the only exception is provided by solvents with maximum swelling potency (see EXPERIMENTAL) for which the dependences of stress on strain rate are nonlinear in the region of high strain rates. This phenomenon is likely to be related to the fact that, upon crazing in the presence of the above media, a marked swelling of PET in the regions of polymer transition to oriented state takes place. In this case, the mechanism of the transfer of a liquid to the region of orientational transformation of polymer is changed. A fast transfer of liquid (viscous flow) through the system of interconnected pores in the craze volume is changed to a much lower process (diffusion) through the swollen polymer layer. Sometimes, this change in the mechanism of transfer of liquid medium may lead to a complete suppression of crazing [20].

In the case of crystallized PET, all the solvents used show a linear dependence of stress maintaining crazing in polymer on strain rate. The latter fact vividly illustrates an important role of the structure of the initial
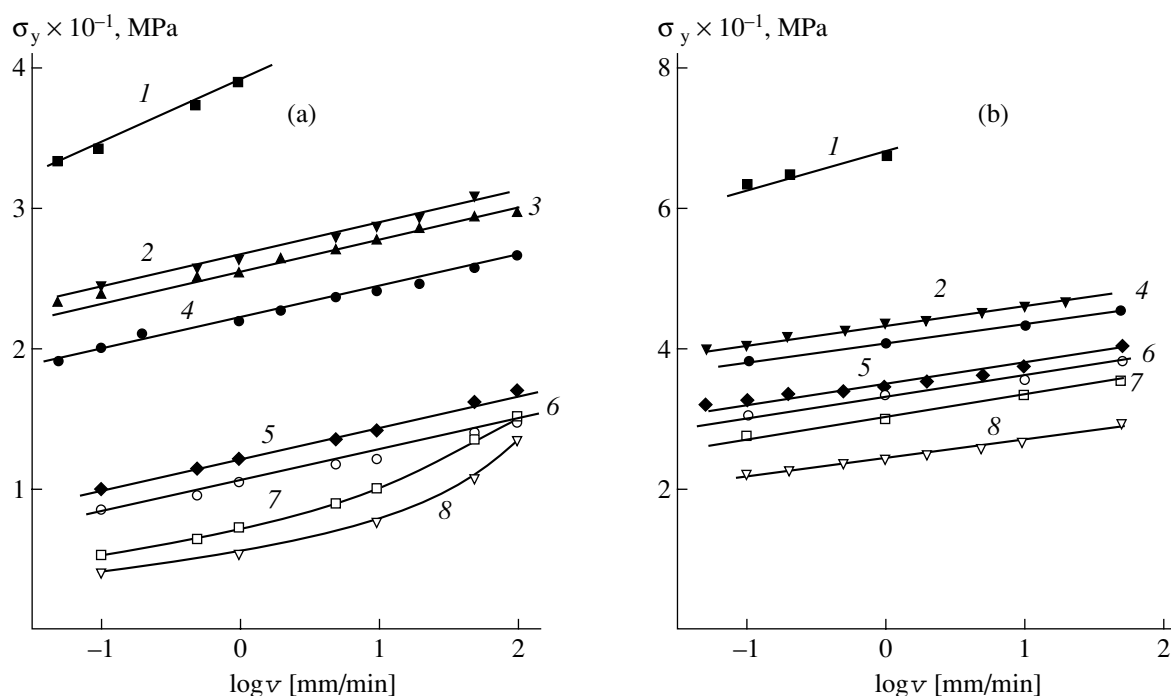
**Fig. 2.** Second yield point vs. logarithm of strain rate for (a) amorphous and (b) crystallized PET. Tensile drawing was performed in (*1*) air, (*2*) ethylene glycol, (*3*) *n*-hexadecane, (*4*) *n*-hexane, (*5*) ethanol, (*6*) *n*-propanol, (*7*) CCl$_4$, and (*8*) 20% solution of methyl ethyl ketone in ethanol.

polymer for the development of solvent crazing and incorrectness of such widely used terms as surface active or plasticizing liquid medium. Actually, as was shown in [21], the effect of a liquid medium on the deformation of each individual polymer may be different. One and the same solvent depending on its ability to swell polymer under given conditions may manifest itself as either a surface active or a swelling solvent. In particular [21], crystallization of PET suppresses its swelling in liquid media; as a result, upon the deformation of the crystallized PET, all solvents become surface active media and promote crazing. This situation is observed when such solvents as CCl$_4$ or solutions of methyl ethyl ketone are used. As was shown above, in the case of amorphous PET, the above solvents swell the deformed polymer. For semicrystalline PET, these media do not swell it to an appreciable extent; as a result, the classical solvent crazing is developed, and a linear dependence of stress on strain rate is preserved.

The above results allow one to suggest that when a linear dependence of stress on the logarithm of strain rate holds, one should primarily expect the surface-active action of liquid medium. First, this finding is proved by the linear dependence of stress on strain rate because, in this case, the transport of a liquid occurs via viscous flow through a system of interconnected pores rather than via diffusion through a swollen polymer layer. Second, the above conclusion may be proved by the data on the deformation of amorphous and semicrystalline PET in the aqueous solutions of normal

alcohols. As was found (Fig. 3), the dependence of the relative decrease in the second yield point on the molar concentration of alcohol in water follows a well-known Duclaux–Traube rule [22] both for amorphous and crystallized PET. The fulfillment of this rule was repeatedly observed in earlier experiments on solvent crazing in polymers. In the systems where the Duclaux–Traube rule holds, the action of a liquid medium is assumed to exhibit a purely surface character [22]. For these systems, one may observe a strictly linear dependence of stress of the logarithm of strain rate. Figure 4 presents this linear plot both for amorphous and semicrystalline PET upon the deformation in aqueous solutions of *n*-propanol.

Hence, in this work, first, the procedure allowing the attainment of a linear dependence of stress on the logarithm of strain rate upon solvent crazing in polymers has been worked out and, second, this dependence has been shown to prove the surface action of a liquid medium on the deformed polymer.

This evidence enables one experimentally estimate for the first time the energy and structural parameters of solvent crazing of polymers. It is important to note that, in the case studied, one may hardly determine the activation energy in its pure form. The point is that [see Eq. (1)], to reach this goal, one should obtain not only the dependences of stress maintaining inelastic deformation of polymer on strain rate (Figs. 2 and 4) but also the corresponding temperature dependences. In the case of solvent crazing, the latter condition cannot
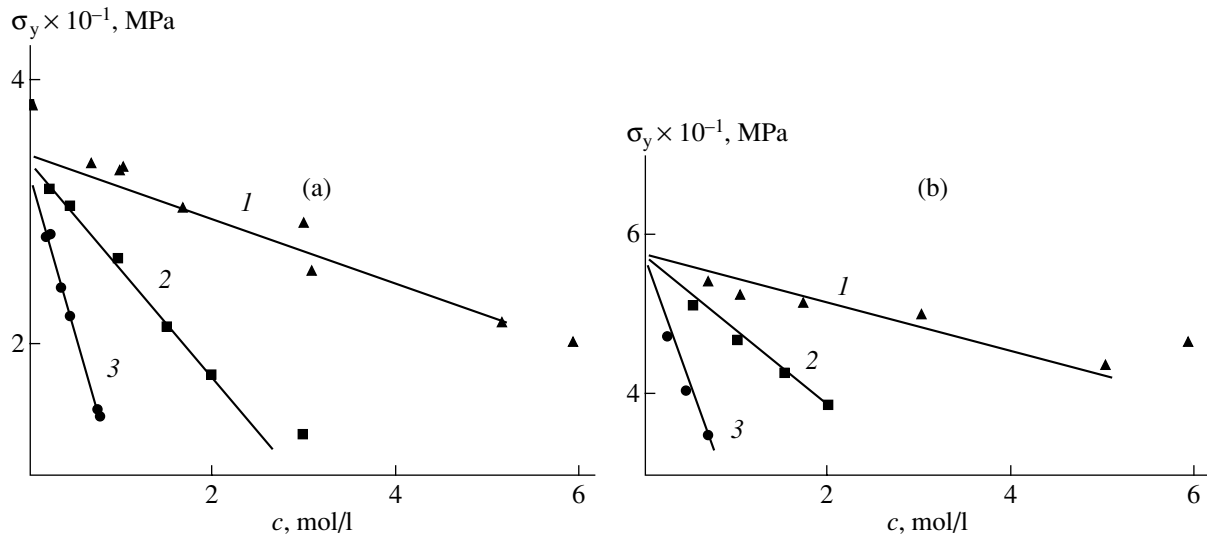
**Fig. 3.** Second yield point of (a) amorphous and (b) crystallized PET vs. concentration of (*1*) ethanol, (*2*) n-propanol, and (*3*) n-butanol in water. Strain rate is 1 mm/min.
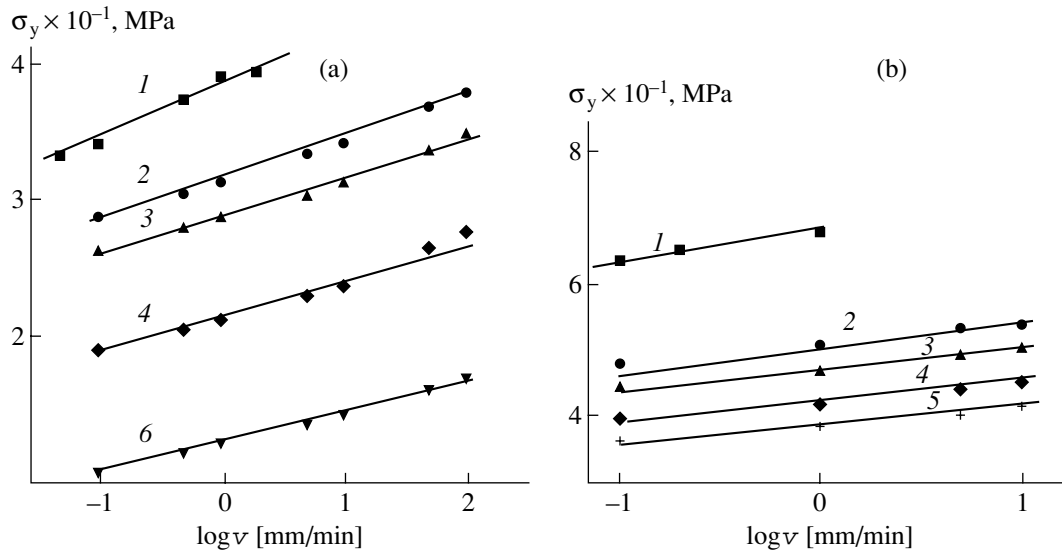


**Fig. 4.** Second yield point vs. logarithm of strain rate for (a) amorphous and (b) crystallized PET. Tensile drawing was performed in (*1*) air and in aqueous solutions of n-propanol with a concentration of (*2*) 0.5, (*3*) 1, (*4*) 1.5, and (*5*) 2 mol/l and (*6*) in n-propanol.

be satisfied, at least, for amorphous PET. As was shown above, upon heating this polymer in the presence of liquid media, the polymer experiences a noticeable swelling leading to dramatic changes in polymer structure, its glass transition temperature, and other mechanical characteristics. In this connection, we used experimental evidence to estimate the values of activation volume $\gamma$ and parameter $\Delta F = U_0 - RT\ln A$ which is related to the activation energy of plastic deformation of polymer.

Tables 1 and 2 present the resultant estimates for amorphous and semicrystalline PET, respectively. First, one should mention the striking constancy of the values of activation volume for all the systems studied. As is seen, independently of the nature of liquid medium and the phase state of polymer, the values of activation volume $\gamma$ appear to lie within the interval of 18–25 $m^3$/mol. Taking into account the scatter in the experimental data, one may conclude that the activation volume of solvent crazing in polymers remains almost unchanged under given experimental conditions. Furthermore, even upon plastic deformation of PET in air, the corresponding activation volume is close to that as observed upon the deformation of PET in the presence of an active liquid medium. At the same time, one may conclude that the principal contribution to changes in the mechanical response of polymer upon its deformation in liquid media is provided by changes in the energy parameter

**Table 1.** Parameters of the Eyring–Lazurkin equation for amorphous PET

| Liquid medium | $\Delta F$, kJ/mol | $\gamma \times 10^4$, m$^3$/mol |
|---|---|---|
| Air | 56 | 14 |
| Ethylene glycol | 63 | 24 |
| Hexadecane | 68 | 27 |
| Hexane | 56 | 25 |
| Propanol | 30 | 24 |
| Ethanol | 28 | 24 |
| Aqueous solutions of *n*-propanol, mol/l | | |
| 0.5 | 59 | 19 |
| 1 | 57 | 20 |
| 1.5 | 42 | 20 |
| 2 | 35 | 19 |

**Table 2.** Parameters of the Eyring–Lazurkin equation for semicrystalline PET

| Liquid medium | $\Delta F$, kJ/mol | $\gamma \times 10^4$, m$^3$/mol |
|---|---|---|
| Air | 90 | 13 |
| Ethylene glycol | 90 | 20 |
| Hexane | 81 | 19 |
| Propanol | 71 | 20 |
| Ethanol | 81 | 24 |
| Carbon tetrachloride | 54 | 18 |
| 20% solution of methyl ethyl ketone in ethanol | 50 | 21 |
| Aqueous solutions of *n*-propanol, mol/l | | |
| 0.5 | 93 | 18 |
| 1 | 88 | 19 |
| 1.5 | 83 | 20 |
| 2 | 80 | 21 |

$\Delta F$. Actually, depending on the nature of active medium and the phase state of polymer, this parameter changes from 28 to 90 kJ/mol. A detailed analysis of this phenomenon and its physical origin is likely to be discussed later.

The most important result of this work concerns the fact that all the dependences of stress on the logarithm of strain rate are characterized by almost the same slopes. This observation implies that, for a given mode of plastic deformation of polymer, the value of activa-tion volume $\gamma$ of solvent crazing is the same and almost independent of the nature of a liquid medium for all cases studied. In other words, in all cases, the mechanism of an elementary deformation event is the same. In the case of the repeated deformation, the shift of the dependences of stress on strain rate along the ordinate axis implies that all changes in the mechanical properties of polymers as observed upon the deformation in the presence of adsorptionally active media are primarily related to changes in the activation barrier of plastic deformation. For example, the higher the decrease in the stress maintaining plastic deformation of polymer, the higher the ability of a given adsorptionally active liquid to reduce the activation energy of the process, and vice versa.

Therefore, we worked the procedure for the preparation of polymer samples which allows one to apply the Eyring–Lazurkin approach for the analysis of structural and energy parameters of solvent crazing of polymers. As was shown, the effect of surface active liquid media on the mechanical response of polymer is provided by changes in activation energy of the process, while, in this case, the activation volume remains almost unchanged.

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