Analysis of thermally activated plastic deformation for glassy polymer poly(methyl methacrylate)

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The uniaxial compression stress-strain curves of the loading and unloading cycle and the corresponding maximum points of yield for poly(methyl methacrylate) in the temperature range, $T = 233$–$343\,\mathrm{K}$ and engineering strain range, $\dot{\varepsilon}_t = 10^{-4}$–$10^{-1}\,\mathrm{s}^{-1}$ are measured. A micromechanics model for the thermally activated plastic deformation of glassy polymer is suggested and the exact theoretical expression for plastic strain rate, $\dot{\varepsilon}_p$, is obtained. The thermodynamic parameters characterizing the plastic deformation process, including activation volume, V_a, activation enthalpy, ΔH, and activation entropy, ΔS, and their curved profiles changing with condition variables T and $\dot{\varepsilon}_t$ are provided. The number of structural repeat units in a V_a for various T and $\dot{\varepsilon}_t$ values are calculated. The changing trends of parameters ΔH and ΔS with V_a and the relationships between ΔH and ΔS for various T and $\dot{\varepsilon}_t$ are presented and compared with that between ΔH_m and ΔS_m for viscous flow in the molten state of the same polymer. The results show that the plastic deformation of glassy polymer can be regarded thermodynamically as the non-Newtonian viscous flow of overcooled melt.

(Keywords: poly(methyl methacrylate); plastic deformation; activation volume; activation enthalpy; activation entropy; non-Newtonian viscous flow)

INTRODUCTION

The more widespread applications of polymers focus greater attention on their mechanical behaviour[1–5]. We have extensively studied the deformation behaviour of perspex used in aviation, namely poly(methyl methacrylate) (PMMA), using various conditions of temperature and strain rate[6–8]. This paper studies plastic deformation behaviour in the range of low and middle strain rates by using the combined methods of macro- and micromechanics analyses for PMMA.

In addition to experimental results, this paper is primarily concerned with the essential features of stress-biased thermally activated plastic deformation, using a micromechanics model known as the slip model for structural repeat units (SRUs) in an activation volume, V_a. An exact theoretical expression for the plastic strain rate, $\dot{\varepsilon}_p$, is provided. The thermodynamic parameters characterizing the plastic deformation process, including activation volume, V_a, activation enthalpy, ΔH, and activation entropy, ΔS, and their curved profiles changing with condition variables, temperature, T, and engineering strain, $\dot{\varepsilon}_t$, are obtained. The relationships between these thermodynamic parameters are presented, and some physical and mechanical characteristics for the plastic deformation process of the glassy polymer PMMA are discussed.

EXPERIMENTAL AND RESULTS

The deformation behaviour of loaded materials is usually characterized by a stress–strain curve of the loading and unloading cycle. A typical curve for a glassy polymer is shown in *Figure 1*[9–11]. The local maximum in the curve is defined as the yield point of plastic deformation and the corresponding stress is the yield stress, σ_s.

There are many different tests to measure the stress–strain behaviour in polymers. The tensile test is the most widely used, but has two main disadvantages: in many polymers, including PMMA, the applied tensile stress may lead to fracture before yield and, even if this does not occur, it is only the extrinsic, but not the intrinsic, yield point that can be obtained. Various compression tests can overcome both of these disadvantages, and have become the recommended methods[2–4,12]. Uniaxial compression tests are adopted in this work. Atactic PMMA (18 mm thick) was machined into square test pieces (9 × 9 × 18 mm), and then carefully polished to ensure that the end sections were as parallel as possible. Other details of the sample preparation, including annealing and drying, were carried out in accordance with ASTM standards. Compression testing was done with an Instron machine using a pair of compressive clamps. The test was automatically controlled by a triangular wave generator and the relative deformation of the sample was measured by an extensometer. Consequently, the data obtained were for a constant engineering strain rate, i.e. constant $\dot{\varepsilon}_t$. (The stress and strain used in this paper are represented by true stress, σ, and engineering strain, ε.)

Experiments were carried out over the ranges for $\dot{\varepsilon}_t$ of 10^{-4}–$10^{-1}\,\mathrm{s}^{-1}$ and for T of 233–343 K. More than 40 groups of stress–strain curves were obtained. Each of these curves could show the maximum yield point and the effect of post-yielding strain softening[11]. The effects

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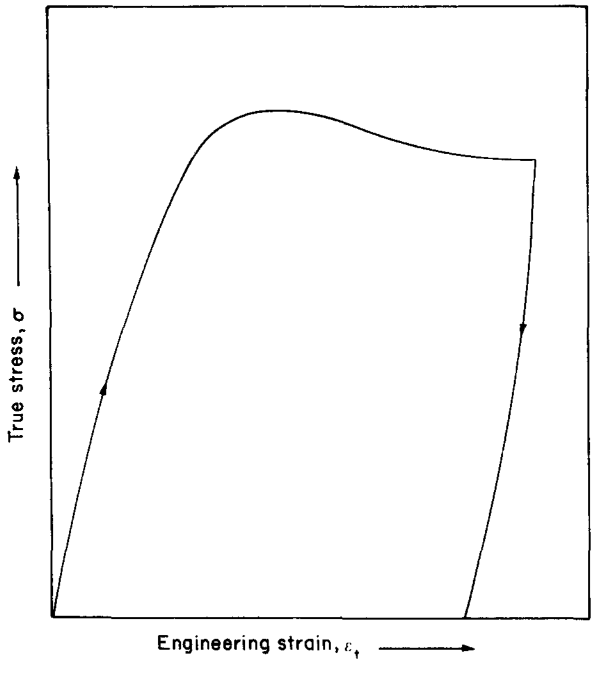

Figure 1 Typical stress–strain curve for a glassy polymer

of strain softening at higher $\dot{\varepsilon}_t$ are more serious than those at lower $\dot{\varepsilon}_t$, since the energy dissipation of plastic deformation brings about a rise in temperature and produces the effect of heat softening which would superpose on the intrinsic softening effect of the material[11].

Figure 2 shows plots of σ_s *versus* T and $\dot{\varepsilon}_t$. The former can be approximately regarded as a group of straight lines approaching zero at the glass transition temperature, T_g. The T_g of pure PMMA is 378 K, but for the aircraft perspex used in this work it is in the range of 363–378 K changing slightly with $\dot{\varepsilon}_t$. The latter for some other polymers, such as polycarbonate and polystyrene, can also be treated as straight lines as reported elsewhere, but the results obtained here and in other related reports for PMMA consistently show that they are non-linear[13–15].

SLIP MODEL AND THEORETICAL EXPRESSION

It is well known that the σ_s of polymers varies with T and $\dot{\varepsilon}_t$. Moreover, it has generally been acknowledged since the initial investigations in the 1940s that the yielding is a process of thermal activation surmounting a potential barrier which can be described by Eyring's theory of absolute reaction rates from chemical kinetics[16].

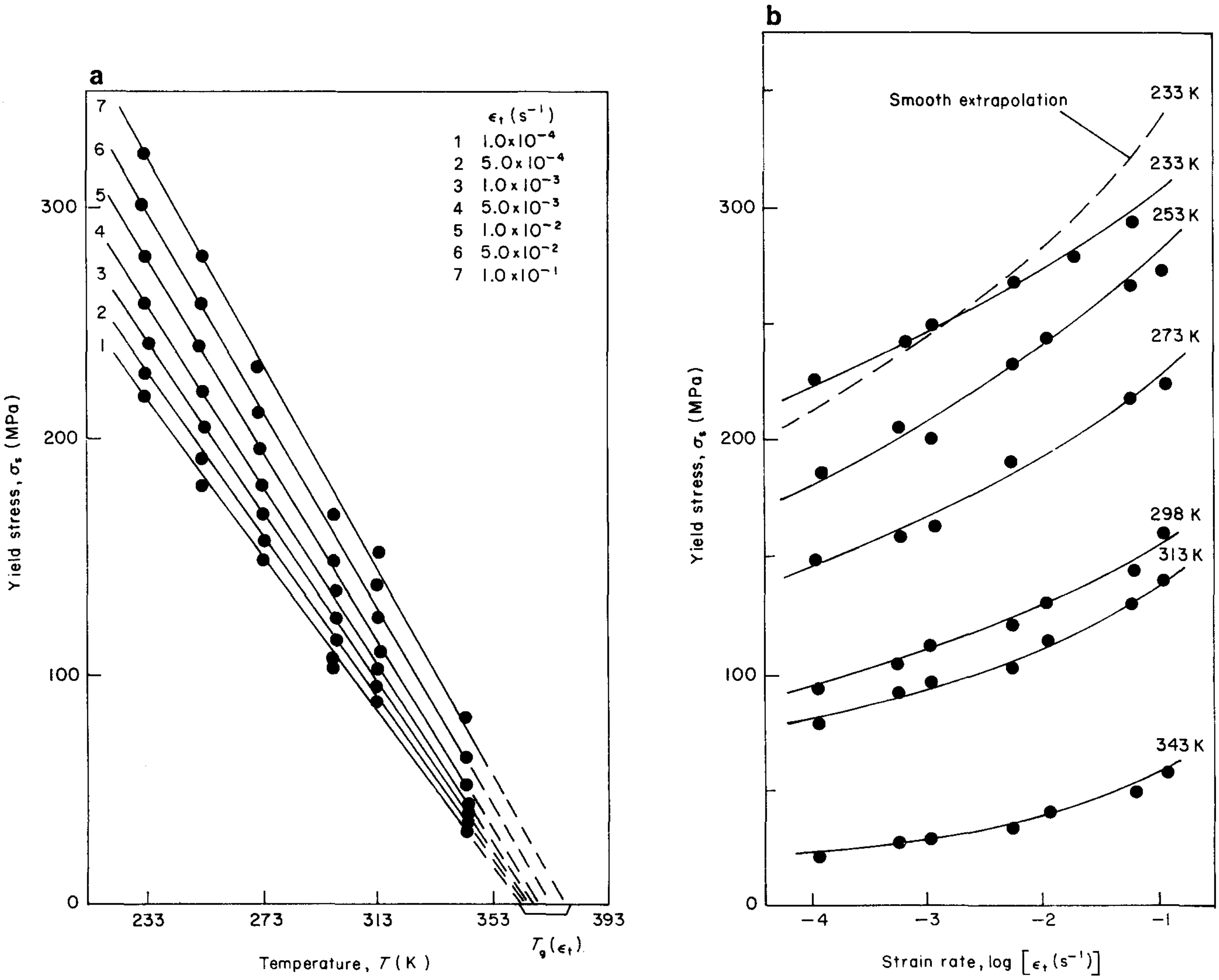

Figure 2 Plots of yield stress *versus* (a) temperature and (b) strain rate for PMMA

On this subject, a more explicit micromechanics consideration for the slip-shearing motion and its exact theoretical expression will now be developed. A glassy polymer is the frozen state of an overcooled melt, and its aggregate structure can be visualized as the packing of elementary structured units in space. According to Flory's random coil model, a molecular chain can be simulated as a group of equal diameter beads strung together by a flexible line, and the glassy structure is composed of a large number of long strings of beads packed in a random form in space[17]. According to the X-ray measurements of Lovell *et al.*[18], the chains are still inclined to form spherically quasi close packed structures in space, since the interactions between neighbouring beads of different molecular chains or different chain segments in the same molecule are those of the central force field produced by Van der Waals' bonds. Any bead, i.e. SRU, in such a structure will have ~10 closest neighbours on average compared to 12 for a perfect close packed structure, and its density differs only by ~15% from that of the perfect crystalline state. In particular, Lovell *et al.* concluded that the glassy structure of a polymer can be best represented as an assemblage of random chains with uncorrelated segments distributed as close packed random spheres[18,19]. A more detailed discussion is presented in the Appendix.

A schematic diagram of an activation unit as a whole passing over a potential barrier is shown in *Figure 3*. The transitional frequencies of the activation unit in opposite directions are equal when there is no imposed stress. When a shearing stress, τ, is imposed along the slip plane and direction, the potential barrier will produce a certain stress bias, and the transitional frequencies in opposite directions will differ. According to the classical approximation of Boltzmann statistics and the theory of absolute reaction rates, this can be expressed as:

$$\begin{aligned} \nu_{\rightarrow} &= \left(\frac{\beta_1}{2} \times \frac{kT}{h}\right) \exp\left(-\frac{\Delta G - V_a\tau}{kT}\right) \\ \nu_{\leftarrow} &= \left(\frac{\beta_1}{2} \times \frac{kT}{h}\right) \exp\left(-\frac{\Delta G + V_a\tau}{kT}\right) \end{aligned} \tag{1}$$

The frequency of net transitions in the direction of τ is:

$$\nu_\tau = \nu_{\rightarrow} - \nu_{\leftarrow} = \left(\beta_1 \frac{kT}{h}\right) \exp\left(-\frac{\Delta G}{kT}\right) \sinh\left(\frac{V_a\tau}{kT}\right) \tag{2}$$

where T is the absolute temperature, h and k are the Planck and Boltzmann constants, respectively, ΔG ($= \Delta H - T\Delta S$) is the height of the potential barrier, and is known as the activation free energy, and ΔH and ΔS are the activation enthalpy and activation entropy, respectively. The term β_1 is a constant between 1.0 and 2.0.

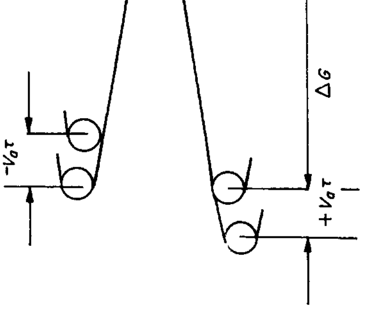

Figure 3 Schematic diagram of a complete activation unit passing over a barrier

The shear strain produced by every activation transition is given by:

$$\gamma_p = \beta_2 \frac{V_a}{V_m} \times \frac{\lambda}{\lambda_1} \tag{3}$$

where λ/λ_1 is the elementary shear strain produced in the V_a described in the Appendix, V_a/V_m is the fraction of the activation volume in a molecular chain, and V_m is the volume of a molecular chain, which in our case can be taken to be 284.24 nm^3 per chain when $\bar{M}_w$ is 2.0×10^5. The term β_2 is a factor considering the effect of non-uniform plastic deformation in a macroscopic specimen. The following expression can be derived by combining the above relations:

$$\dot{\gamma}_p = \gamma_p \nu_\tau = \beta\left(\frac{V_a}{V_m}\right)\left(\frac{kT}{h}\right) \exp\left(\frac{\Delta G}{kT}\right) \sinh\left(\frac{V_a\tau}{kT}\right) \tag{4}$$

where $\beta = \beta_1\beta_2(\lambda/\lambda_1)$. The magnitude of β is taken as a constant (2.0) since the primary results obtained from the basic rate equation are essentially unaffected by varying the value of β by an order of magnitude.

In order to convert the shear stress, τ, into the uniaxial compression stress, σ, the following relation, first derived by Brady and Yeh, may be used[15]:

$$\tau = \xi\sigma \tag{5}$$

The factor ξ can be derived according to the Bowden–Jukes' yield criterion, a modified Coulumb–Mohr's yield criterion, and in our case can be expressed as[20,21]:

$$\xi = \frac{1}{2}[\cos\phi - (1 - \sin\phi)\tan\phi] \tag{6}$$

where $\tan\phi$ is the coefficient of internal friction contained in the expression of yield criterion, and for PMMA it may be taken as 0.158 according to the result reported by Bowden and Jukes[20]. By inserting this value into the above equation, a value for $\xi = 0.427$ can finally be obtained.

In order to convert the shear strain rate, $\dot{\gamma}_p$, into the uniaxial compression strain rate, $\dot{\varepsilon}_p$, the relationship between shear strain, γ, and principle strains ε_i may be used[22]:

$$\gamma = (ll'\varepsilon_1 + mm'\varepsilon_2 + nn'\varepsilon_3) \tag{7}$$

where (l, m, n) and (l', m', n') are the direction cosines of the normals of the slip plane and its normal plane. In our case, the angle of the normal of the slip plane with the axis of compression may be taken as ~45°. When selecting the coordinate system of principle strain and taking $\varepsilon_1 = \varepsilon_p$ and $\varepsilon_2 = \varepsilon_3 = -\varepsilon_p/2$, the following relations can be obtained:

$$\gamma_p = \frac{3}{2}\varepsilon_p \qquad \dot{\gamma}_p = \frac{3}{2}\dot{\varepsilon}_p \tag{8}$$

By inserting these relations into equation (4), the exact theoretical expression for $\dot{\varepsilon}_p$ can be obtained:

$$\dot{\varepsilon}_p = \left(\frac{4}{3} \times \frac{V_a}{V_m} \times \frac{kT}{h}\right) \exp\left(-\frac{\Delta G}{kT}\right) \sinh\left(\frac{\xi V_a\sigma}{kT}\right) \tag{9}$$

Equation (9) means that the yield stress should be the stress when $\dot{\varepsilon}_p$ is equal to the loading strain rate, $\dot{\varepsilon}_t$, and this result can be considered as another, but equivalent, definition for the yield point[3]. Taking into account $\sigma_s \gg 1$, $\sinh(\xi V_a \sigma_s / kT)$ will be equal to $\exp(\xi V_a \sigma_s / kT)/2$, and the above equation can be represented as:

$$\dot{\varepsilon}_t = \left(\frac{2}{3} \times \frac{V_a}{V_m} \times \frac{kT}{h}\right) \exp\left(-\frac{\Delta G}{kT}\right) \exp\left(\frac{\xi V_a \sigma_s}{kT}\right) \tag{10}$$

This is the basic theoretical formula adopted in this paper.

It should be noted that the deformation behaviour described by equations (9) and (10) has already been referred to as 'an activation dashpot' by Eyring, since these equations, which provide the relationships between $\dot{\varepsilon}_p$ and σ and $\dot{\varepsilon}_t$ and σ_s, are analogous to the viscous flow of a typical Newtonian dashpot[16].

CHARACTERISTIC THERMODYNAMIC PARAMETERS

By taking the logarithm of equation (10), and exchanging relative terms and inserting ΔH and ΔS, the following equation can be obtained:

$$\frac{\sigma_s}{T} = \frac{5.3925k}{V_a} \left[\log \dot{\varepsilon}_t - \log\left(\frac{V_a}{V_m}\right) - \log\left(\frac{2}{3}\frac{kT}{h}\right) + 0.434\left(\frac{\Delta H}{kT}\right) - 0.434\left(\frac{\Delta S}{kT}\right) \right] \tag{11}$$

This equation can be partially differentiated with respect to $\log \dot{\varepsilon}_t$ under the condition that T is constant, and with respect to $1/T$ under the condition that $\dot{\varepsilon}_t$ is constant. In operations the thermodynamic parameters V_a, ΔH and ΔS can be regarded as constants, in other words, they do not change with condition variables T or $\dot{\varepsilon}_t$ in a first approximation. Thus, the following can be obtained:

$$\left(\frac{\partial \sigma_s}{\partial \log \dot{\varepsilon}_t}\right)_T = \frac{5.392kT}{V_a} \tag{12}$$

$$\left[\frac{\partial(\sigma_s/T)}{\partial(1/T)}\right]_{\dot{\varepsilon}_t} = \frac{1}{0.427V_a}(\Delta H + kT) \tag{13}$$

From the plots of σ_s *versus* T and $\log \dot{\varepsilon}_t$ shown in *Figure 2*, the parameters V_a and ΔH can be calculated as functions of T and $\dot{\varepsilon}_t$ by making tangents to the fitting curves. By inserting the obtained values of V_a and ΔH into equation (11), parameter ΔS as a function of T and $\dot{\varepsilon}_t$ can also be determined.

At this point it should be noted that a model containing two activation dashpots has been used by Ward *et al.*[23,24] in order to consider the non-linearity of σ_s *versus* $\log \dot{\varepsilon}_t$. It is mathematically equivalent to fit the non-linear σ_s *versus* $\log \dot{\varepsilon}_t$ curves using two straight lines. Recently Nanzai has suggested that the non-linear curves can be segmentally fitted by a group of straight lines[25]. In this paper, a limiting method by taking tangents to the non-linear curves is used, and thus the functional relationships of the thermodynamic parameters V_a, ΔH and ΔS with the condition variables T and $\dot{\varepsilon}_t$ can be more explicitly obtained. From the mathematical viewpoint, the approximation contained in our tangent method is equivalent to an iterative procedure from a first approximate value to a more exact result in second approximation.

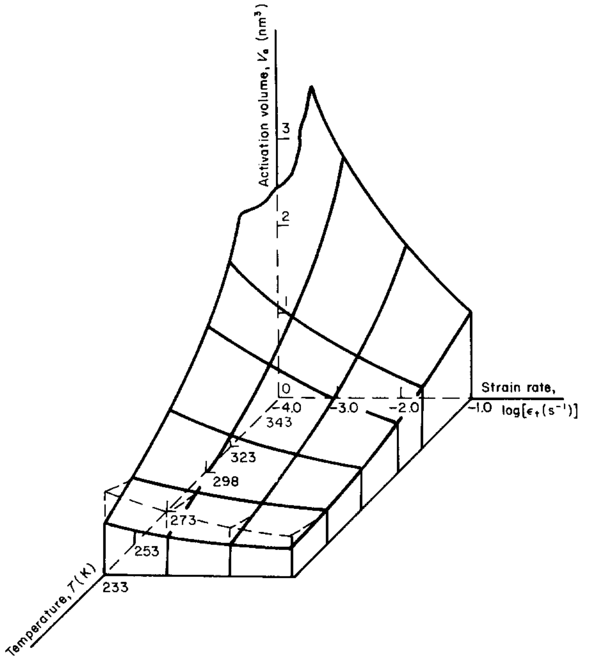

Figure 4 Profile of activation volume *versus* temperature and strain rate

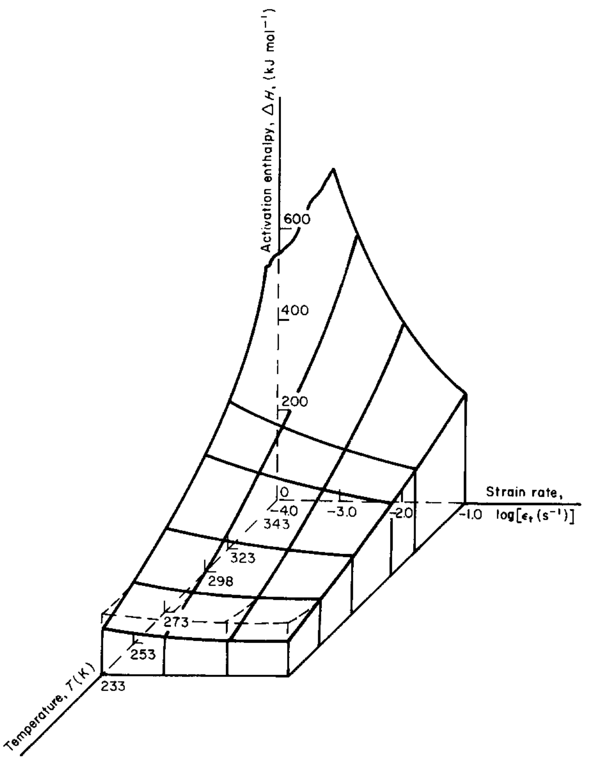

Figure 5 Profile of activation enthalpy *versus* temperature and strain rate

Figures 4–6 show the profiles of V_a, ΔH and ΔS *versus* T and $\log \dot{\varepsilon}_t$ for PMMA. These figures illustrate the change in trends of parameters V_a, ΔH and ΔS in the ranges of the temperatures and strain rates investigated. The data at 233 K appear abnormal. Thus, the results obtained from measured data and smooth extrapolative values are provided in *Figures 2b*, *4*, *5* and *6* for comparison.

THE NUMBER OF SRU

Parameters V_a, ΔH and ΔS can be regarded as a group of characteristic thermodynamic parameters which can

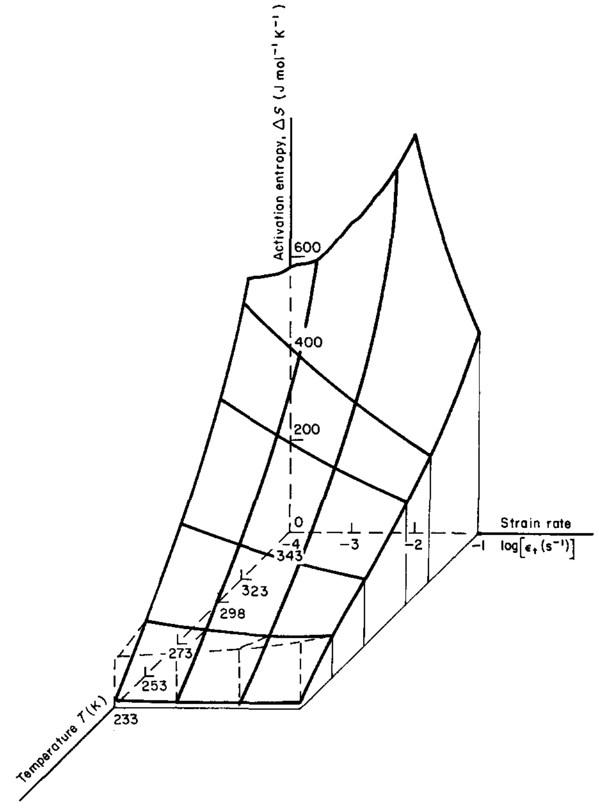

Figure 6 Profile of activation entropy *versus* temperature and strain rate

determine the behaviour of the stress-biased thermally activated process of plastic deformation. The characteristics of plastic deformation can be further understood by analysing the changes in these parameters. V_a is the volume of chain segment producing the slip motion in stress-biased thermal activation. If divided by 0.1421 nm^3, the volume of the SRU of PMMA, the number of SRUs and atoms taking part in the activation deformation can be determined[26]. *Figure 4* can also indicate the number of SRUs and atoms taking part in the activation process, which changes with T and $\dot{\varepsilon}_t$. Some calculated results for various typical condition variables are given in *Table 1*.

Figure 7 shows plots of ΔH and ΔS *versus* V_a at various condition variables T and $\dot{\varepsilon}_t$. The relations between ΔH and V_a at various strain rates are a group of straight lines converging to the origin. This situation shows that the

Table 1 Number of SRUs in the activation process and the volume occupied in a molecular chain as a percentage (in parentheses)

	Log[$\dot{\varepsilon}_t$(s^{-1})]						
T(K)	−4.0	−3.5	−3.0	−2.5	−2.0	−1.5	−1.0
343	49.8 (2.49)	38.4 (1.92)	27.5 (1.38)	19.2 (0.96)	13.5 (0.68)	10.0 (0.50)	7.5 (0.37)
298	11.6 (0.58)	10.2 (0.51)	8.9 (0.45)	7.7 (0.39)	6.7 (0.33)	5.8 (0.29)	5.0 (0.25)
253	5.8 (0.29)	5.1 (0.25)	4.5 (0.23)	4.1 (0.20)	3.7 (0.19)	3.4 (0.17)	3.2 (0.16)

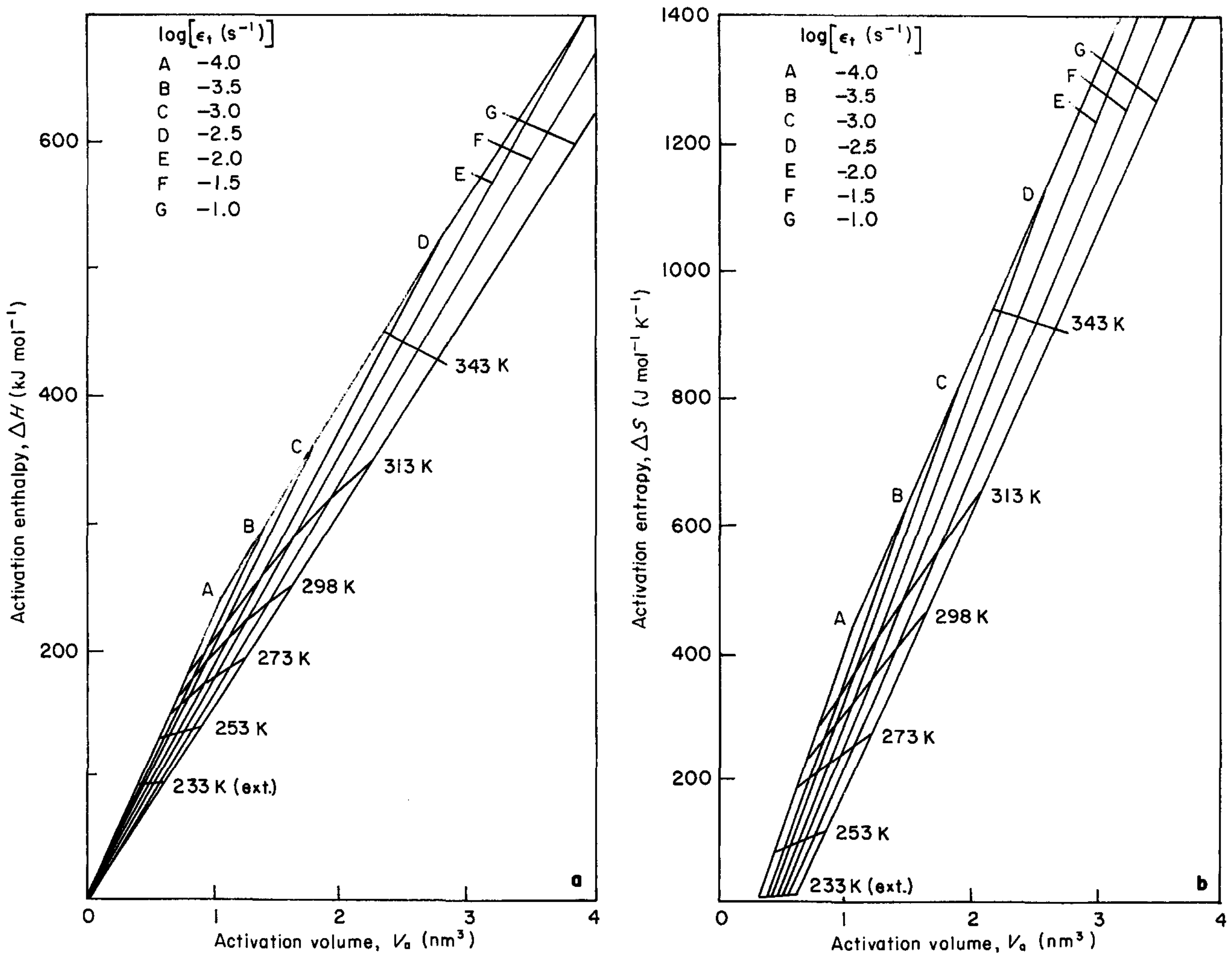

Figure 7 Plots of (a) activation enthalpy and (b) activation entropy *versus* activation volume

ratio of ΔH to V_a at different strain rates does not change with T in the range of measurements (but slightly decreases with increasing $\dot{\varepsilon}_t$), i.e. even though the number of SRUs and atoms taking part in the thermal activation increase with increase in temperature, the activation enthalpy activating each SRU or atom remains constant in the range of temperatures investigated. The ratio of ΔS to V_a does not show such behaviour; the values change not only with $\dot{\varepsilon}_t$ but also with T, although the variations are not large. It should be noted that the largest error produced in calculations of the parameters V_a, ΔH and ΔS will be involved in the activation entropy, ΔS, since the latter contains a logarithm term of a coefficient which is arbitrarily taken to be 2.0 in this paper.

NON-NEWTONIAN VISCOUS FLOW

According to the curves of ΔH and ΔS *versus* V_a shown in *Figure 7*, relationships between ΔH and ΔS for thermally activated plastic deformation at various conditions of T and $\dot{\varepsilon}_t$ can be obtained by using V_a as a varying parameter. It can be seen that the data obtained at different conditions may be represented by a single curve (*Figure 8*).

In the following discussion the relationship between ΔH_m and ΔS_m for the viscous flow of PMMA in the molten state will be derived.

From the Williams–Landel–Ferry (WLF) equation Ferry derived a theoretical expression for the activation enthalpy of viscous flow for molten polymer[1]:

$$\Delta H_m = \frac{2.303RC_1C_2T^2}{(T-T_g-C_2)^2} \qquad (14)$$

where R is the gas constant, and T_g in our case can be taken to be 368.16 K. C_1 and C_2 are material constants contained in the WLF equation, and can be taken to be 17.4 and 51.6 K, respectively, i.e. their common values.

According to the idea that the temperature $(T_g - C_2)$ is a thermodynamic transformation temperature, the approximate formula for the activation entropy of viscous flow in molten polymer can be represented as[3]:

$$\Delta S_m = \frac{2.303RC_1C_2(T_g - C_2)}{(T-T_g-C_2)^2} \qquad (15)$$

By combining these two relations and inserting various constants, the following expression can be obtained:

$$\Delta S_m = 3.159\,\Delta H_m\left(1-\sqrt{\frac{17.189}{\Delta H_m}}\right)^2 \qquad (16)$$

where the units of ΔH_m and ΔS_m are kJ mol^{-1} and J K^{-1} mol^{-1}, respectively. The corresponding curve of ΔH_m *versus* ΔS_m is plotted in *Figure 8*, and shows that the relationship between ΔH and ΔS for thermally activated plastic deformation discussed in this paper is in good agreement with that of ΔH_m *versus* ΔS_m. The results for commercial PMMA in the range of 323–388 K obtained by Nanzai are also plotted in *Figure 8*, and show good agreement with the other values[25]. These results demonstrate that the thermally activated plastic deformation of an amorphous polymer, such as PMMA, in its glassy state is equivalent to the viscous flow in its molten state from the thermodynamic viewpoint.

It should be noted that the result discussed above is both interesting and useful. It shows that the glassy state of amorphous polymer is practically the frozen state of overcooled melt. Although this is a well known viewpoint, obtaining this conclusion from a discussion of plastic deformation is novel and has not been reported in the literature previously. The practical significance is that the abundant data and information accumulated for the viscous flow of molten polymers can also be applied to the plastic deformation process of glassy polymers by extrapolation.

Although the plastic deformation of glassy polymer can be regarded as the viscous flow of its overcooled melt, this viscous flow is apparently non-linear and non-Newtonian. If this behaviour is illustrated using Newton's law of viscous flow, an apparent viscous coefficient for plastic deformation can be defined as:

$$\eta_p = \frac{\tau}{\dot{\gamma}_p} = \frac{2\xi}{3}\times\frac{\sigma}{\dot{\varepsilon}_p} = \frac{2\xi}{3}\times\frac{\sigma_s}{\dot{\varepsilon}_t} \qquad (17)$$

Figure 9 shows plots of the apparent viscous coefficient, $\log \eta_p$, *versus* $\log \dot{\varepsilon}_t$ and $\log V_a$ at various conditions according to the measured data for PMMA.

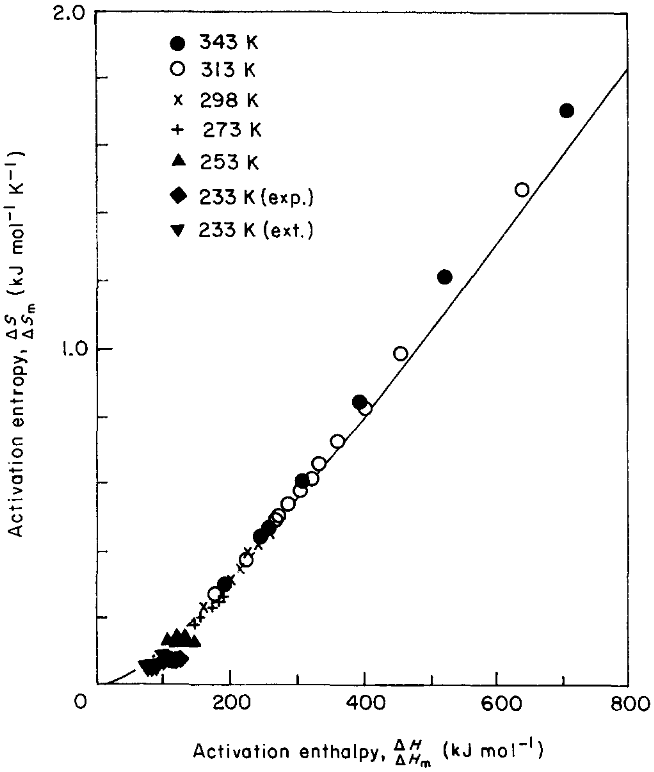

Figure 8 Relationship between activation entropy and activation enthalpy for plastic deformation of glassy PMMA and comparison with viscous flow in the molten state: (—) molten state; (○) Nanzai's data[25]

DISCUSSION AND CONCLUSIONS

An interpretation for the abnormal results measured at 233 K is now offered. It can be seen that this situation would be reflected in all the relevant parameters. Our tentative opinion is that the model of slip-shear suggested cannot perhaps be applied to such a low temperature. For example, Ward, Bowden and Argon have all indicated that the plastic deformation of glassy polymers at higher temperatures is inclined to produce thermally activated slip-shear, and at lower temperatures to form kinks by thermal activation[3,12,27]. Our experiments also support this. In the uniaxial compression tests for

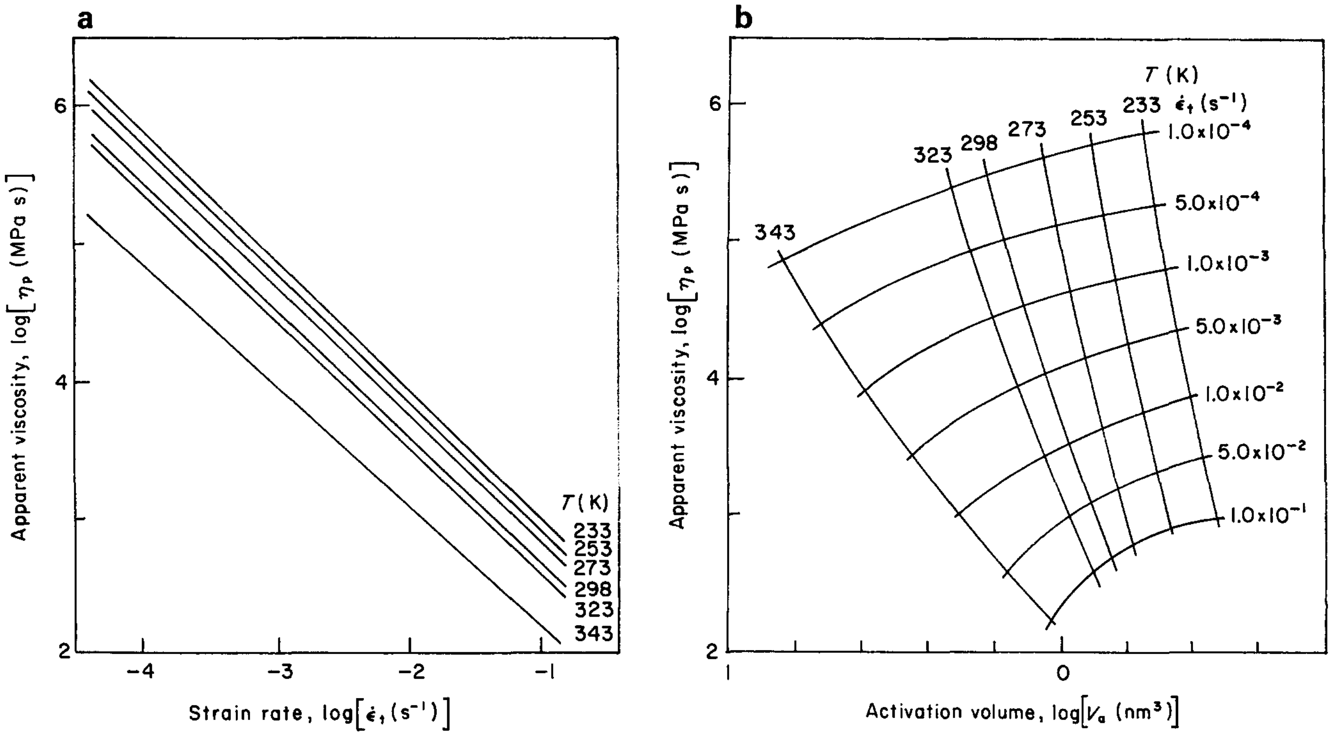

Figure 9 Plots of apparent viscosity *versus* (a) strain rate and (b) activation volume

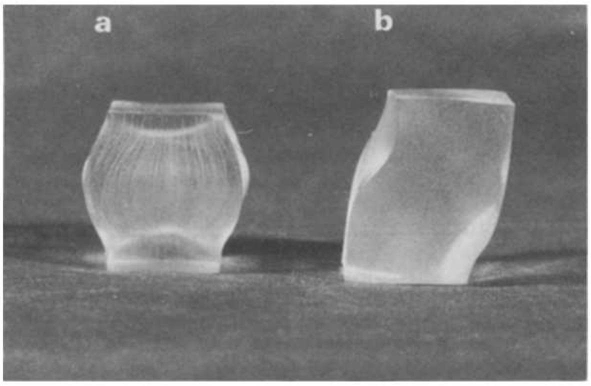

Figure 10 Photograph of test pieces loaded to very large deformation at (a) high temperature and (b) low temperature

PMMA, slip deformation is preferred at higher temperatures, and, in contrast, at lower temperatures kink deformation and break down occurs. *Figure 10* shows a photograph of typical testing pieces obtained by loading to very large deformation ($\varepsilon_t > 0.80$) in order to strengthen the deformation process in the material.

Some conclusions are now briefly summarized:

1. Experimental measurements for the uniaxial compression stress–strain curves of the loading and unloading cycle and the corresponding maximum yield points for PMMA in the ranges of $T = 233$–343 K and $\dot{\varepsilon}_t = 10^{-4}$–$10^{-1}$ s^{-1} have been carried out, and plots of σ_s *versus* T and $\dot{\varepsilon}_t$ are presented.
2. A micromechanics model, which can be referred to as the slip model between SRUs in the V_a for thermally activated plastic deformation of glassy polymer is suggested. Its exact and comprehensive theoretical expression for $\dot{\varepsilon}_p$, according to Eyring's theory of absolute reaction rates, is worked out.
3. The thermodynamic parameters V_a, ΔH and ΔS characterizing the process of stress-biased thermally activated plastic deformation and their curved profiles changing with testing conditions T and $\log \dot{\varepsilon}_t$ are calculated and discussed.
4. The number of SRUs and atoms taking part in the activation deformation are discussed. Plots of ΔH and ΔS *versus* V_a are presented and their changing behaviour is discussed.
5. The relationships between ΔH and ΔS at various conditions are derived and compared with that between ΔH_m and ΔS_m for the viscous flow of the same polymer in the molten state. Finally, it was concluded that the glassy state of amorphous polymer practically is the frozen state of overcooled melt, and the plastic deformation of glassy polymer can be thermodynamically regarded as the viscous flow of its overcooled melt.

Finally, a thermodynamic picture which is both more explicit and comprehensive than those previously reported in the literature for the thermally activated plastic deformation of glassy polymer PMMA has been presented.

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APPENDIX

On the micromechanics mechanism of plastic deformation in the form of slip-shear for glassy polymer

It is well known that slip-shear is the primary form of plastic deformation for the glassy state of amorphous polymer, but the generally accepted and common opinion about the micromechanics mechanism of plastic deformation has not been reported in the literature. There are some theories that take a molecular viewpoint, such as chain flexing by Robertson, chain twisting by Yannas and Lunn, chain bending via disclinations by Argon, a dislocation analogue mechanism by Bowden and Raha, the breaking of the Van der Waals' bonds by Brown, and a co-operative model of molecular interactions by Joseph[28–33].

During the 1980s, investigations of the slip-shear mechanism on a molecular level concentrated on the aggregate state of glassy polymers and its relationship with slip-shearing deformation. A common and generally accepted viewpoint has already been formed for the former, i.e. the glassy state of amorphous polymer can be visualized as the frozen state of overcooled melt, and can be more explicitly described by Flory's random coil model[17]. The main points relating to the packing structure are as follows:

1. The elementary structural unit of packing in space is the SRU of a molecular chain. Atoms in the SRU are fixed by covalent bonds with strong directionality, and can barely produce relative displacements with respect to each other except for rotational motions of the C—C covalent bond.
2. The long chain of molecules remains sufficiently flexible through permissible bond rotations of C—C covalent bonds in the backbone, although the SRUs between nearest neighbours are fixed by covalent bonds. One can imagine that a molecular chain can be simulated as a group of equal diameter beads strung together in a flexible line.
3. The glassy structure is composed of a large number of long strings of beads with different lengths packed in a random form in space. Different strings of beads can penetrate and entangle with each other, and then form the well known entanglement structure.

In the packing structure formed according to the above model, the neighbouring SRUs which belong to different chains or different chain segments of the same molecule are bonded by Van der Waals' bonds, having central force fields and spherical isopotential surfaces, and they are still inclined to form a spherically close packed structure. The strong covalent bonds in the backbone exert some restraints on this structure, so the packing is not as close as in a perfect close packed structure. For example, according to the measurements performed by Lovell *et al.* the average number of closest neighbours is ~10 compared with 12 for the perfect structure, and the density differs by ~15% from that of the crystalline state. In particular, they concluded that the glassy structure of polymer can be best represented as an assemblage of random chains with uncorrelated segments distributed as close packed random spheres[18,19].

According to the characteristics of the aggregate structure discussed above for glassy polymers, a micromechanics mechanism can be proposed for the slip-shear process of plastic deformation. The main points are as follows:

1. The slip-shear process of plastic deformation is a motion of relative sliding of neighbouring SRUs against the interaction of Van der Waals' bonds in transition from one equilibrium position in a potential well to a neighbouring one.
2. The motion of relative sliding is characteristic of stress-biased thermal activation. The transitional frequencies in opposite directions are different, and thus directional flow in the direction of stress, i.e. irreversible plastic deformation, appears.
3. The V_a of the elementary unit of thermally activated motion, can contain a different number of SRUs. The transitional frequency and position of such an activation unit is in accordance with the statistical rules of thermal motion of molecules.
4. When producing thermal activation, every SRU would face different heights in the potential barrier and produce different relative displacements, but there should be statistical average values for these quantities. The former is the ΔG ($=\Delta H - T\Delta S$) discussed in this paper, and the latter corresponds to a certain value of elementary shear strain:

$$\gamma = \frac{\lambda}{\lambda_1} \tag{A1}$$

5. The yielding deformation is unaffected by the entanglement structure, although the effect of strain hardening will perhaps be affected.

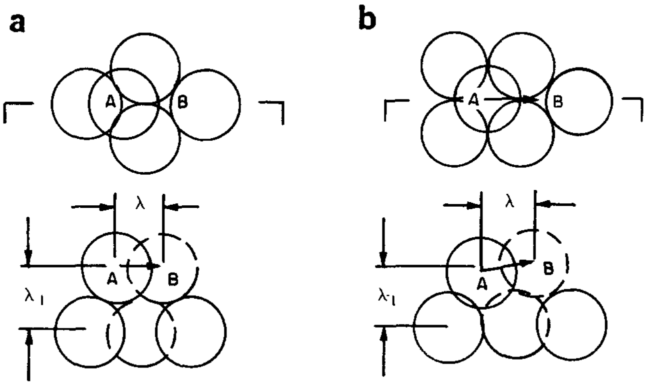

Figure A1 Schematic diagram of the transitional displacement of an SRU: (a) close packed structure; (b) quasi close packed structure

Figure A1 shows schematic diagrams for the transitional displacement of an SRU in both close packed and quasi close packed structures.

When discussing the micromechanics mechanism described above two novel papers by Brown[34] and Stachurski[35] should be considered. Brown suggested three possible forms of motion for the long chain molecules under simple shear in the spherically close packing or quasi close packing structures. The first is the relative slipping between two neighbouring segments located in parallel slip planes, referred to as Shearon. The second is the rotational motion of a chain segment located in a glissile position, referred to as Roton. The third is the slip motion of a particular chain segment relative to its stationary nearest neighbours, referred to as Tubon. The three forms of motion have different characteristics, different probabilities of taking place, and different resistances. However, it can be seen by analysis that the elementary motion of the various forms remains the elementary slip-shear motion of the SRU described above. (It should be noted that the term 'atom' used in Brown's paper should be taken generally as the elementary building block, i.e. the SRU, of the packing structure in space.) Stachurski's paper discussed in detail the packing structure and its relationship with the plastic deformation of yield for glassy polyethylene. He noted that, in contrast with the plastic deformation in crystal, which is produced by the motions of some imperfections, i.e. dislocations, in a more perfect crystal structure, the plastic deformation of glassy polymer is produced by the motions of more perfect structural units, i.e. SRUs, in a more imperfect packed structure of molecular chains. For this reason, the activation unit will undergo a process from one equilibrium state to a new equilibrium state through a corresponding combination and fitting up in each transition. Every SRU will also face different heights in the potential barrier and different amounts of elementary shear strain.