

modified to $(\partial V/\partial \ln \sigma)_P (\partial \ln \sigma/\partial P)_\epsilon$; and the latter derivative may be found in Fig. 6. For the change of volume with stress we estimate the true stress by multiplying the nominal stress by $1 + \Delta l/l_0$. For the region beyond the Lüders strain, with which we are concerned, this is a reasonably reliable procedure. The values of $(\partial V/\partial \ln \sigma)_P$ thus obtained scatter between -14 and $-64 \text{ \AA}^3$ over the range of 1 atm to 5 kbar for samples tested in water; we approximate the derivative in this region with a mean value of $-37 \text{ \AA}^3$. Above 5 kbar, $\partial V/\partial \ln \sigma$ is ~ 0 . For pentane, $\partial V/\partial \ln \sigma$ is $\sim -26 \text{ \AA}^3$ from 0–4 kbar and 0 at higher pressures. From these data, and from those in Figs. 6 and 8, one can then estimate $(\partial V/\partial P)_\sigma$ and this is shown in Fig. 9 for the (nominal) tensile stress appropriate to a value of $V^* \approx 266$ at 1 atm in water (~ 195 bar) and $230 \text{ \AA}^3$ in pentane (~ 180 bar).

It is evident that the decrease of V^* with P at constant stress is only about 60% of that at constant strain rate. We also note in Fig. 9 that V^* in pentane is always less than that in water; the coincidence of V^* at high pressure in Fig. 8 is caused by a combination of high pressure and high stress. At 8 kbar V^* is decreased by $\sim 30\%$ relative to its value at 1 atm. Some of this decrease must be ascribed to the hydrostatic compression of the material, which for the bulk polymer amounts to $\sim 10\%$ at 8 kbar. On the other hand, because pentane influences V^* and it is expected that the pentane is absorbed primarily in the amorphous region, this suggests that the decrease of V^* might reflect the compression of the amorphous

component. According to the work of Pastine¹³ this amounts to about 16% at room temperature and 8 kbar. At any rate, for the condition of constant stress and allowing for the compressibility of the material, V^* decreases by only 15–20% at 8 kbar. Such a decrease has also been found for metals.^{14,15}

The ultimate goal in determining the activation parameters which characterize plastic flow is to understand the nature of the micromechanical deformation mechanism. In this regard the influence of pentane on V^* is important, because it suggests that the rate-limiting step controlling deformation (beyond the Lüders strain) may operate in the amorphous region. One can imagine that in the already swollen polymer the difference in volume between the ground state and the activated state will be smaller except, apparently, under a combination of high pressure and high stress. According to the model of deformation developed by Peterlin¹⁶ the structure of cold-drawn PE is characterized by stacked crystalline lamellae interconnected by many tie molecules which bridge the quasiamorphous region between lamellae. The formation of free radicals on deformation, as detected by electron-spin resonance experiments,¹⁷ suggests that in order for plastic flow to proceed it is necessary to sever the tie molecules. We suggest then that the transient local volume change, which occurs in the unswollen polymer (AC 1220) at 1 atm during rupture of a tie molecule, probably amounts to $\sim 265 \text{ \AA}^3$. Because the activation energies of mechanical destruction and thermal degradation in many polymers are approximately equal,¹⁸ we speculate that the activation volume for the process of thermal degradation of PE is also approximately of this magnitude. The analogous situation for metals is the correspondence of the activation volumes of creep and diffusion.

The strain dependence of the parameter m observed here for PE offers an interesting contrast with that generally observed for metals. As noted above, m decreases with increasing strain while for metals m usually increases with strain. In the latter case it is believed that the applied stress σ_a is separable into the sum of two components, a long-range internal stress σ_i , and an effective stress σ_e acting on a mobile unit.⁴ By definition⁴ m is given by $\partial \ln \dot{\epsilon}/\partial \ln \sigma_e$. It is assumed that the change of applied stress $\delta \sigma_a$ which occurs in a cyclic test is equal to the change of effective stress $\delta \sigma_e$. However, $\delta \sigma_e/\sigma_e > \delta \sigma_a/\sigma_a = \delta \sigma_e/(\sigma_e + \sigma_i)$ if σ_i is not small. As σ_i increases, m will increase and hence work hardening in metals is ascribed to the generation of a long-range internal stress which screens the applied stress from the mobile unit. In the present case m decreases with strain

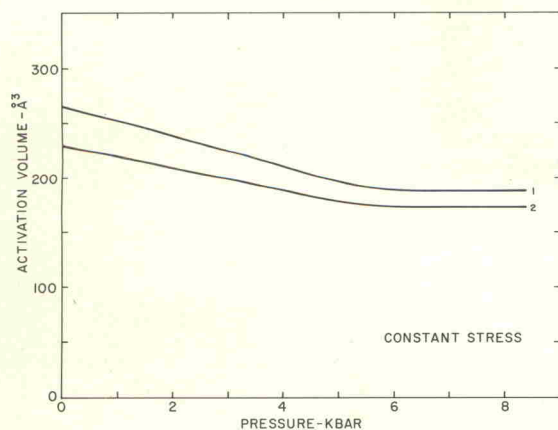


FIG. 9. Activation volume as a function of pressure at constant (nominal) stress equal to ~ 195 bar for curve 1 (water) and ~ 180 bar for curve 2 (pentane), which corresponds roughly to the 1-atm flow stress at $\epsilon = 1.25$ in each case; the true stresses are in approximately the same ratio. If the same true stress were used for both curves, the spread between the two curves would be slightly greater.

and hence work hardening is probably not associated with an increasing internal stress.

It has been noted that the ratio of yield stress to Young's modulus σ/E for polymers is approximately independent of T , $\dot{\epsilon}$, and P ¹⁹; this is roughly true in the present work. In the case of metals this is taken as evidence for an athermal process because E is not rate dependent, i.e., thermally activated, in the normal testing range and $\sigma_i \approx \sigma_a$. For polymers, however, both E and σ are rate dependent, and constant σ/E implies that they have similar activation parameters (though not necessarily similar mechanisms).

CONCLUSIONS

It is found that the inverse strain-rate sensitivity, m , of AC 1220 high-molecular-weight PE increases with pressure and decreases with strain (Figs. 4 and 5). The pressure derivative of the flow stress $(\partial \ln \sigma / \partial P)_T$ for this material decreases strongly with pressure (Fig. 6) and increases with strain. As the strain and pressure dependences of these parameters are of opposite sign, on calculation of the activation volume V^* from their product (and kT) it is found that V^* is only a moderately decreasing function of pressure, especially at constant stress (Fig. 9); it is only slightly dependent on ϵ at low pressure and independent of ϵ at high pressure. Samples tested in pentane are observed to have a lower activation volume than samples tested in water, except under a combination of high pressure and high stress. As pentane is absorbed primarily in the amorphous region, the influence of pentane on V^* suggests that the thermally activated mechanism which controls deformation probably operates in the amorphous region. We suggest that V^* may be the transient local volume change which occurs

on the breaking of a tie molecule during deformation.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Richard Fehrman for his assistance with the high-pressure experiments, to Miss Lucille Snyder for her patience with typing the manuscript, and to Dr. J. C. M. Li for many stimulating discussions.

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