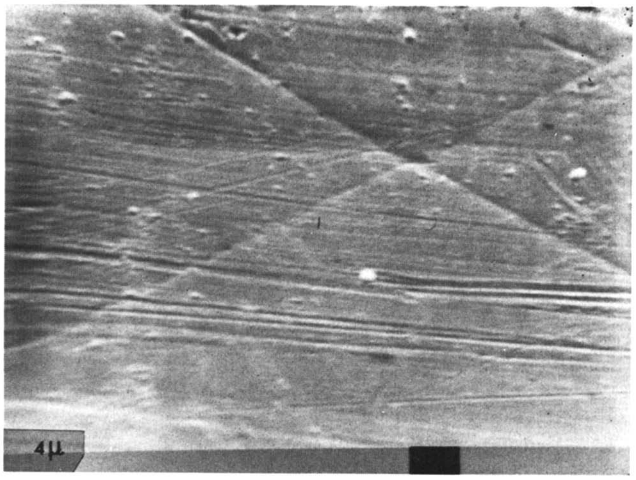

Figure 4 Intersections of shear bands and scratches in aged polycarbonate. Neck velocity = 0.002 mm s^{-1}. The micron marker refers to the length of the black band

However, in common with other papers in this field, no explanation for this phenomenon can be readily provided.

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An approach to the mechanism of environmental stress cracking by theoretical kinetics

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Environmental stress cracking (*ESC*) in polyethylene (PE) has been studied both from scientific and technological viewpoints. A study based on the fracture mechanics of a continuum body was reported by Williams *et al.*[1]. Two different molecular mechanisms have been proposed. One was based on a surface energy reduction by *ESC* active liquids[2] and the other[3,4] attributed *ESC* to stress-induced plasticization. A study of PE *ESC* growth rate in our laboratory[5] has indicated that the thermal motion of PE segments at crack tips is enhanced by active liquids. Although the two theories of Brown[3] and Gent[6] for treating stress-induced plasticization are adequate, they are equilibrium theories. Because cracking is not a thermodynamically reversible process, a sound approach to the problem should take irreversibility into account. The theory presented here, which represents the role of stress as a promotion of the compatability of active liquids with polymers, is developed from irreversible statistical mechanics. The results seem to give us a deeper insight into *ESC* in PE and other polymers. The *ESC* growth rate is assumed to be so slow that the flow of liquids is not rate-controlling.

We consider a system composed of phases I and II. Phase I, representing a polymer crack tip region, is a mixture of n_r r-mers and n_s s-mers. The former are polymer molecules and the latter are *ESC* active molecules and phase II represents an *ESC* active liquid. Phases I and II are in contact and s-mer molecules can migrate between the both phases. Phase I is subjected to a dilative stress P_1 due to the stress concentration at the crack tip and II to P_2 (negative) due to atmospheric pressure. The whole system is maintained at a temperature T. Assuming local equilibrium and using the Flory–Huggins lattice theory, the Gibbs free energy of the system is given by:

$$G/kT = n_r \ln(1-\varphi_s) + n_s \ln\varphi_s + \chi_{r,s} r n_r \varphi_s - s n_s (p_1 - p_2)/kT + \text{constant} \qquad (1)$$

where φ_s is the volume fraction of the s-mer in phase I and $\chi_{r,s}$ is the interaction parameter defined for a pair of segments, one r-mer and one s-mer.

The free energy G *versus* φ_s, calculated for a system of 100-mers and 3-mers with $\chi_{r,s}=1$ and various effective dilative stresses $\Delta p=(p_1-p_2)/kT$ are shown in *Figure* 1. For Δp positive or zero, the free energy has a minimum near $\varphi_s=0$, i.e., the r-mers and the s-mers are almost incompatible. As Δp becomes more positive G exhibits a minimum and a maximum and tends to $-\infty$ as $\varphi_s \rightarrow 1$. With further increase in Δp, it decreases monotonically, When Δp is positive, the most stable state of phase I is thus the state $\varphi_s=1$. At the moment when the loading by p_1 on phase I and the contact of phase I and II starts, the system is at the state $\varphi_s=0$ and then is shifted towards the stable state $\varphi_s=1$ by the thermodynamical force. The shift rate will be slowed down in the interval between the two free energy extremes. When the concentration of the s-mer in phase I reaches a value, say φ_s^* phase I will not support the dilative stress and will collapse, which is regarded here as

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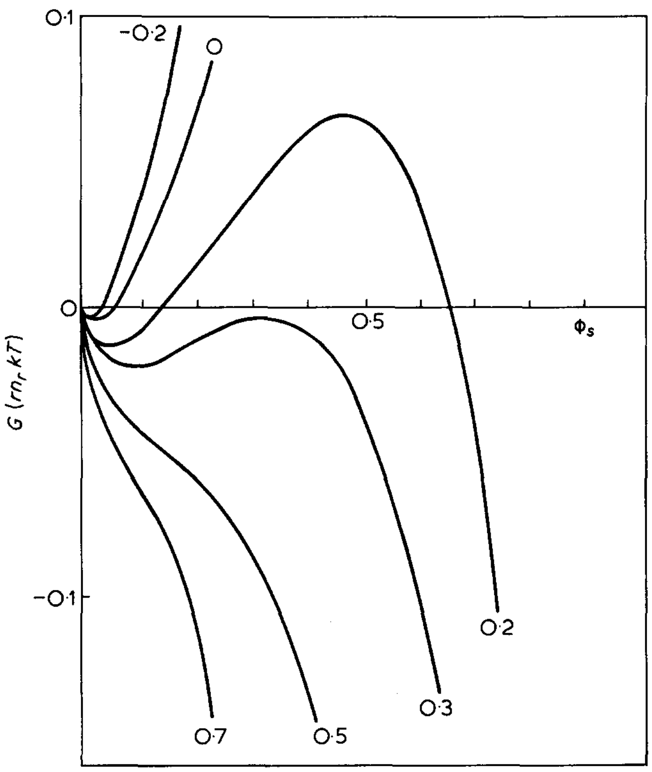

Figure 1 Gibbs free energy *versus* ϕ_s calculated by equation (1). The values of the parameters are $r = 100$, $s = 3$, $\chi_{r,s} = 1$ and the values of $(p_1 - p_2)/kT$ are indicated in the Figure

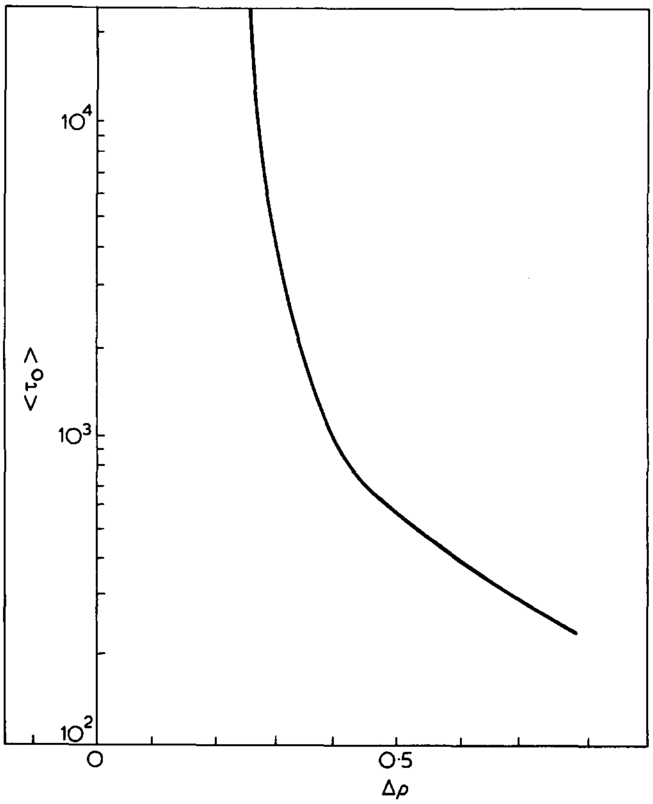

Figure 2 Mean fracture time $\langle\tau_0\rangle$ *versus* the effective dilative stress $\Delta p = (p_1 - p_2)/kT$. The values of the parameters are $n_r = 10$, $r = 100$, $s = 3$, $\chi_{r,s} = 1$ and $\phi_s^* = 0.107$

ESC. The free energy curves are not greatly affected by polymer molecular weight and curves calculated by $r = 1000$ cannot be separate in the Figure. It is quite natural to assume that φ_s^* is changed by polymer molecular weight so that the higher the molecular weight, the larger the value of φ_s^*.

An elementary manipulation of irreversible statistical mechanics with an assumed value of φ_s^* leads to a formula predicting the mean time to collapse of phase I, $\langle\tau_0\rangle$, in undetermined time units. Numerical calculations are now in progress. An example is shown in *Figure* 2, where $\langle\tau_0\rangle$ is plotted against the effective dilative stress Δp. The free energies used are given in *Figure* 1 and φ_s^* is assumed to be 0.107. For a certain amount of Δp, $\varphi_s'_{\min}$, the concentration giving minimum free energy, exceeds φ_s^* and *ESC* will then proceed in a moderate time. With a decrease in Δp, $\varphi_s'_{\min}$ decreases and becomes smaller than φ_s^* and the time to collapse suddenly increases. The critical stress below which *ESC* does not occur will be the level of stress giving a sudden increase in $\langle\tau_0\rangle$. Another example (not shown here) indicates that a small difference in φ_s^* resulting from difference in molecular weight results in a considerable difference in $\langle\tau_0\rangle$. This corresponds to a marked influence of polymer molecular weight on *ESC* which is well known.

Various experimental data on PE *ESC* growth rate are being accumulated in our laboratory; some of them are rather puzzling. For example, the order of the activity of PE *ESC* active liquids are sometimes reversed by polymer molecular weight. Preliminary analysis, however, shows that the present kinetic theory is promising for solving these problems. The reported kinetic data on environmental stress crazing and cracking in glassy polymers are also being compared. The trends in the stress *versus* craze initiation time[7] are similar to that shown in *Figure* 2.

A fuller account, the formula of $\langle\tau_0\rangle$, and the comparison with the experiments will be published soon.

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