both PMMA and PET are in some disagreement with independent measurements. The only comparison for PMMA is with the value predicted from T_g using the Gibbs-DiMarzio relationship $\Delta E = 3.81\ T_g$ cals/mole. It can be seen that the value obtained from this investigation is only about 60% of this prediction. Our value of ΔE for PMMA should be compared with the value of 0.9 kcals/mole for polystyrene, obtained from ultrasonic measurements [21]. For PET we calculate $\Delta E = 1.91$ kcals/mole. This should be compared with the Gibbs-DiMarzio value of 1.38 kcals/mole. However, the work of Riveros and Bright Wilson [22] using microwave spectroscopy yields a value of 0.186 ± 0.060 kcals/mole for the difference in energy between the rotational isomeric states of ethyl formate, separated by a barrier height of 1.1 ± 0.25 kcals/mole for upward transitions.

The value of 0.186 kcals/mole was used by Walker and Semlyen [23] for the methyl group rotation, in a calculation which accurately predicted the measured cyclic trimer concentration in the melt of poly(ethylene terephthalate). The results would imply that the barriers to conformational changes at yield are higher than those measured in the melt. This might be because the stiffness of the terephthaloyl units is more effective in the denser material.

6. Conclusion

A modification of Robertson's molecular theory of yielding has been presented which allows the hydrostatic pressure, temperature and rate-dependence of yield to be discussed within a common formalism. Although the details of the theory are complex the theory is attractive for several reasons. Firstly because it emphasizes that yield is not a unique point on the stress-strain curve, but merely the point at which the plastic strain-rate produced by the stress just matches the machine displacement rate and secondly, it does not require that a horizontal log strain-rate shift will produce a yield master curve. Thirdly, it predicts that yield is governed by a temperature dependent activation energy (formally introduced via the WLF equation). It also suggests a possible molecular mechanism of yield in polymers.

The accuracy of the fit obtained is very promising, but clearly it is desirable to find a material with which it is possible to do tensile and compression tests over a wider temperature range and also torsion tests under hydrostatic pressure.

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The slight disagreement between the data for PMMA and the theory may arise in part because of the use of a crude planar zig-zag model of the polymer chain and from the approximation used for calculating χ maximum. However, we believe that the fit is sufficiently good to warrant three tentative conclusions.

(1) The difference between tensile and compressive yield stresses for PMMA may be attributed to interaction with the hydrostatic component of stress. N.B. In principle this technique should be capable of distinguishing between a modified von Mises and a Coulomb criterion, i.e. between the expressions $\Delta E - \tau v + P\Omega$ and $\Delta E - \tau v - \sigma_N \Omega'$ respectively, for the stress-modified energy difference between the two states. For the torsion tests $p = -\sigma_N$ and so $\Omega = \Omega'$ to explain the pressure dependence in torsion correctly. However, for the axial tests $\sigma_N = \pm \sigma/2$ and $p = \pm \sigma/3$, so $\Delta E - \tau v + p\Omega \neq \Delta E - \tau v - \sigma_N \Omega$. It is not felt, however, that from the present results we can choose unequivocally between these criteria.

(2) The general features of the rate dependence of yield stress may be represented in terms of an effective viscosity, that is pressure, temperature and shear stress dependent.

(3) The effective viscosity relates directly to the low strain relaxation behaviour through the constants which appear in the WLF equation. This is at first sight surprising, in view of the fact that yield occurs at much higher levels of stress and strain than is usual in linear visco-elasticity.

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