

experimental details entailed. Thus the volume correction of eqn. (3) results in better agreement than Ainbinder's (1969) simpler relationship for superposing the effect of pressure and temperature with respect to yield stress.

### 3.2.3. Free volume and yield strains

Free volume theories require a net dilational component to explain yielding. Such a formulation for tensile tests was proposed by Litt, Koch and Tobolsky (1967) and simplified by Rusch and Beck (1969) to a form

$$e_y(1 - 2\nu) = (\alpha_g - \alpha_c)(T^* - T), \quad (4)$$

where  $e_y$  is the yield strain,  $\alpha_g$  and  $\alpha_c$  are the coefficients of thermal expansion for the glassy and crystalline states, respectively,  $T^*$  is the temperature at which the molecular relaxation processes occur at the same rate as that at which the polymer is being strained, and  $T$  is the test temperature. The variables  $\alpha_g$ ,  $\alpha_c$ ,  $\nu$  and  $T^*$  could be expected to change with pressure, thus changing  $e_y$ .  $T^*$  is closely associated with  $T_g$ , 160°C compared to 145°C at atmospheric pressure for polycarbonate, using the values of Litt *et al.* (1967) and so might vary with pressure in the same manner. The volumetric data of Matsuoka and Ishida (1966) indicate an increase of  $T_g$  by about 50° between atmospheric pressure and 1 kb for polycarbonate. Since the values of  $\alpha_g$  and  $\alpha_c$  are of the same order (Bondi 1968) one might expect their dependence on pressure to be about equal, thus negating the effect of pressure on their differences; lacking appropriate data on the crystalline state, this assumption will be made. Gielessen and Koppelman (1960) found only a three per cent increase of  $\nu$  up to 1 kb for PMMA, an increase which will be assumed here using an initial value of  $\nu = 0.35$ . Using these assumptions and a test temperature of 25°C the equation predicts a ratio of 1.47 for  $e_y(1 \text{ kb})/e_y(0 \text{ kb})$ . The experimental ratio for polycarbonate was 1.29 for engineering strains, 1.36 for true strains. Thus, free volume could account for the increased strain to yield.

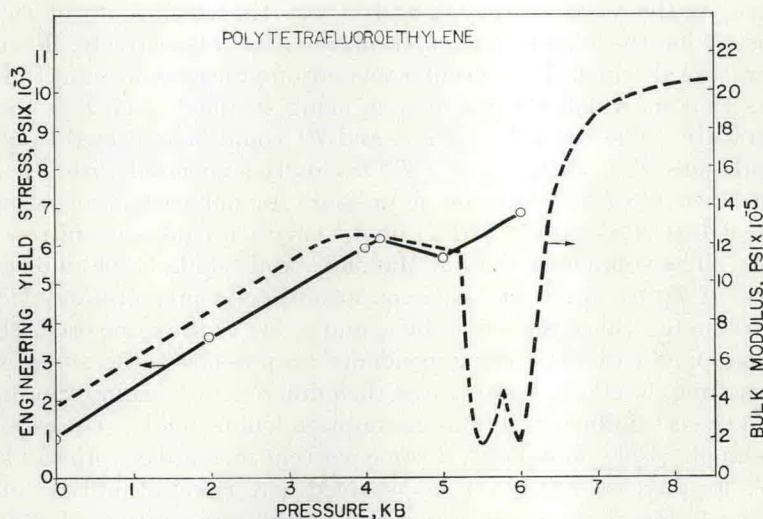
### 3.2.4. Behaviour of PTFE at high pressure

The yield stress of PTFE, as defined above, increases with pressure much as do those of the other polymers, up to 4 kb. Then a systematic change is noted. This can be seen in fig. 8. It is known that PTFE has a solid-solid phase transition at about 5.5 kb, judging by the dilatometric data of Weir (1951). Wood (1964) has calculated bulk modulus values at various pressures from these dilatometric results, and his relationship has been superimposed on the present nominal yield stress versus pressure results in fig. 8. There is an obvious similarity in the deviation of yield stress around 4–5 kb and then a likely increase at higher pressures to the behaviour of the bulk modulus. (The behaviour of Young's modulus included in a later discussion, shows a similar deviation.) An exact correspondence is not expected considering the different natures of the phenomena.

### 3.2.5. Behaviour of Young's Modulus

The values of Young's modulus obtained from the present work were low, not because of an insufficiently stiff system, but because of other experimental considerations. Nevertheless it is still instructive to note the change of modulus as a function of pressure. To this end the relative values have been plotted for the four polymers in fig. 9. Also included are data for POM taken from the work of Sardar *et al.* (1968), using the same experimental conditions as in the present work.

Fig. 8



Engineering yield stress and bulk modulus of polytetrafluoroethylene as a function of pressure. Bulk modulus data after Wood (1964).

There is no correlation of the pressure dependence of modulus either with the class of polymer or with the yield parameter  $\mu$ . It is likely that the pressure dependence of the modulus, as with the temperature dependence, depends on the nearness of relaxations and the changes of modulus associated with these, such as in the elastomers studied by Paterson (1964).

The present data do not support the contention that yielding is uniquely associated with a particular ratio of yield stress and modulus. For polycarbonate, the modulus increases by about 40% up to 8 kb whereas the yield stress increases by 240% over the same pressure range. This indicates that the factors controlling the modulus of polymers are not entirely the same as those governing plastic flow. Matsuoka (1965) has briefly touched on the various morphological and structural variables affecting different mechanical properties.