Table 1 Values of $T_{g,\infty}$, A and B for various liquids

Liquid	$T_{g,\infty}$ (K)	A (kg/mol)	B (g/mol)	$A/B - T_{g,\infty}$	m_e (g/mol)
Poly(dimethyl siloxane)	149	7580	42.8	+28.1	23
n-Alkanes	184	30 200	195	−29.1	−31
Polypropylene	270	49 800	267	−83.5	−83
Poly(vinyl chloride)	351	85 800	382	−126	−138
Polystyrene	373	100 000	378	−109	−110
Poly(methyl methacrylate)	387	270 000	2880	−293	−2180
Polycarbonate	436	259 000	1270	−232	−676
Poly(α-methystyrene)	446	448 000	2400	−259	−1400

in the Table it may be seen that with the sole exception of the siloxane liquids these values are negative, i.e. $\Delta\nu_0/\Delta\alpha < 0$. We now enquire whether this result is reasonable.

The full form of this ratio may be expressed as:

$$\frac{\Delta\nu_0}{\Delta\alpha} = \frac{\nu_0(1) - \nu_0(\infty)}{\alpha_1 - \alpha_\infty} \qquad (7)$$

From direct measurement, it is found that α invariably decreases as the molecular weight increases[2], and hence $\alpha_1 - \alpha_\infty > 0$ always. By the same token, the specific volume of a liquid at a given temperature invariably decreases as the molecular weight increases[2] and hence $\nu(1) - \nu(\infty) > 0$ always. This is true at any temperature in the liquid range and since there is no reason to suppose that the V,T response for members of a family of liquids interset, then $\nu(1) - \nu(\infty) > 0$ for the hypothetical liquid at $T = 0$ and thus we have $\nu_0(1) - \nu_0(\infty) > 0$. Since both numerator and denominator of equation (7) are positive the ratio will also be positive.

It has been shown that the right hand side of equation (7) is greater than zero while the data in *Table 1* show that the left hand side of the equation is less than zero. This is an impossible situation and hence the values of A and B cannot have the physical significance that the Fox and Loshaek treatment would attribute to them.

Using an entirely different approach, Kanig[3] derived a relationship between T_g and the degree of polymerization, P, which was originally cast as

$$\frac{1}{T_g} = \frac{a}{P} + b \qquad (8)$$

where a and b are parameters with the units moles of monomer per mole of polymer chain and reciprocal absolute temperature, respectively, and whose precise meanings are of no concern here. This expression can be readily transformed into:

$$T_g = T_{g,\infty} - \frac{A}{M + B}$$

where now A is given by:

$$A = maT_{g,\infty}^2$$

and

$$B = maT_{g,\infty} - m_e$$

Hence, the relationship can be derived that m_e, the molecular weight of the end-groups, is given by:

$$m_e = \frac{A}{T_{g,\infty}} - B \qquad (9)$$

which contains only quantities whose values have already been estimated from the fit of equation (1) to the experimental data. The final column in *Table 1* contains the values of m_e calculated according to equation (9). With the exception of the siloxane fluids, the required m_e values aside from their inappropriate magnitudes are all negative which again is a physically impossible situation. It can easily be shown, in common with the Fox and Loshaek treatment that a positive value of m_e will lead to values of the quantity $A/B - T_{g,\infty} > 0$.

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The generality of the plastic fracture process

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In uniaxial tension, the post-yield fracture of several glassy polymers is known to be initiated from 'diamond shaped' cavities which grow from defects in the drawn material. Previously the materials examined were PVC[1,2], nylon fibres[3], and at elevated temperatures poly(ether sulphone)[4], polycarbonate[4], PMMA[4] and polystyrene[5]. It is now known that poly(ether sulphone)[6] and polycarbonate produce diamonds at room temperature. Also several other polymers can be added to this list. *Figure 1* shows diamonds in five polymers drawn at 25°C. The polymers in question are

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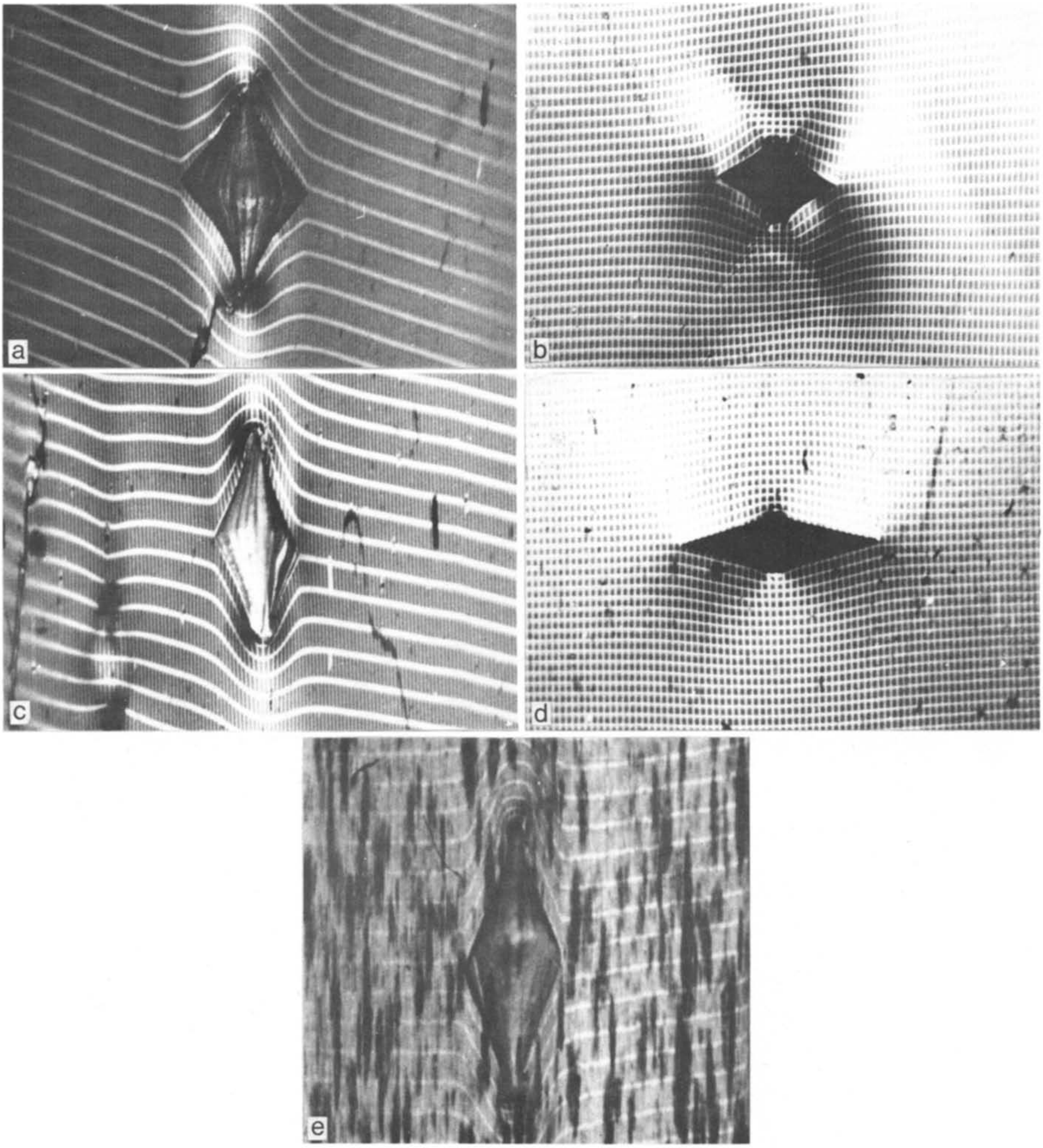

Figure 1 The shape of diamond cavities in (a) Polyethylene terephthalate, (b) Polycarbonate, (c) Plasticised PVC, (d) Plasticised Cellulose Acetate, (e) U. H. M. Polyethylene

polycarbonate (Makrolon), poly(ethylene terephthalate) (isotropic Melanex), plasticized PVC (30% DOP in Breon) plasticized cellulose acetate and an ultra-high molecular weight polyethylene (Hostalen GUR). Each test specimen was a conventional dumb-bell (narrow section 12.7 x 60 mm) cut from 1 mm thick sheet. The plasticized PVC and UHM polyethylene were compression moulded from commercially obtained granules, while the other three were cut from commercial sheet. Prior to extension, a square grid was placed on each specimen surface by evaporating gold-palladium alloy through a gauze lying on the surface of the specimen. The grid squares were approximately 64 μm in length. Each specimen was then extended at 0.2 cm/min in an Instron machine

Polycarbonate and polyethylene terephthalate are glassy polymers which neck and cold-draw and are similar to materials examined previously. However, the two plasticized polymers draw uniformly, and since they do not craze, dia-

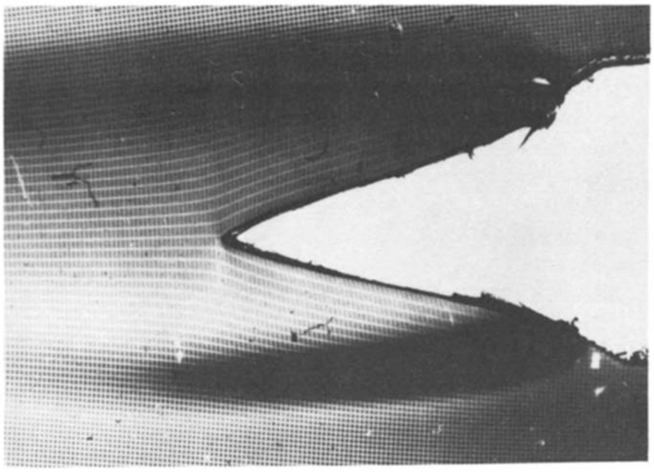

Figure 2 The crack in a notched tensile specimen of rigid PVC

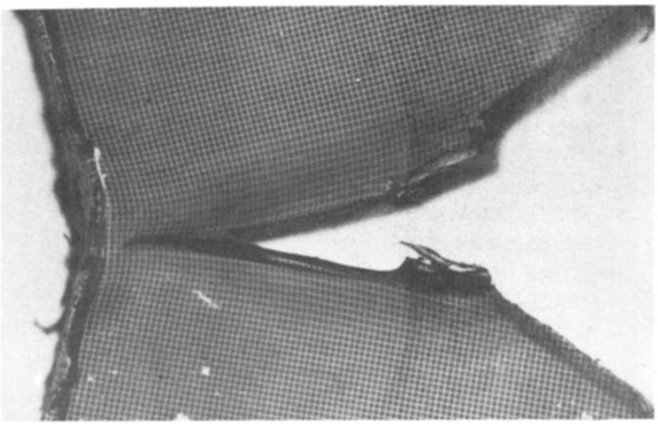

Figure 3 A plane stress Charpy impact specimen in polycarbonate

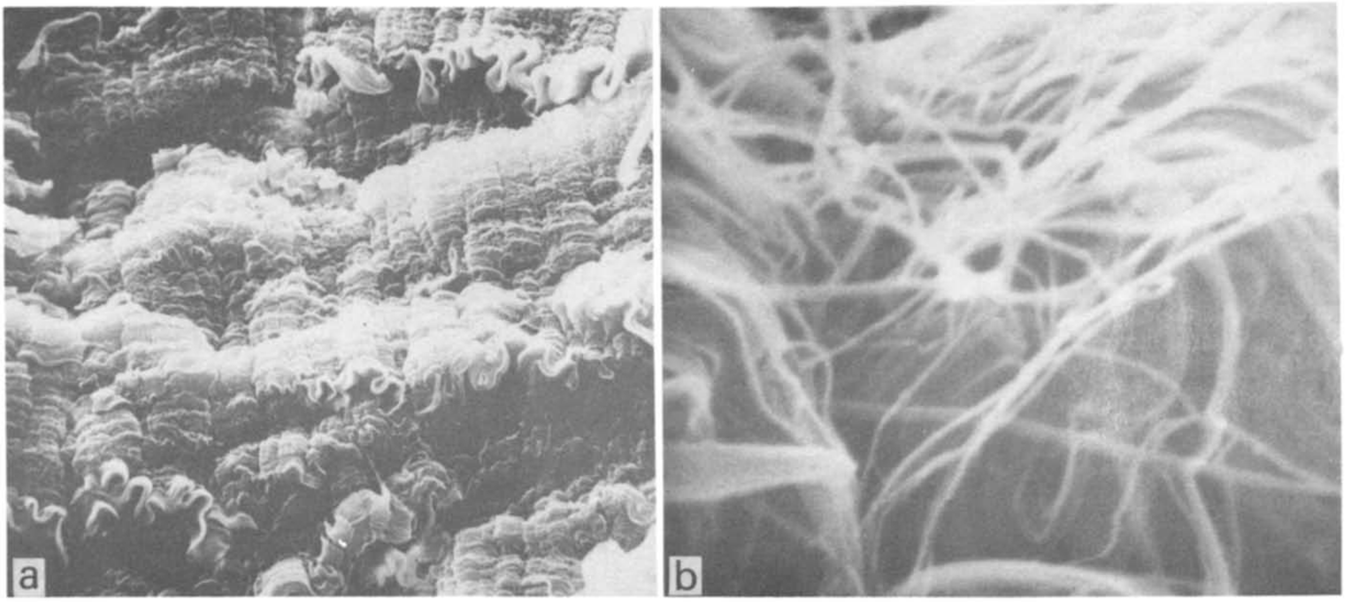

Figure 4 The fracture surface of a diamond cavity grown in U. H. M. polyethylene. (a) 1000x (b) 25 400x

mond growth followed by a fast fracture is the only fracture process reported in these polymers. The UHM polyethylene has a number average molecular weight near 4 x 10^6. Although this is a linear polyethylene its crystallinity is particularly sensitive to crystallization conditions. The particular sample had a density of 0.928 and so was about 50% crystalline[7]. At room temperature the material draws uniformly and generally fractures at extension ratios around 4 or 5 [7]. This is therefore the first reported case of diamond cavities in a partially crystalline polymer. The opaque regions around the diamond are produced by areas of whitening which are assumed to be aggregates of voids.

Around each of the diamonds in *Figure 1* the characteristic simple shear deformation described previously[1] can be seen. In the polymers with the higher draw ratios the vertical lines are difficult to resolve but at higher magnification the simple shear is obvious. The maximum shear and consequently the angle subtended by the diamond faces varies in each polymer. Apparently the degree of anisotropy of the matrix controls the shape of the diamond since the angle at the diamond tip increases with draw ratio.

Diamonds have only been studied in simple tensile tests. However, it appears that this type of fracture process is a general phenomenon associated with bulk yielding in tension. *Figure 2* shows a crack tearing through the plastic zone at a notch in a tensile specimen of rigid PVC. The specimen has a standard fracture toughness geometry (200 x 50 mm with a 5 mm notch) but is only 1 mm thick so that plane stress yielding occurs. The crack has straight faces and the adjacent areas appear to have deformed predominantly in simple shear. In the plastic zone the extension ratio varies considerably, but in the vicinity of the diamond it is roughly equal to that found in cold-drawing experiments (~2.4). Therefore the crack closely resembles an edge diamond in PVC published previously[1] and is obviously the same fracture mechanism.

The experiments described above were performed at reasonably low extension rates to minimize thermal effects, but diamonds are also seen at the highest rates possible on the Instron. In order to examine whether this type of plastic fracture occurs at even higher deformation rates, Charpy impact specimens of 2 mm thick quenched polycarbonate were gridded and then fractured. *Figure 3* shows the resulting deformation. The fracture is not complete since in plane stress a plastic 'hinge' forms on the opposite side to the notch and the specimen deforms by bending around this hinge. Consequently, as the crack propagates, the orientation of the grid lines with respect to the tensile stresses in the specimen changes markedly and the simple shear deformation is not as obvious as around the cracks shown above. However, the faces of the crack appear to be quite straight, and from the elements adjacent to the crack faces we can deduce that considerable plastic shear parallel to the tensile axis deformation has occurred. It is therefore reasonable to assume that this type of fracture is similar to the diamond growth process.

As yet the mechanism by which a diamond grows has not been determined. Electron microscopy shows that the fracture surfaces of diamonds grown in glassy polymers are almost featureless[1]. Present studies involve determining the effect of thermal history and molecular weight on the growth rates of diamonds in PVC and polycarbonate. By this means we hope to determine the parameters which control diamond growth and possibly deduce the growth mechanism.

However, the fracture surfaces of diamonds in UHM polyethylene are far from featureless. *Figure 4(a)* is a scanning electron micrograph of the fracture surface of a diamond which shows a corrugated surface and also folded contours a few microns thick. At higher magnification (*Figure 4b*) the surface of the corrugations appears as a tangled mat of fibrils and ribbon-like structures. The diameters of the fibrils range from 40 to 150 nm. No fibrils were found on the specimen side surface or the final fast fracture, which indicates that they are produced by the propagation of the diamond and are not artefacts. Calorimetry measures the zero rate of heating melting point as 411K for the drawn material, which would indicate that the mean lamellae thickness was around 65 nm[8]. The growth of diamonds in these experiments is nearly isothermal and there appears to be no cavitation or 'plastic zone' at the diamond tip. We are therefore led to the suggestion that these fibrils are part of the internal structure of the drawn polymer. Experiments are in progress to determine whether such a fibrillar structure does exist and also to determine the origin of the folded and corrugated structures observed on the fracture surface.

In summary, it appears that the plastic fracture process associated with diamond formation is a general phenomenon which occurs in the plane stress fracture of glassy polymers. We have also shown that at least one partially crystalline polymer also produces diamond cavities.

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Crystallization of poly(γ-benzyl-L-glutamate) from dilute solutions of hexafluoroisopropanol

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Several studies[1–4] showed that polypeptides in the α-helical conformation could crystallize from certain solvents to form well-defined lamella crystals with folded molecular chains. These crystals displayed many of the morphological features normally associated with the crystallization of more flexible polymers such as polyethylene[5]. In contrast, from many other α-helical supporting solvents polypeptides were found to crystallize in a fibrillar manner[6,7]. The fibrils, which were of various thicknesses, were found associated in bundles, and inter-woven and twisted to form ropes up to 200 nm in diameter. Besides long fibres other objects built up from fibrillar units were observed such as short twisted spindles, toroids and globules. The assembly of these various fibrillar structures from individual α-helices was partially explained[6] in terms of the relative tendencies for end-to-end and side-by-side associations in the various solvents used. It was argued that a high degree of solvation diminished side-by-side associations and thus favoured the formation of thin fibrillar structures. On the other hand the length of such fibrils was thought to be governed by the extent of end-to-end association.

In the present Communication we present preliminary evidence of a different type of mechanism by which α-helices can assemble to form ribbon-like structures. Investigations were carried out on various fractionated samples of poly(γ-benzyl-L-glutamate), PBLG, in hexafluoroisopropanol, HFIP. Previous work reported by us[3] showed that PBLG could crystallize from dilute HFIP solutions to form lamella crystals having a regular hexagonal habit; in some cases the lamellae were found to exhibit distinct sectorization. More detailed studies now under way have revealed conditions for the growth of lamella crystals in the form of semi-

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