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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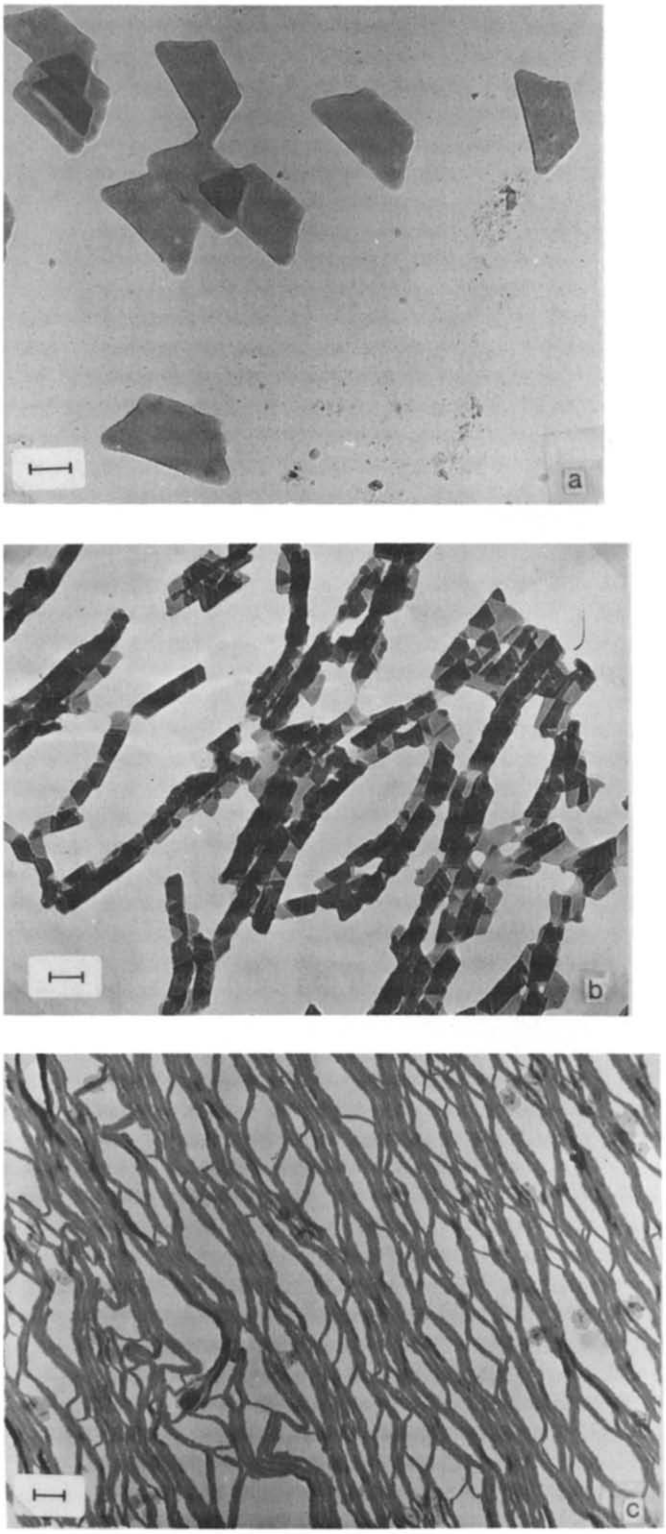
hexagons. These semi-hexagons have been found to have a strong tendency to associate to form ribbon-like structures as shown by the electron micrographs in *Figures 1a–1c*.

Crystallization conditions

Because of the low boiling point (58.5°C) of the solvent, all experiments were carried out in sealed thin-walled glass tubes (3 mm diameter x 100 mm length); prior to sealing the solutions were degassed on a vacuum line. Crystal growth was controlled by a self-seeding technique of the type developed by Blundell *et al.*[8,9] for polyethylene. The polymer/solvent system was first warmed up slowly until the solution became clear. It was then allowed to cool to 0°C. The system was then plunged into a thermostat bath at some temperature T_d above the clearing temperature, T_x, of the solution and held there for a given time Δt_d. Finally the system was plunged into a thermostat bath set at the chosen crystallization temperature, T_c.



Electron micrographs showing how lamella semi-hexagonal crystals grown from hexafluoroisopropanol associate to form ribbon-like structures. (The scale mark represents 500 nm in (1a), 1 μm in (1b) and 2 μm in (1c)).

The crystals obtained were mounted on a carbon substrate, shadowed with Pt/C and studied with an AEI 6G electron microscope. As with a number of other polypeptide crystals[1] no electron diffraction pattern could be observed even when utilizing very low beam currents. It is believed that parts of the chain are solvated in the crystals and that on removal of the solvent under high vacuum conditions some loss of local order occurs due to chain crumpling.

For a PBLG sample having M_w = 104 000 and M_w/M_n = 1.06, the set of crystallization conditions giving the semi-hexagons shown in *Figures 1a* and *1b* were as follows: solution concentration = 3×10^{-3} g cm^3, T_x = 21.5°C, T_d = 26°C, Δt_d = 10 min and T_c = 0°C (for one day).

Both fully-hexagonal and semi-hexagonal crystals have been grown from HFIP for solution concentrations in the range 0.001–0.005 g cm^{-3} and for molecular weights between 50 000 to 200 000. Our present view is that it is the values chosen for $(T_d - T_x)$ and Δt_d, that govern whether full hexagons or semi-hexagons initially grow from solution. Reducing $(T_d - T_x)$ and Δt_d gives rise to crystals containing large distinct seeds, and under these conditions semi-hexagons are not observed. On the other hand the semi-hexagons invariably have a narrow size distribution suggesting a self-seeding process is involved. There is no evidence that semi-hexagons are formed by the fracture of full hexagons. If semi-hexagons are allowed to stand in dilute solution for long periods (say three weeks), they slowly disintegrate, whilst full hexagons become larger and generally develop much smoother surfaces.

The thicknesses of the lamellae were determined from measurements of shadow lengths. The semi-hexagons were found to be approximately the same thickness as the full hexagons. This ruled out the possibility that the semi-hexagons were merely the product of crystal folding. The thicknesses observed were in the region of half the value expected for an unfolded α-helical chain (e.g. the thickness of the crystals in *Figures 1a* and *1b* is 42 ± 5 nm compared with 72 nm for the fully extended length of the PBLG chains). Evidence that PBLG exists as an α-helix in HFIP was provided by circular dichroism measurements.

The formation of ribbon-like structures occurred only with the semi-hexagons. Full hexagons appeared only to associate by stacking symmetrically one on top of the other.

On moving to PBLG samples with molecular weights above 150 000 the tendency for fibrillar structures started to assert itself. For a polymer with M_w = 340 000, conditions could not be found which permitted the growth of lamella crystals from HFIP. It was found however that if a poly(D,L-leucine) block was copolymerized onto the PBLG polymer then hexagonal crystals could be readily grown from the PBLG blocks of the copolymer. The poly(D,L-leucine) blocks provided the crystals with an outer fringe which became thicker and more globular as the molecular weight of the poly(D,L-leucine) was increased. The growth of semi-hexagons was not observed for the copolymers. Destabilization of the α-helix was not responsible for the enhanced tendency of the copolymers to form lamella crystals, since n.m.r. measurements showed that the poly(D,L-leucine) block had little or not effect on the stability of the PBLG α-helix.

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Protonation and complex formation of some novel poly(amido-amines)

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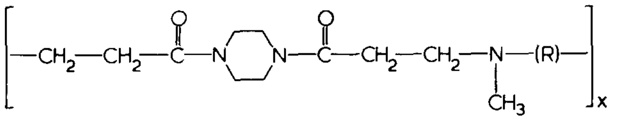
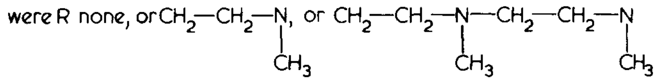
In previous research, we have found that tertiary amino polymers belonging to a new class, poly(amido-amines), show an unusual behaviour towards both protonation[1–3], and complex formation with metal ions such as Cu^{2+} [4] and Ni^{2+} [5].

In fact, 'real' basicity and stability constants could be determined in the case of poly(amido-amines). To our knowledge, no other polyelectrolytes showing this kind of behaviour have previously been described. In all previous cases, only 'apparent' constants were determined[6].

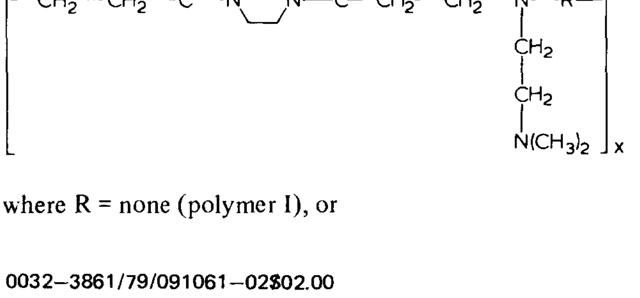
The poly(amido-amines) studied in our previous work had the following structure:



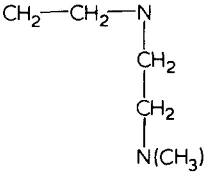


$$\text{were R none, or } CH_2-CH_2-\underset{CH_3}{\underset{|}{N}}, \text{ or } CH_2-CH_2-\underset{CH_3}{\underset{|}{N}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{N}}$$

It may be noted that in all cases the tertiary amino groups were present as a part of the main chain. We thought it interesting to study the behaviour of poly(amido-amines) having a similar structure, but carrying additional amino groups as side substituents. Therefore, we synthesized the following new polymers:



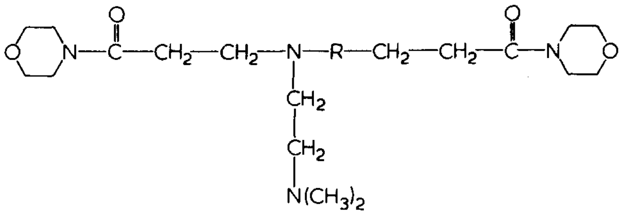
where R = none (polymer I), or



$$CH_2-CH_2-\underset{N(CH_3)_2}{\underset{|}{\underset{CH_2}{\underset{|}{\underset{CH_2}{\underset{|}{N}}}}}}$$

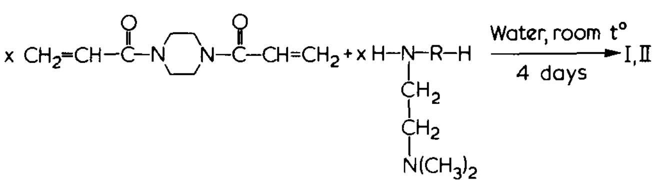
(polymer II).

We also, synthesized the corresponding non-macromolecular models:



where R has the same meaning as in the previous case.

The polymers were synthesized by polyaddition of 1,1-dimethylethylenediamine (I), or 1,1,10,10-tetramethyltriethylenetetramine (II), to 1,4-bisacryloylpiperazine, according to the following scheme:



The intrinsic viscosities of the polymers were 0.19 and 0.25 dl/g, respectively. They were measured in chloroform at 30°C. The C, H and N analyses gave satisfactory results.

The models were synthesized in a similar way, starting from the same amines, and N-acryloylmorpholine in a 1:2 molar ratio. They were viscous oils, and gave quite satisfactory analytical results.

The potentiometric titrations were performed as previously reported[1,2]. The results are summarized in *Table 1*.

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