The Fracture Surfaces of Polystyrenes having Different Molecular Weights

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*Compression moulded samples of narrow molecular weight distribution poly-
styrene have been fractured and the fracture surfaces studied by electron
micrography. Three different molecular weight polymers were used with
molecular weights of 35 000; 82 000 and 220 000. The lowest molecular weight
polymer gives a generally smoother fracture surface than the other polymers,
a characteristic which is ascribed to the virtual absence of entanglement.
When broken at −196°C, all three polymers give nodular areas and the nodule
size is observed to depend on the molecular weight. The actual sizes are of
the same order as the expected end-to-end molecular distance in a theta solvent.
When fractured at room temperature the high molecular weight material,
and also a commercial wide distribution polymer of similar molecular weight,
gives rise to very small, highly extended filaments. It is suggested that these
filaments are formed by the rapid, adiabatic extension of material which has·
been heated and softened during the propagation and separation of a craze.
However, although these features are well developed and indeed striking, the
electron micrograph information by·itself does not unambiguously prove that
melting has occurred, although it certainly supports this concept. Neither can
it be unequivocally shown that the fibrils are solid and not hollow.*

RECENTLY Bird, Mann, Pogany and Rooney[1] have studied the fracture
surfaces of polystyrene by electron micrography. They used two methods
for breaking their specimens; according to one procedure they extended
their specimen relatively slowly in tension until fracture occurred; in their
other method, the specimen was broken quickly in bending. In the former
case they were able to observe a number of characteristic features, such as
parabolic structures, which were formed in the mirror area of the fracture
surface, and which are characteristic of a number of organic glasses[2]. In their
fast bending experiments they observed a characteristic distribution of tiny
nodules or hillocks, whose size appeared to depend on the molecular weight
of the polystyrene used. However, as their conclusions were only tentative
and as their polystyrenes were of the conventional free radical type con-
taining a distribution of molecular weights, it seemed of interest to repeat
their experiments using anionic polystyrenes of narrow molecular weight
distribution. It was also desirable to cover a wider range of molecular
weights than those employed in the previous work[1].

MATERIALS

Three polystyrenes were prepared by Dr B. W. Brooks‡ using anionic
polymerization. Under the conditions employed, the molecular weight
predicted from catalyst addition was in each case close to that derived
from the intrinsic viscosity of the polymer. The three polymers are
described in *Table 1*.

Table 1. Materials used

Material	Intrinsic viscosity in toluene dl/g	Molecular weight§
ANIONIC POLYSTYRENE		
Low molecular weight polystyrene	0·23	35 000
Medium molecular weight polystyrene	0·44	82 000
High molecular weight	0·915	222 000
COMMERCIAL POLYSTYRENE		
Carinex HR	0·94	230 000

§Determined according to the equation of Krigbaum and Flory[2].

Some experiments were also carried out with a commercial (wide distribution) polystyrene, Carinex HR having an intrinsic viscosity of 0·94. This material was similar to the 'high molecular weight' polystyrene used by Bird *et al.*[1].

FRACTURE
This was executed manually as described by Bird *et al.*[1]. Two temperatures were used, viz. liquid nitrogen temperature ($-196°C$) and room temperature ($20°$ and $25°C$).

ELECTRON MICROSCOPY
Self shadowed direct carbon replicas were prepared from the freshly fractured polystyrene surfaces. The procedure employed was to evaporate a thin carbon layer on to the fracture at an angle of $45°$ to the fracture surface and normal to the direction of crack propagation. After scribing the carbon film into suitably sized pieces, the replicas were removed by partial dissolution of polymer in toluene. Washing of the replicas in fresh toluene, before collecting them for examination, was performed to remove the last traces of polystyrene.

RESULTS AND DISCUSSION
As the initial intention was to study the effect of molecular weight on the fine structure observed by Bird *et al.*[1] especially under conditions of low temperature fracture, the first pictures were taken from fractures made at $-196°C$. We show in *Figures 1* to *3* low and high magnification photographs of the fracture surface replicas. In each case the low magnification picture indicates the type of area from which the high magnification picture could be obtained.

Low molecular weight polystyrene (Figure 1)
The low magnification photographs show that this polymer contains some relatively plane areas, some of which show features rather like those observed for glass at $300°C$ by Bird *et al.*[1] and some of which are more complex. Close examination of these photographs shows that they are
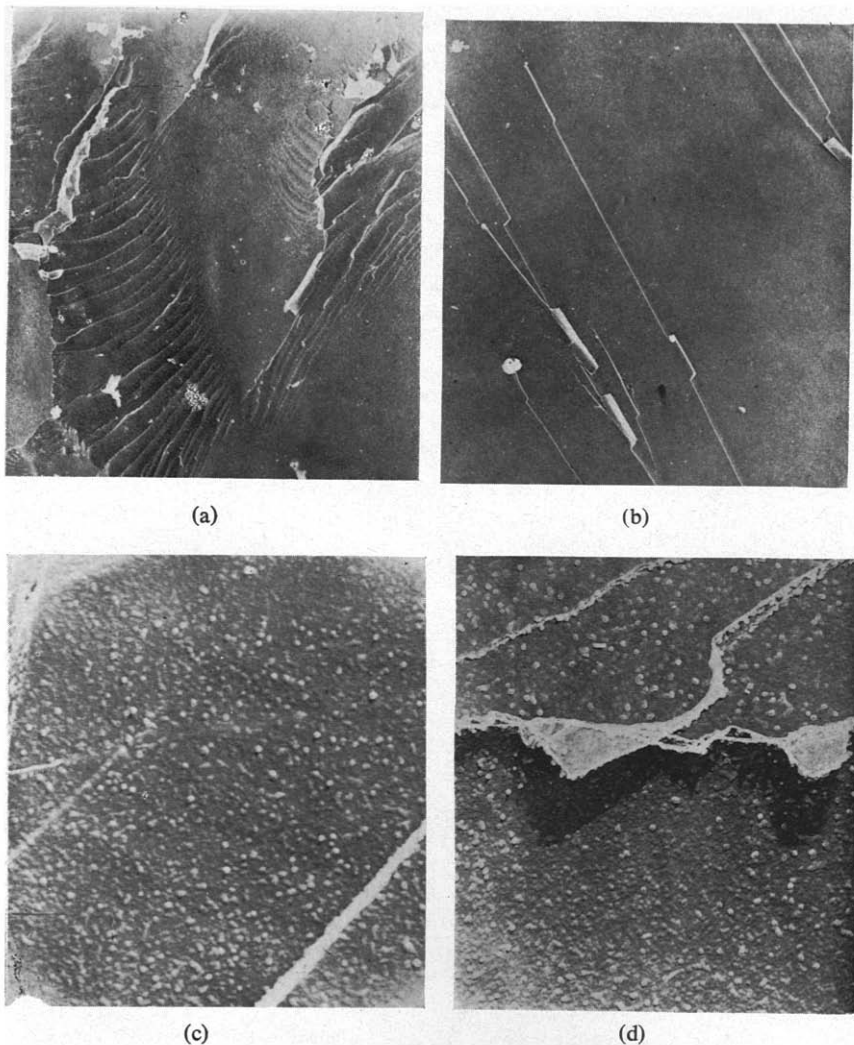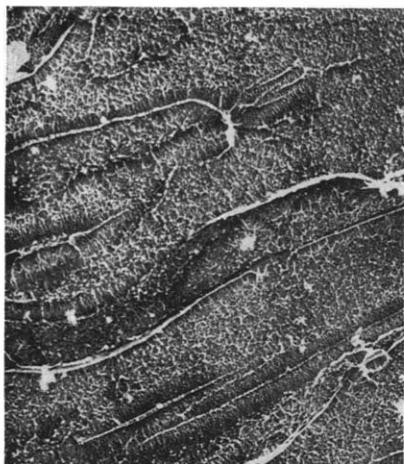
Figure 1—Low molecular weight polystyrene fracture at −196°C. (a)×1 350; (b)×1 800; (c)×18 000; (d)×18 000

covered with a very fine 'grain'. The nature of this surface 'grain' is shown up in the high magnification pictures as tiny round hillocks.

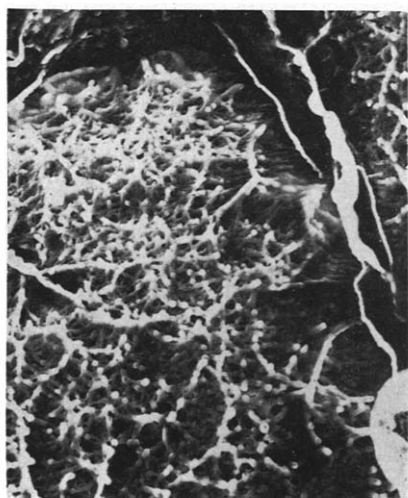*Medium molecular weight polystyrene (Figure 2)*

As shown on the low magnification print this polymer shows extensive rough areas, with a fine, almost sandy texture. Higher magnification shows that these areas have an almost fibrous appearance, with numerous small bumps, reminiscent of those previously reported[1]. These bumps are connected up and appear larger than those observed with the low molecular weight material.

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(a)
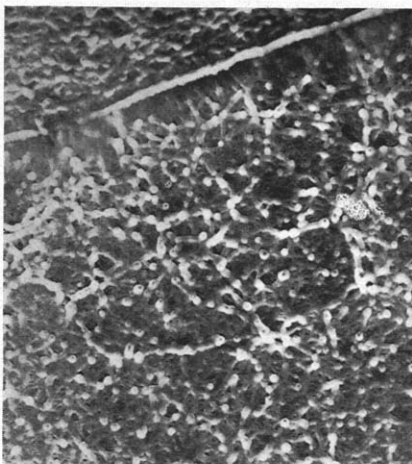
(b)

(c)

Figure 2—Medium molecular weight polystyrene fractured at −196°C. (a)×4 800; (b)×18 000; (c)×18 000

High molecular weight polystyrene (Figure 3)

With this material the rough areas were harder to find. There were considerable regions with an appearance similar to those found by Bird *et al.* for high molecular weight styrene–acrylonitrile copolymer and for polycarbonate. However, as shown in *Figures 3 (a)* to (c) it was possible to find areas of granularity very similar to that observed with the medium molecular weight material, although the scale of the structure appears to have increased further. There is also a noticeable tendency for the structures to become blurred, as if they had been smoothed out {bottom part
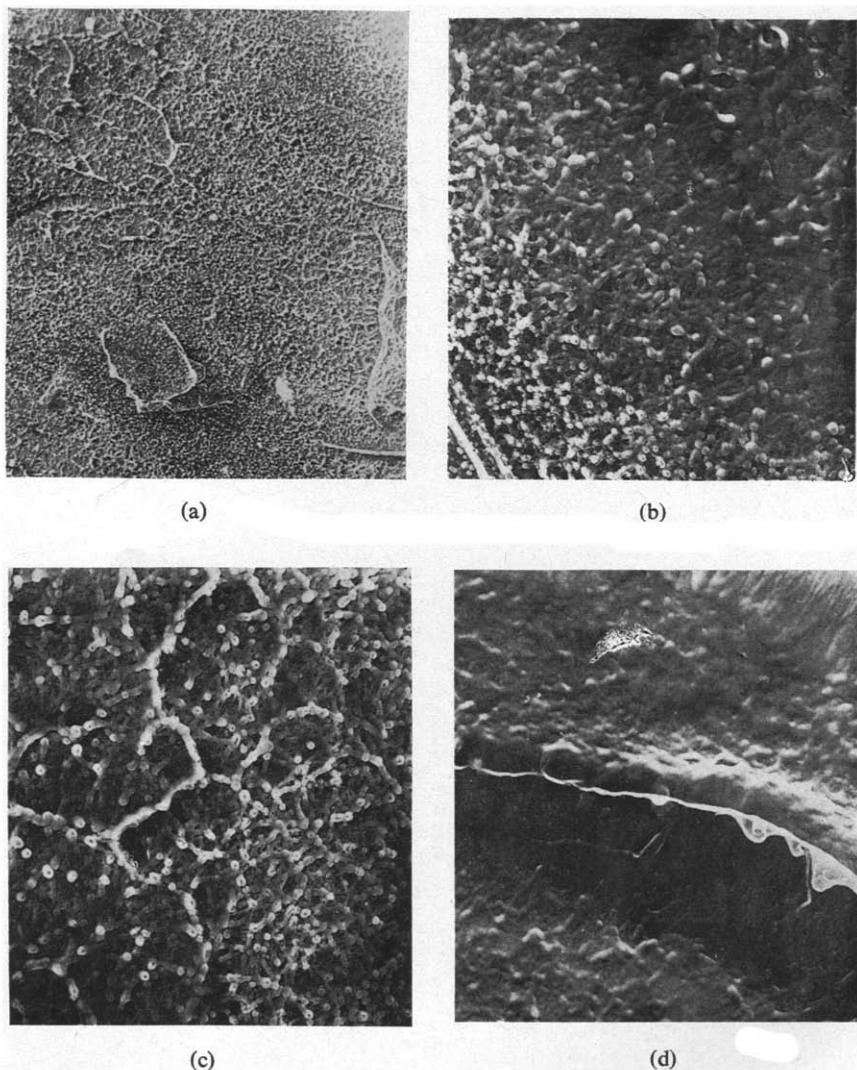
Figure 3—High molecular weight polystyrene fractured at −196°C. (a)×4 800;
(b)×18 000; (c)×18 000; (d)×21 000

of *Figure 3 (b)*]. Other pictures (not included here) show extensive areas with a structure rather similar to the blurred part of this picture.

Comparison between the results with the three types of polystyrene shows that there is a major difference in the surface structure of the low molecular weight polymer and the other two. This change occurs between molecular weights of 35 000 and 82 000. Now it has been proposed elsewhere[4] that the large deformations which can be observed with glassy thermoplastics are governed by the existence of entanglements between the polymer chains. Further, the approximate frequency of these entangle-

ments can be obtained by reference to the review by Porter and Johnson[5] which shows that, within a factor of two, there are some 500 chain atoms between entanglements with polystyrene, corresponding to a molecular weight of 25 000; more recently this figure has been revised[6] to 35 000. Only molecules considerably larger than this can be expected to pass through more than one entanglement. Thus in the molecular weight range in which the most striking differences in fracture surface are observed we change over from a condition of single to multi-entanglement along the polymer chain. It was also found that the low molecular weight material was extremely brittle and had to be handled with great care to avoid fracture of the test pieces. The two other polymers, although still brittle in the way that many glassy thermoplastics are brittle below T_G, had an appreciable strength and could be handled without any great problems. This experience parallels other observations with high-density polyethylene[4] where a changeover to brittle behaviour may also be related to entanglement density.

The size of the visible nodules

Examination of the high magnification photographs in *Figures 1* to *3* shows that with all three polymers certain spherical structures or nodules are visible. In order to test the observation of Bird *et al.*[1] which indicated a possible relation between the nodule size and molecular weight, we have measured the average size of the characteristic nodules by the following procedure. First a series of replicas was examined visually and three representative areas were photographed from different replicas of the fracture surface of each polymer, where the characteristic nodular features were well developed. From the prints obtained at least 50 and in most cases 100 different nodules were measured. The three sets of diameters, with

Table 2. Dependence of average nodule size on polymer molecular weight

Molecular weight	Ave. nodule diameter A.U.	Coefficient of variation, %	Estimated root mean square end separation of the same polymer in a theta solvent[6]* $(R^{-2})^{\frac{1}{2}}$ A.U.
	168	28	
35 000	293	31	190
	377	22	
Ave.	286		
	443	28	
82 000	537	15	290
	429	21	
Ave.	470		
	486	39	
	755	26	
220 000	569	27	470
	1010	18	
	555	30	
Ave.	670		

*The apparently reasonable assumption that the conformation of the polymer molecules in the glassy state is approximately similar to that found in a theta solvent has recently found some experimental support, from crosslinking studies by Alberino and Graessley (*J. phys. Chem.* 1968, **72**, 4229), and mechanical measurements (Bueche, Kinzig and Coven, *Polymer Letters*, 1965, **3**, 403, and Haward and Thackray[4]).

their respective coefficients of variation as obtained for each polymer, are given in *Table 2*. In the same table we give the expected root mean square end-to-end distance of the polymer chain in a theta solvent[7]. Although the variation of the nodule size was generally rather large there was no overlap in the average values for the low and high molecular weight polymers. It therefore seems reasonable to conclude that the size of these features does vary with molecular weight. Comparison with the estimated end-to-end distance also shows that these two quantities are in the same size range.

In electron micrography it is, of course, always necessary to consider how far the observed features might have been affected by the specimen preparation. Specifically in this case the measured size of the nodules might have been affected by the thickness of the carbon deposited upon them. To meet this point we prepared a completely new set of specimens in which a germanium preshadowing technique (at 45° angle) was applied before depositing the carbon. Although in these replicas we did not examine the nodules very extensively we were able to demonstrate that both nodules and shadow were of a similar size (*Figure 4*), thus indicating that
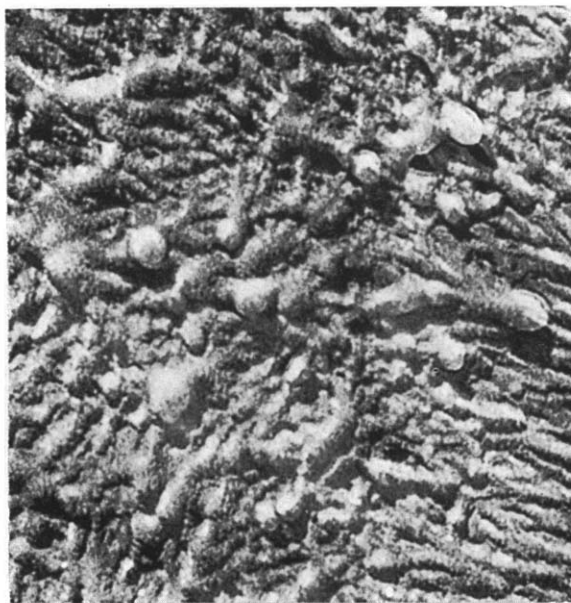

Figure 4—A shadowed electron micrograph of nodules from high molecular weight polystyrene (×72 000). Note shadows are essentially same size as nodules; also they have a short 'spike' or 'knob' at the top

the nodule had not been changed in size during replication. The shadows also elucidated the shape of the nodules and indicated how they may have been formed. Each nodule appears to have a small spike at the top, as if it had been formed by the relaxation of a short filament. It is perhaps

interesting to speculate that if a filament is drawn out to a width which is small compared with the dimensions of a random molecular coil, then on relaxation (which here would also imply that the filament had been heated during the extension process) it would expand to a diameter at least as great as the normal end-to-end distance of a random molecular coil. This concept is supported by the occurrence of a short filament on the right hand side of *Figure 3 (d)* and further illustrated in *Figure 5*.
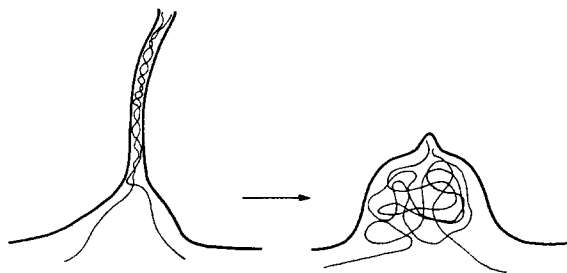
Figure 5—Diagram illustrating a possible method of formation of the nodules

Fractures at ambient temperatures

As previously stated fractures at room temperatures were made at 20° and 25°C, i.e. our specimens were very slightly warmer than those used by Bird et al.[1]. Under these conditions we found it difficult to observe any well defined surface granularity suitable for measurement. Instead we observed some apparently novel but characteristic features which occurred extensively on the fracture surfaces. For example, *Figure 6 (a)* and *(b)* show low magnification electron micrographs taken with the high molecular weight polystyrene and also from Carinex H.R. High magnification pictures are shown in *Figure 7*. It will be seen that at unconformities or steps on the fracture surface long 'rats tails' of fibrillar polystyrene are pulled out. These features seem to be different from those reported by Bird et al. and their suggestion that the fibrils are formed by the rolling up of initially flat sheets does not seem applicable to the structures which we observe. Instead we would propose that the fibres have been drawn out from material which has been temporarily heated up during adiabatic deformation preceding the growth of the crack. This explanation is strongly suggested by the shape of the fibril base from which the drawing apparently took place [*Figure 7 (a), (b), (c)*].

Closer examination of the two smaller fibrils and their shadows at the top right hand corner of *Figure 7 (b)* also seems instructive. In both cases the fibril appears to have fallen on to a lower polymer surface and stuck to it, thus suggesting that both the surfaces and the fibril were hot. Further the steep angle and linear form of the free fibrils (and their shadows) suggests that they had developed a tension during relaxation and cooling. The idea that these fibres were formed by the adiabatic pulling out of a softened layer of polymer also accounts for the fibres all being oriented in a single direction [*Figure 6 (a)*], and for the twisted structure visible in
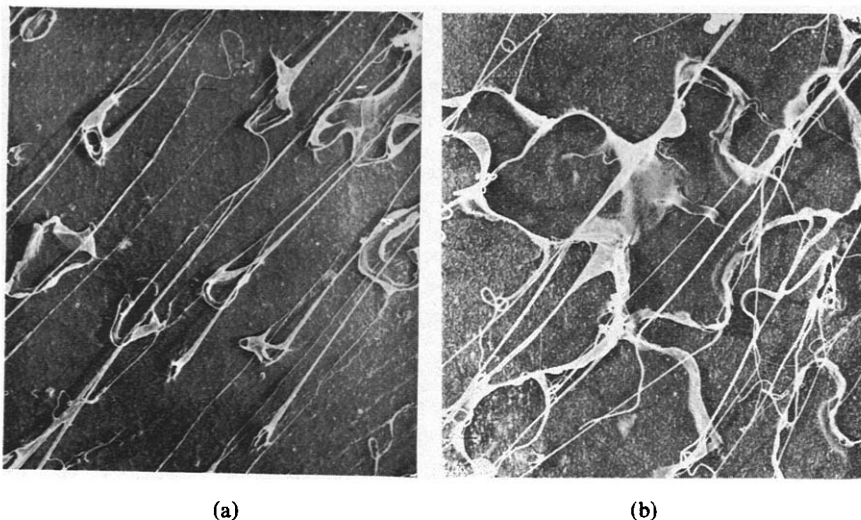
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(a)   (b)

Figure 6—(a) High molecular weight polystyrene, (b) Carinex H.R. fractured at 25°C (×2 250). No particular significance attached to differences in the two materials

Figure 7 (*b*) which could be formed when the hot fibre relaxes before cooling below the glass transition temperature.

That plastic materials can heat up during deformation has been known for a long time[8]. Indeed, certain rounded features in the fracture of polycarbonate crazes have already been ascribed to thermal effects by Spurr and Niegisch[9]. Naturally the extent to which local heating can take place during the propagation of a craze or a crack will depend on the rate at which the fracture takes place. This aspect has recently been studied by Kambour[10] with polycarbonate crazes. He showed that the heat generated would cease to be conducted away when the rate of craze propagation was greater than 1 000 cm/sec. This rate would be exceeded in our specimens if they broke in less than one millisecond, and this seems probable. Again these conclusions have been supported by Regel *et al.*[11], who found by examining the volatile products formed during the fracture of polymethyl methacrylate, polystyrene and polypropylene in a mass spectrograph, that the same chemical decomposition products were produced in fracture as in thermal degradation.

When fully adiabatic deformation occurs it is of course possible to modify any given stress/strain relationship to include the effect of heating. An attempt to do this for polystyrene has recently been reported[12]. In these calculations[12] it was shown that the adiabatic extension of a material like polystyrene by 200 per cent at room temperature should lead to a temperature rise of some 60 deg. C. At larger deformations, such as those present here, the temperature should approach T_G. Therefore this figure of 60 deg. C is almost certainly an underestimate for the heating which occurs during a fast process of deformation such as that under consideration, since extension in the time range of one millisecond instead of the normal
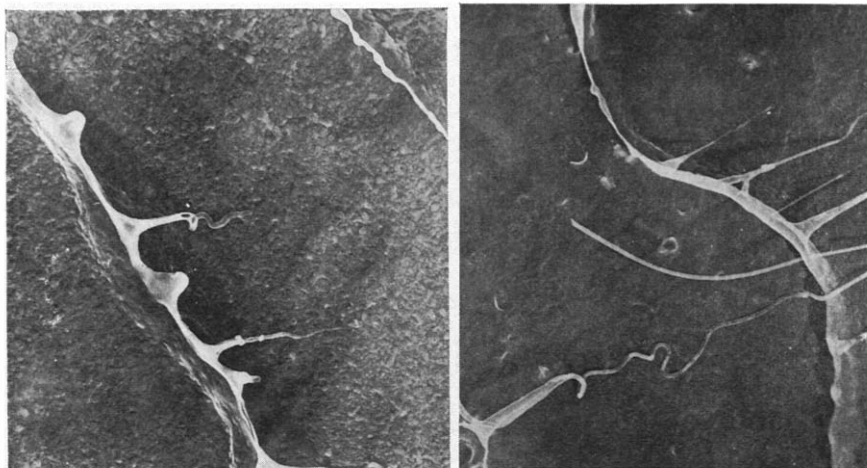
(a)

(b)
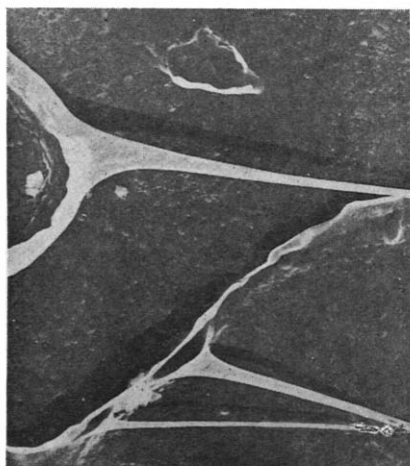
(c)

Figure 7—Further details of the fibrils observed in high molecular weight polystyrene fractured at 25°C: (a)×9 000; (b)×9 000; (c)×12 000

time interval of 100 to 1 000 seconds in which T_G is measured, would be expected[13] to increase the level of T_G by 50 to 100 deg. C. Thus immediately after drawing, the filaments are likely to be above their effective T_G and their behaviour will depend on the competition between cooling and relaxation.

Further evidence for the idea that thermal effects occur during fast cracking processes comes from Vincent and Gotham[14]. They found that the fracture energy due to crack growth in polymethyl methacrylate initially increases with increasing velocity of fracture and then falls. The fall at high velocity was ascribed to adiabatic heating.

Thermal effects may also explain the evidence of *Figure 3* which shows a progression from a clearly defined structure to one in which the same

structure has been smoothed out. This could occur through the speeding up of the crack with the consequent heating and relaxation (smearing out) of surface forms. This direction coincides with the line of crack propagation relating to *Figure 3* (b), although we do not know for certain in this case the sense in which the crack front moves along that line. The fact that the characteristic 'rats tails' are largely absent from the low temperature fractures is, of course, in conformity with our proposals.

FURTHER PROBLEMS OF INTERPRETATION

Use of the scanning electron microscope

One difficulty which arises in evaluating conventional electron micrographs, concerns the possible heating of the specimen during deposition of the carbon replica. It is very difficult to be completely certain on this point though the definition of the smallest shadows in the top right hand part of *Figure 7* (b) and also *Figure 7* (c) argues against any movement during replication. We therefore went on to repeat the 20°C fracture of the high molecular weight polymer and, after deposition of silver under conditions which are less likely to heat the specimen than those which occur during carbon replication*, they were examined in the scanning electron microscope. No change in the picture (e.g. movement of the fibrils) was observed during scanning. The picture shown in *Figures 8* (a) and
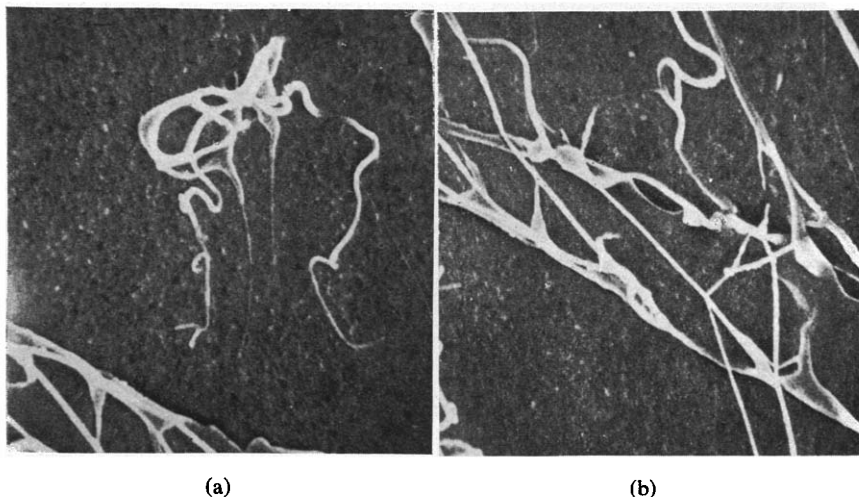

(a)   (b)

Figure 8—Scanning electron micrographs of fibrils from high molecular weight polystyrene fractured at 25°C (×17 400)

(b), although they lack the high resolution associated with the replica method, confirm the form of the fibrils which has been previously observed. These fibrils show the same tendency to retract and coil. Thus it seems safe to conclude that significant heating of the fibrils did not occur during deposition of the carbon.

*During the deposition of the very thin layer of silver, just enough to give a conducting layer, the specimen is rotated at a high speed at a distance of approximately 10 in from the heated tungsten wire with the silver source.

Are the fibrils hollow?

Considerably greater difficulties arises from the possibility that the original fibrils are hollow†. In fact we are unable to offer conclusive evidence at this point. Obviously the carbon *replicas* will be at least partly hollow, having the form of tubes whenever the polystyrene inside the replica has been successfully dissolved away. Certain features of the apparent hole in the filament at the bottom right hand side of *Figure 7 (c)* might indicate that the original fibrils were also hollow. In order to throw further light on this aspect we examined a number of cases where coiling and bending of the fibrils had taken place. These pictures are shown in *Figures 9 (a)*
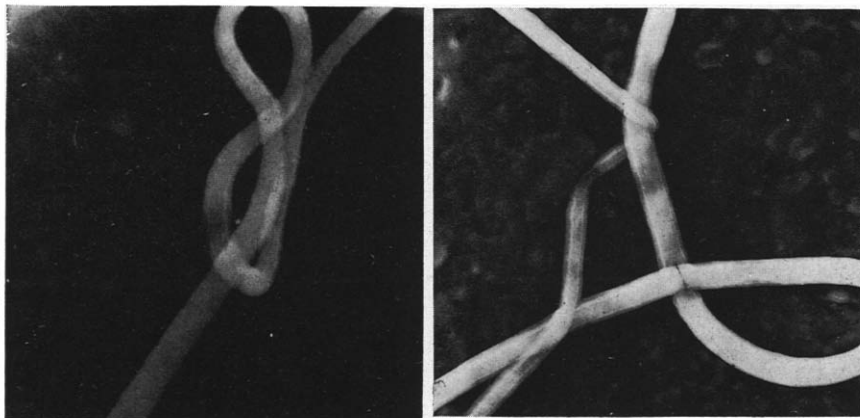

Figure 9—Two electron micrographs (×24 000) showing details of fibril coils from high molecular weight polymer fractured at 25°C. The hair crack in (b) may be caused by a fracture of the replica

and (*b*). On the whole we think that their forms suggest that the original specimen was solid since they provide no indication of kinking where bends of small radius are present. However, even if the fibrils should prove to be hollow we would still doubt the possibility of their being formed by the rolling up of a film. A process of drawing out softened material would still seem a more probable explanation.

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†We are indebted to Dr A. Keller (Department of Physics, University of Bristol) for pointing out to us this possibility.

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