Surface Morphology of Polystyrene Fractured in Liquids

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Synopsis

Polystyrene test pieces broken by flexure in the presence of *n*-propanol and other alcohols have been examined by scanning electron microscopy. Two regions on the fracture surface are observed; a narrow band near to the tension surface corresponds to fracture through a solvent craze, but the remainder of the surface is identical to fracture surfaces produced in air. The solvent-crazed region has a cellular structure decreasing in scale toward the tip of the craze. An explanation of these features is offered in terms of the changing conditions of stress and solvent content ahead of the growing craze.

INTRODUCTION

It is well known that organic fluids encourage crazing and subsequent fracture of glassy plastics. Even apparently innocuous liquids can have a very marked effect; for example, alcohols can reduce the fracture energy of poly(methyl methacrylate) by a factor[1] of 100 and the strain at which crazing initiates in polystyrene, by a factor[2] of 10.

The present project consisted of two concurrent studies of solvent crazing, one relating to the strain conditions under which crazing initiated[2] and the other being a study of the effects of liquids upon the fracture surface morphology. Data from the latter are given in the present paper.

EXPERIMENTAL

The polymer used in these experiments was Carinex GP (Shell Chemicals Limited), a suspension polystyrene with $\bar{M}_w = 2.3 \times 10^5$ and $\bar{M}_n = 1.05 \times 10^5$ (data supplied by Shell Carrington Plastics Laboratory). This was compression molded into sheets in a frame mold at 200°C. Five alcohols were employed which were all of laboratory reagent grade.

Polystyrene is almost completely insoluble in the lower alcohols, but they are known to encourage crazing in it. Therefore, alcohols were chosen for use in these experiments so as to minimize destruction of the

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fracture surfaces by dissolution by the liquid subsequent to fracture.   For
the same reason, only a trace of crazing liquid was used in the early experi-
ments.

Fracture by Manual Flexing

In our early experiments, strips of polystyrene (40 mm $\times$ 8 mm $\times$ 2.5
mm approx.) were rapidly flexed by hand to fracture after applying a trace
of n-propanol to the middle of one large (i.e., molded) surface, which was
put in tension.   The time to fracture from the initial application of stress
was about 0.5 sec.

The resulting fracture surfaces each contained two regions: a band of
variable width, adjacent to the tension face, within which there was evi-
dence of solvent effects; and the remainder of the surface, which contained
typical features such as have been observed on polystyrene fractured in
air.[2-5]   Within the solvent-attacked region were areas of cellular structure
and pitted areas (e.g., Fig. 1).   The cell size generally decreased inward
from the tension face of the sample (Figs. 2 and 3) to 50–100 nm at the
front of the solvent-crazed region (Fig. 4).

The area shown in Figure 5 is repeated at lower magnification in Figure
6, in which the lower two thirds of the micrograph show a surface which is
typical of slow fracture in the absence of solvent.   The horseshoe features
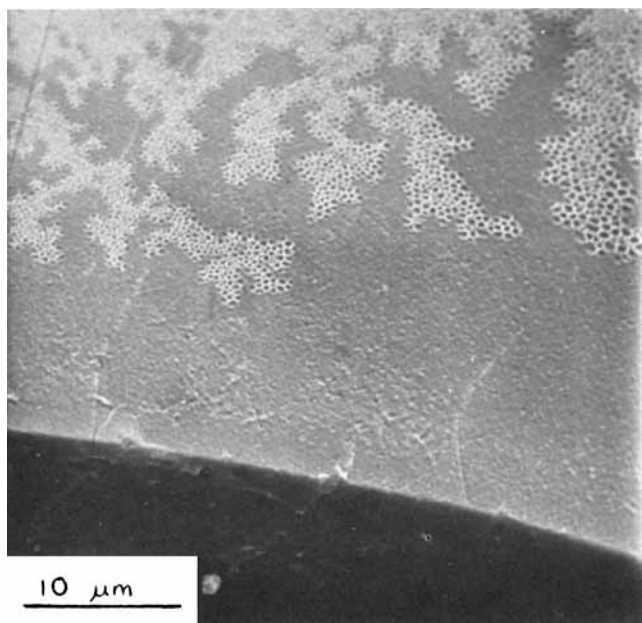are secondary fractures such as are commonly observed on slow fracture

Fig. 1. Fracture surface on polystyrene which was manually flexed to fracture after
applying a trace of n-propanol to the surface.   Intersection of fracture surface with
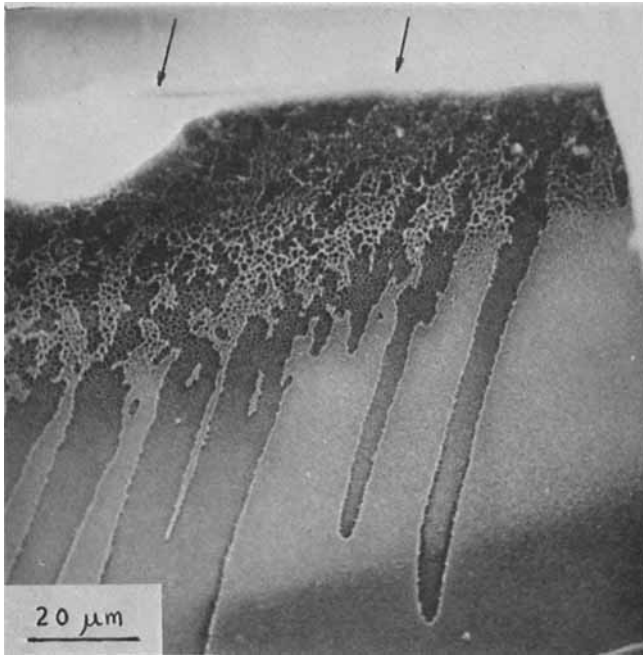molded surface is shown.

Fig. 2. General view of the craze region of the fracture surface on another polystyrene sample manually flexed after a trace of *n*-propanol had been applied. Arrows indicate position of molded surface at which craze originated.
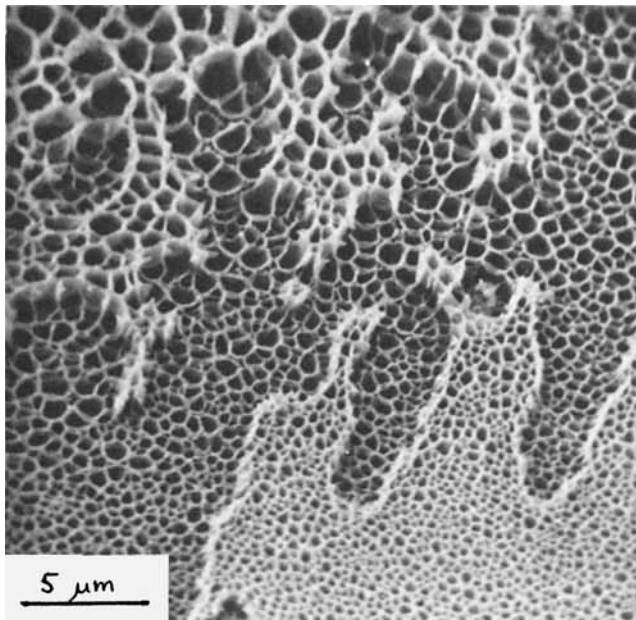

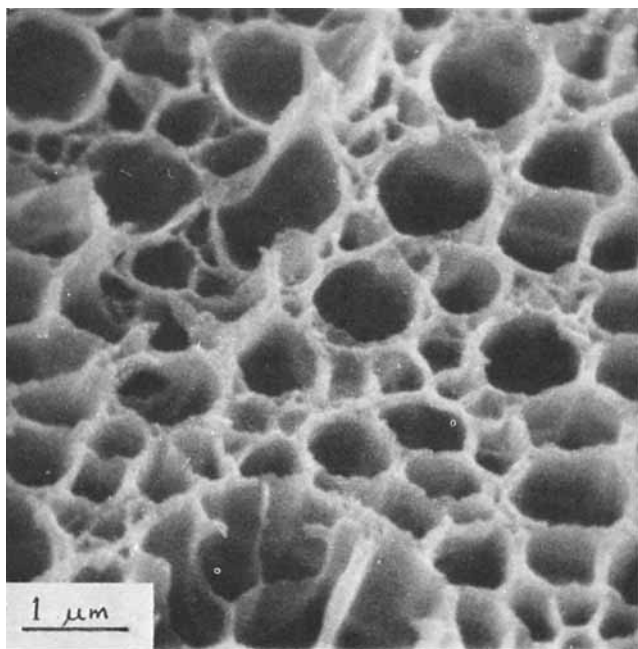Fig. 3. Detail of central area on Fig. 2.

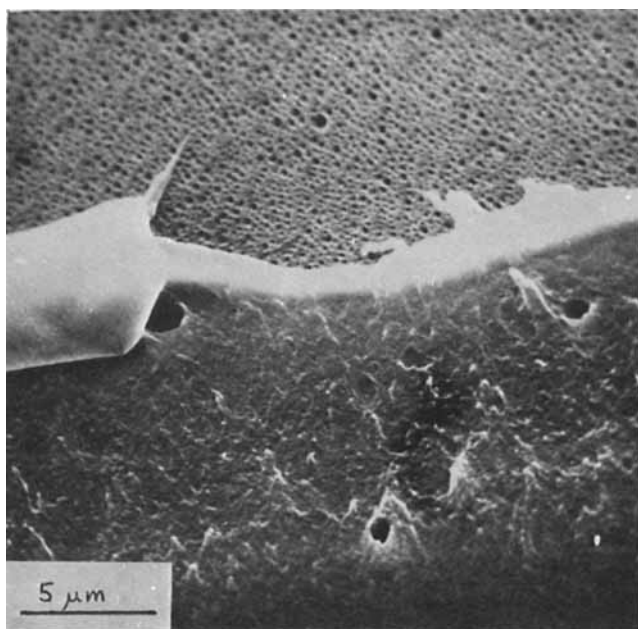Fig. 4. Detail of part of the cellular structure on Fig. 2.

Fig. 5. Craze tip on a polystyrene sample manually fractured after applying a trace of n-propanol. Fracture commenced at the molded surface which is off the top edge of the micrograph.
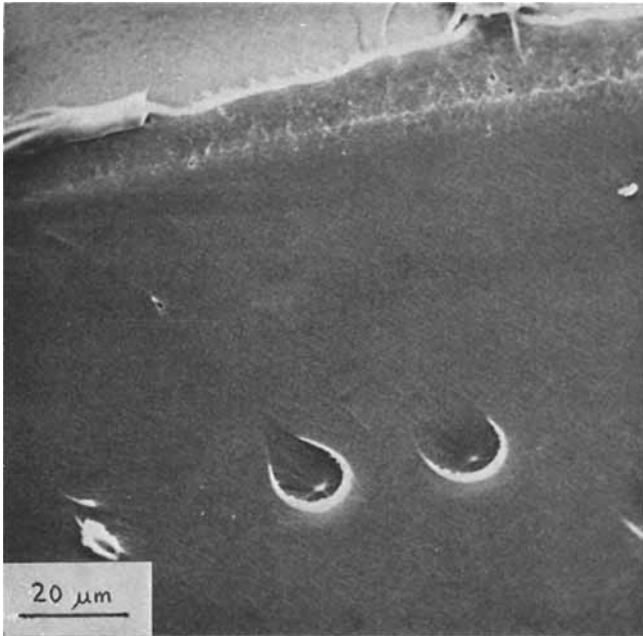
Fig. 6. Same region as Fig. 5 but at lower magnification. Secondary fractures indicate that the crack propagation direction was reversed near bottom of micrograph.
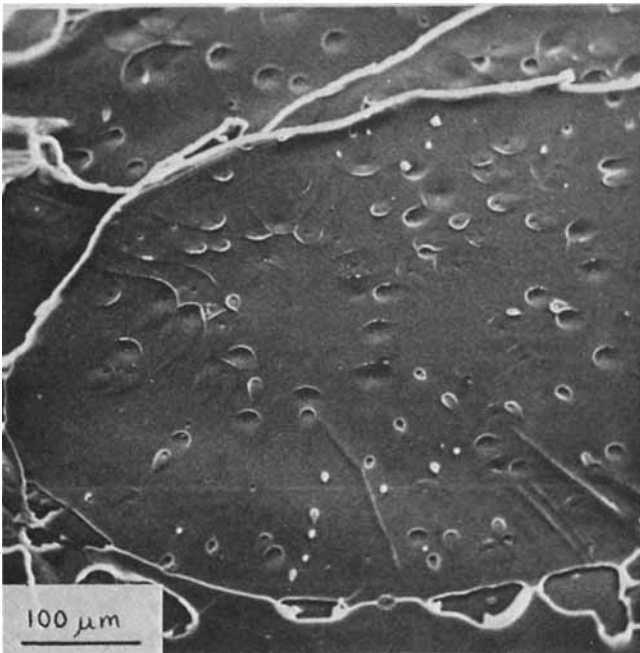

Fig. 7. Polystyrene sample broken by applying 36 N/mm² outer fiber stress and then wetting with *n*-propanol. Reinitiation ahead of the craze tip is shown. Principal crack propagation direction was left to right.

surfaces produced in air. The orientation of these features indicates that the crack was propagating from the bottom edge of the micrograph though the tension surface of the sample was off the top edge of the micrograph; i.e., locally there was a reversal of the crack propagation direction. This effect occurred in all of the test pieces, and often one or more regions of fracture reinitiation were found such as that shown in Figure 7. Around the perimeter of the roughly circular region of surface in this figure, the orientations of the secondary fractures indicate that the main crack was growing radially in all directions and had therefore initiated within the region shown.

Referring again to Figures 5 and 6, ahead of the solvent craze front there is a band, about 10 μm wide, of slightly different structure which may correspond to material penetrated by the n-propanol. If craze growth is encouraged by the alcohol owing to its softening effect, the liquid diffusion front must precede the craze tip. However, the fact that fracture occurred within 0.5 sec of load application indicates that craze growth must have been rapid, and it is therefore surprising that the solvent front could be 10 μm ahead of the solvent craze front.

Flexure With Constant Outer Fiber Stress

It was considered essential at this stage to carry out tests under more strictly defined stress conditions. For these experiments, polystyrene test pieces of dimensions 75 mm $\times$ 12 mm were cut from 0.9 mm thick compression-molded sheet and annealed between plate glass. These strips were fractured at room temperature by first applying a load to produce an arbitrary outer fiber stress of 36 N/mm^2 and then wetting the tensile face with an alcohol from a teat pipet.

In order to find whether the cell size was dependent upon the alcohol molecule size, five alcohols were used: methanol, ethanol, n-propanol, n-butanol, and cyclohexanol. On all of the samples, the tip of the solvent-crazed region was examined, and no difference was found between the cell sizes on the various test pieces. The cell diameter in this region was somewhat variable on all the samples but was generally 50 to 100 nm, with occasional regions of 25 nm in diameter. The depth to which the craze had penetrated decreased as the size of the alcohol molecule increased, but it appeared that the structure at the tip of the craze was independent of the chemical nature of the alcohol.

It was expected that frozen-in free volume might affect the cell size observed on the fracture surfaces. Test pieces were quenched into liquid nitrogen from 20°, 90°, 115°, 130°, and 148°C and then allowed to warm to room temperature before being fractured as before, at 36 N/mm^2 outer fiber stress, wetted with n-propanol from a teat pipet. The cell sizes on some regions of these samples were irregular, but no trend of change was observable as a result of the different thermal treatments. All the samples had approximately the same cell structure at the craze tip. (Subsequent
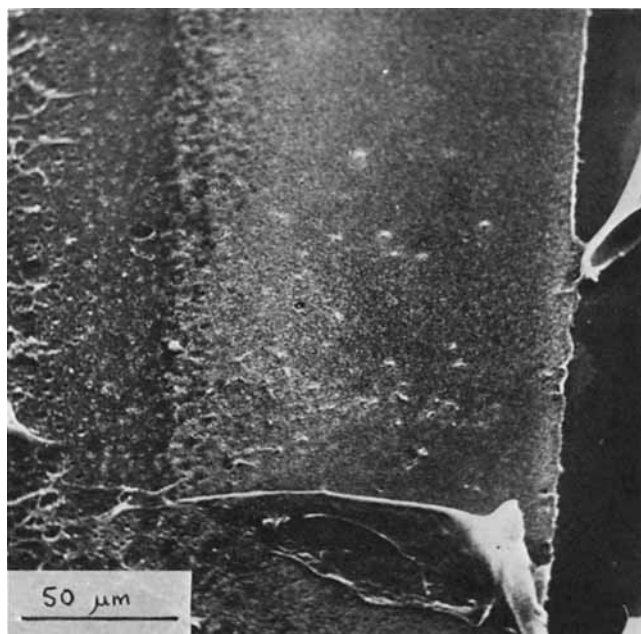
Fig. 8. General view of the craze region on a polystyrene test piece fractured at 36 N/mm² after quenching from 148°C into liquid nitrogen. Craze tip is near right edge. Fracture direction from left to right.

density measurements on similarly quenched samples suggest, however, that quenching from temperatures above 90°C caused no additional increase in frozen-in free volume; densities 1.0477, 1.0455, 1.0451, 1.0453, and 1.0452 g/ml at 21.5°C after quenching from 20°, 90°, 115°, 130°, and 148°C, respectively.)

It was noted that the surfaces produced in these two experiments contained larger pitted areas than were observed on the manually flexed test pieces. This may have been due to the larger amount of alcohol applied in the controlled-stress experiments compared to the experiments in which the test piece was broken by hand.

Figures 8–11 are examples of the surface features observed on the quenched materials. Figure 8 shows a low magnification view of part of a test piece which had been quenched from 148°C into liquid nitrogen. The fracture propagation was from left to right and the pitted area is close to the tension surface. It is apparent that the cell size decreases as the solvent craze tip is approached. Figure 9 is part of the corresponding area on the other fracture surface (therefore propagation was right to left), and this shows again the effect upon the structure of increasing distance from the solvent-wetted tension face of the test piece. Figure 10 is part of the craze front on the same sample as Figure 8. In this sample, the n-propanol has penetrated only 1–2 μm ahead of the craze tip as judged by the appearance of the surface. Figure 11 is part of the craze tip on a sample
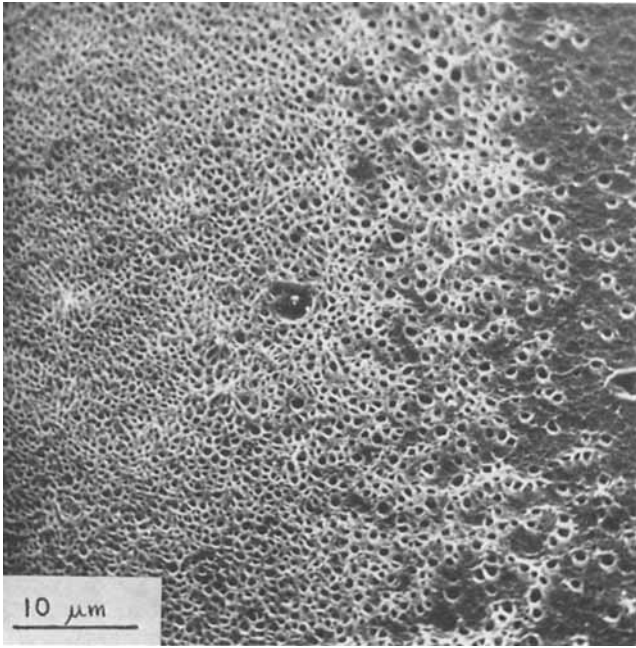
Fig. 9. Part of the corresponding region to Fig. 8 on the other fracture surface.   Fracture
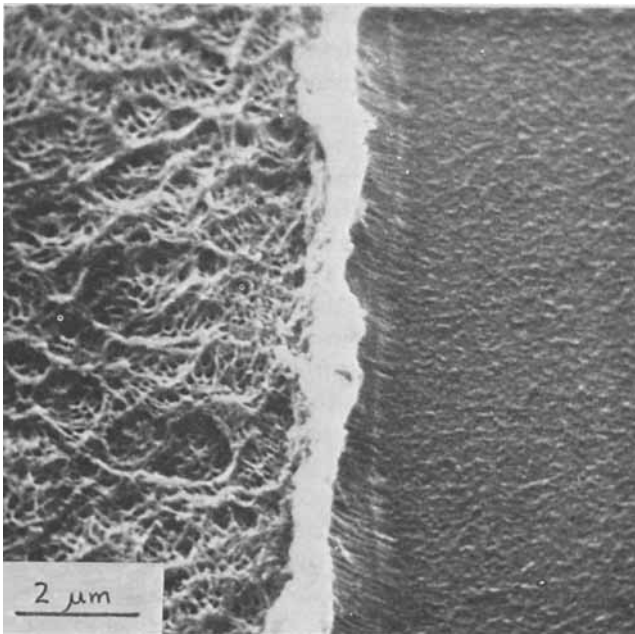direction right to left.

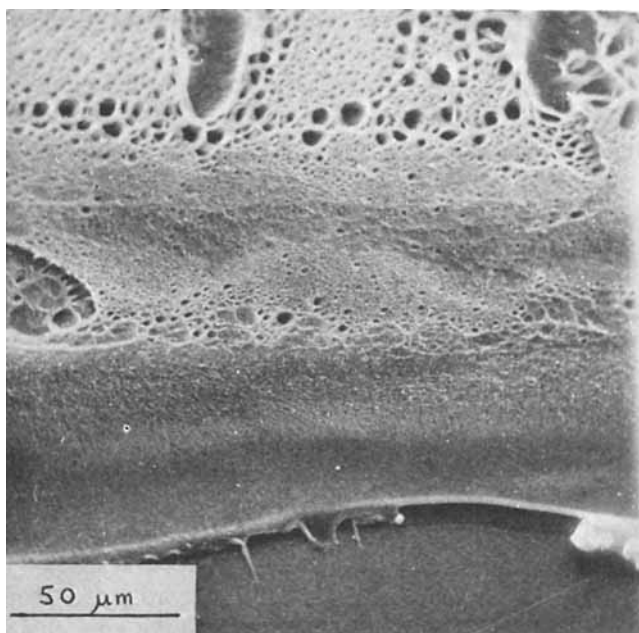Fig. 10. Detail of part of the craze tip on same sample as Fig. 9.

Fig. 11. Sample similar to that shown in Figs. 8–10 but quenched from 130°C into liquid nitrogen, showing an irregular structure. Fracture direction top to bottom.

quenched from 130°C, demonstrating the structural irregularity which was sometimes observed.

Treatment of Polystyrene Dry-Fracture Surface with *n*-Propanol

It was just conceivable that the porous structures being observed on the solvent-fractured surface were due to attack on the dry-fracture surface by the alcohols. Accordingly, areas on polystyrene slow-fracture surfaces which had been produced in air at ambient temperature were wetted with *n*-propanol, and after allowing time for the alcohol to evaporate, they were examined by optical and scanning electron microscopy. The region which had been wetted with the propanol showed slightly altered interference patterns when examined in sodium light under the optical microscope. No changes were detectable in the scanning electron microscope at magnifications from ×20 to ×20,000, and the treated regions were only locatable by means of marker scratches on the surface.

It was inferred, therefore, that the surface structures described in the above sections were formed due to the presence of the alcohols within the polymer prior to craze fracture and probably prior to craze formation.

DISCUSSION

Kambour[6,7] has provided evidence that crazes in glassy polymers contain many small voids which can be 10 nm in diameter when the crazes are

formed in air or in very weak crazing liquids. The occurrence of such a structure within crazes has been explained by Gent[8] as being due to the effect of the dilatational component of the local stress acting upon a random distribution of microvoid flaws. (NB: These flaws range in size from perhaps 1 nm and hence are very much smaller than the flaws which initiate secondary fracture in polystyrene.) According to this theory, these microvoids vary in magnitude, and therefore the proportion of them which is caused to grow depends upon the local stress. If crazing occurs in air, many of the flaws will be activated and the resulting voids will be small. If, however, the crazing stress is low, as occurs in solvent crazing, relatively few flaws will cause cavitation, and the cavities which do form will then grow to a greater size. The presence of a coarse cellular structure on the solvent-fractured surface can be understood on the basis of Gent's theory. The decreasing average cell diameter as the solvent front is approached could be due to reducing solvent content causing an increase in the crazing stress.

An alternative theory which could explain the variation in craze cell diameter has been proposed by Murray and Hull,[4] who studied the surface morphology of polystyrene fractured in air. According to them the craze forms as a fine cell structure; but then, progressive void coalescence can occur so as to produce an increasingly coarse structure. In the present series of micrographs, the differences in cell diameter would then be due simply to different intervals of time between formation and fracture of the craze in each region, i.e., near to the molded surface the craze is coarsest because it formed first, and near to the craze tip the craze is finest because it formed only just before the instant of fracture.

On the available evidence, it is not possible confidantly to prefer either of these two approaches. Occasionally, evidence of void coalescence is observed, e.g., center left of Figure 11; but at high magnification, many of the larger cells contain no evidence of residual cell walls within them such as would be expected if they were formed by coalescence of smaller voids.

The pitted regions are not formed by solvent attack upon the cellular structure. This has been shown by fracturing polystyrene immersed in crazing liquids so that the surface was completely wetted by crazing liquid after fracture, and it was found that the cellular structure remained on the surface. (These results will be reported in a subsequent paper.) Therefore, the generation of such surfaces must be caused by some feature of the fracture process itself and not by solvent attack subsequent to fracture. Due to the dilatational stress acting upon the volume of material ahead of the craze, it becomes capable of absorbing a larger volume of liquid than it could absorb under zero stress conditions. We believe that the relaxation of the structure occurs during the period of beyond-equilibrium swelling.

The sequence of events during fracture in alcohol is probably as follows: Solvent crazes initiate at or close to the tension surface of the sample under conditions of low stress and maximum solvent availability. The resulting surface is pitted. Further into the sample, the craze tip begins to be

starved of solvent, and the coarse cell structure consequently appears, decreasing in size away from the tension face.   The presence of the solvent within the highly stressed region at the craze tip has two opposing effects; it softens the penetrated volume but it also swells the penetrated volume so as to reduce the dilatational stress within it.   Softening promotes cavitation, but decrease in the dilitational stress inhibits cavitation.   It appears that as the solvent content of the material ahead of the craze decreases and the cavitation stress increases, there comes a point at which initiation of a dry-craze some microns ahead is more favorable than propagation of the existing solvent craze.

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