that values of force constants for smaller molecules[10] can be transferred to polyalkenamers then there would be an approximately two-fold increase in force constant at the double bond. Secondly, the introduction of a double bond brings about at conformational change to skew (+120°), *trans*, skew (−120°). This lateral displacement of the chain at the double bond[1] may be regarded as a type of defect. It is to be noted that calculations[11] have indicated that the *LAM* corresponding to the whole chain traverse is greatly reduced in intensity when conformational defects are introduced into an all-*trans* chain. We would suggest that these two effects in conjunction could be responsible for decoupling the *LAM* at the double bond in polyalkenamers.

In summary, therefore, we looked for, but did not find, a *LAM* corresponding to the thickness of polyalkenamer lamellae. However, a band has been found which displays the characteristics of a *LAM* of the repeat unit of a polyalkenamer. From this we conclude that the *LAM* may be decoupled by double bonds. This conclusion is in line with an observation made elsewhere[12] that in salts of an unsaturated dicarboxylic acid two *LAMs* are seen which are characteristic of the lengths of chain on either side of the double bond. Similarly, by comparison with normal paraffins, it appears that in polyalkenamers the *LAM* gives a measure of the number of carbon atoms in the repeat unit of the polymer.

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Evidence for crystallinity in poly(ether sulphone)

Certain polymers appear to be incorrigibly non-crystalline and are customarily described as amorphous. The stiff, bulky chains of poly(ether sulphone), (PES), constitute a severe challenge to any attempt to produce an ordered structure. Direct crystallization has so far failed but other approaches are possible. Some polymers, including poly(ethylene terephthalate), are prone to solvent-induced crystallization and this has been well documented in recent years[1]. PES must now be added to the list of polymers which can develop crystallinity with the assistance of a solvent.

Recent work[2,3] has shown that the systems formed by PES and organic solvents are exceedingly complicated with features including lower critical solution temperatures, gelation and solvent-induced resistance. The last mentioned feature led directly to the discovery of crystallinity in a sample. In the course of experiments on the kinetics of dissolution of PES in organic solvents[2,3] it was noted that the polymer could be made virtually insoluble in dichloromethane by a previous controlled encounter with the same solvent. This strongly suggested that a crystalline structure was being produced and the conclusion was confirmed directly by X-ray diffraction as shown in *Figure 1* and *Table 1*. Solvent-resistant samples of the polymer could be obtained in a number of ways of which the following is typical.

A clear solution of the polymer was prepared at 40°C by dissolving some PES in four times its own weight of dichloro-

Figure 1   Typical X-ray diffraction pattern produced by polyethersulphone containing dichloromethane

Table 1 Spacings from most significant crystalline peaks

d spacing Å	Comparative Intensity
5.02	Weak
4.50	Strong
3.93	Medium
3.63	Medium
3.32	Medium—strong
2.98	Weak
2.45	Weak

methane. The solution was cooled to 5°C and held at that temperature overnight, the result being a whitened solid mass. The solid lost solvent gradually over a period of one month at room temperature but about 21 wt % of solvent was still present when the X-ray analysis was performed. Reasonably rapid removal of this solvent requires heating under vacuum and such treatment appears to destroy the X-ray crystallinity if the temperature exceeds 150°C. (The glass transition temperature of PES is 220°C.) In an attempt to orient the sample the X-ray crystallinity was also destroyed by cold rolling.

A remarkable property of samples of PES which have been crystallized and then stripped of solvent is shown by their resistance to dissolution when they encounter the solvent a second time. This appears to be because recrystallization occurs so rapidly that it forestalls dissolution at any temperature up to the boiling point of the solvent. The recrystallization has been confirmed by X-ray diffraction and it is now proposed that polymer exhibiting this property should be known as 'susceptible polymer'. This susceptibility to rapid recrystallization is obliterated only by heating to the glass transition temperature.

The possibility that crystallinity is due to a stoichiometric adduct of polymer and solvent is attractive but not yet established.

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Volume strain measurement during the creep of polymers in liquid environments

In the course of a detailed study on the engineering properties of unfilled polyamide-6,6 (PA 66) and short glass fibre reinforced polyamide-6,6 (GFPA 66) injection mouldings, all three orthogonal strains were measured during uniaxial tensile creep on specimens tested in air or in distilled water. This permitted the calculation of the variation of volume strain with time during tensile creep. The purpose of this Letter is to summarize some of the very interesting trends observed.

If $\Delta V/V$, $\Delta l/l$, $\Delta t/t$ and $\Delta w/w$ are the volume, axial, thickness and width strains respectively, then:

$$\frac{\Delta V}{V} = \left(1 + \frac{\Delta l}{l}\right)\left(1 + \frac{\Delta t}{t}\right)\left(1 + \frac{\Delta w}{w}\right) - 1 \qquad (1)$$

with all strains measured at any one creep time.

Figure 1 plots volume strain against log(creep time) and axial strain against log(creep time). The data from these two graphs may be combined to produce a linear plot of volume strain against axial creep strain where both strains are measured at the same creep time (and stress).

Bucknall[1] has shown that this linear volume strain versus axial strain plot can provide valuable indications of the mechanism of deformation during tensile creep. In mechanisms which involve crazing, a slope of one on this plot indicates that all deformation is due to volume processes, whereas a horizontal line (i.e. a slope of zero) indicates that deformation arises from shear effects.

Observations of volume strain behaviour during creep in air of short glass fibre reinforced thermoplastics have also

been undertaken and it has been found that an upturn in the volume strain—axial strain plot for these materials may provide an indication of the onset of permanent damage during creep[2]. Thus it would seem that evaluation of volume strain during tensile creep *in liquids* may also provide insight into the underlying mechanisms of deformation and absorption.
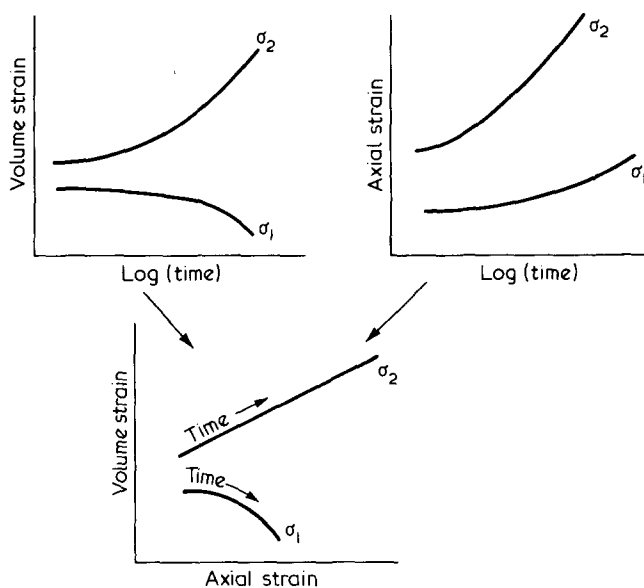

Figure 1 Derivation of volume strain—axial strain plot. σ is the applied tensile stress and $\sigma_2 > \sigma_1$