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The effect of temperature on crazing mechanisms in polystyrene

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At room temperature scission is the dominant mechanism for the modification of the entanglement network required for craze formation in polystyrene, but as the temperature is increased towards T_g, there is the possibility that disentanglement processes may contribute. These will be most important for short chains. If disentanglement can occur, a molecular weight dependence of the crazing stress as a function of temperature will result. This prediction is tested by straining thin films of a range of monodisperse samples of polystyrene at temperatures between 40 and 90° C. The nature of the ensuing deformation has been characterized by transmission electron microscopy. It is observed that whereas only crazing occurs over the entire temperature range for the lowest molecular weight sample, shear processes become important for higher molecular weight materials. For the longest chains, crazing is almost entirely suppressed at 80° C, with the preferential formation of shear deformation zones occurring. These observations are consistent with the idea that disentanglement is playing a significant role in craze formation at sufficiently high temperatures.

1. Introduction

Because the formation of crazes usually precedes fracture in brittle, glassy polymers, crazes have been the subject of extensive study (for a recent series of reviews, see [1]). From the results of a transmission electron microscopy (TEM) study of a wide range of homopolymers, copolymers and blends, it has recently become apparent that the entanglement network plays an important role in determining craze microstructure and properties [2–5]. Based on the assumption that the entanglement network of the melt is unchanged when "frozen in" in the glass, melt elasticity measurements can be used to give a value of M_e, the molecular weight between entanglements in the glass. With a knowledge of M_e, two further parameters governing the entanglement network can be determined. The chain contour length between entanglements, l_e, is given by

$$l_e = l_0 \frac{M_e}{M_0} \qquad (1)$$

where l_0 is the length of a fully extended chain unit of molecular weight M_0. The mesh size of the entanglement network, d, is equal to the root-mean-square end-to-end distance of a chain of molecular weight M_e, and can be written as

$$d = k(M_e)^{1/2} \qquad (2)$$

where k may be determined from neutron or light scattering experiments. For a single chain in the entanglement network extended along its end-to-end vector, such that the entanglement points remain unbroken, a maximum extension ratio, λ_{max}, can be defined:

$$\lambda_{max} = l_e/d \qquad (3)$$

Measurements of craze extension ratios, λ_{craze} via TEM, have shown a strong correlation exists between λ_{craze} and λ_{max} [2, 3], thereby demonstrating the importance of the entanglements in craze formation.

For polymers with a high entanglement density, ν_E, given by

$$\nu_E = \varrho N_A / M_e \qquad (4)$$

(where ϱ is the density and N_A Avogadro's number) such as polycarbonate, PC, and poly(2,6-dimethyl-1,4-phenylene oxide), PPO, in the thin films required for examination in the TEM, crazing tends to be suppressed in favour of the formation of shear deformation zones (DZs), unless physical ageing of the films (e.g. by annealing just below T_g) has occurred [4]. As the density of the entanglement points decreases, crazing becomes increasingly favoured such that for polystyrene, PS, with $\nu_E = 3.28 \times 10^{25}$ chains m^{-3} (compared with values of 28.95×10^{25} and 14.81×10^{25} for PC and PPO, respectively) [6] deformation zones have not to date been observed. For blends of PS with PPO, for which the entanglement density can be systematically varied by compositional variations, the changing appearance of crazes can be explored as shear deformation becomes increasingly favoured with increase in PPO content (and hence in ν_E). In pure PS, the crazes are long and thin, but as PPO is added, shorter, wide crazes ("cigars") with shear blunting at their tips form and finally true DZs, with no voids [4].

In the derivation of λ_{max} (Equation 3), it is assumed that all entanglement points remain intact during crazing. Clearly this is an oversimplification, since the generation of voids, necessary for the formation of the craze fibril structure, must entail significant modification of the entanglement network. This modification could occur either by chain scission or by slippage of the entanglement points via reptation [7, 8]. Kramer [9] has convincingly argued that for PS at room temperature scission is the dominant mechanism. This conclusion was reached by noting that both the uniaxial stress for crazing [9] and the craze fibril extension ratio [10] remain essentially constant for monodisperse PS specimens with molecular weights above 200 000. Additionally, light crosslinking of PS does not modify the craze microstructure relative to uncrosslinked PS [11, 12]. These observations are not consistent with the idea that chain disentanglement is important in the formation of the craze structure.

However, since chain disentanglement via reptation must involve mobility of the polymer chains, it may be expected that at elevated temperature the effective contribution of chain scission to craze deformation may be reduced. In this paper, the effect of temperature on deformation mechanisms in a series of monodisperse samples of PS is examined to explore this premise. Optical microscopy and TEM are used to characterize the deformation behaviour.

2. Experimental details

Samples of monodisperse PS ($M_w/M_n < 1.07$) were obtained from Polymer Laboratories, with molecular weights of 115 000, 350 000, 515 000 and 1 150 000. These will be referred to as MPS 100, 350, 515 and 1150, respectively. The polymers were dissolved in toluene. Thin films ($\sim 0.5\,\mu$m thick) were prepared by drawing glass slides at a constant rate from solution. The films were floated off on a water bath and picked up on an annealed copper grid which had been precoated with the same polymer. Bonding of the film to the grid was achieved by a short exposure to the solvent vapour.

After drying, the specimens were mounted in a straining rig and this was placed in an oven at the selected temperature (in the range 40 to 90° C) for 10 min prior to straining. The specimen was then strained, still inside the oven, and left for a further 5 min before being removed and air-cooled. The specimen was then observed with an optical microscope, and suitable grid squares cut out for observation in a Siemens 102 electron microscope operating at 100 keV. This method is analogous to that used by Kramer's group for studies of crazing at room temperature [2, 3, 13, 14].

The volume fraction of material in either a craze or a deformation zone may be obtained by microdensitometry of the electron image plate [14, 15]. The optical densities of the craze/DZ ($\phi_{craze/DZ}$), film (ϕ_{film}) and a hole through the film (ϕ_{hole}) are measured. The volume fraction, v_f ($= 1/\lambda$), is then given by

$$v_f = 1 - \left[\frac{\ln(\phi_{craze}/\phi_{film})}{\ln(\phi_{hole}/\phi_{film})}\right] \qquad (6)$$

3. Results

The effect of temperature upon the model of deformation on specimens of MPS 515 can be seen in Fig. 1. It is clear from Fig. 1, that there is an increasing propensity for shear as the temperature is raised. The first appearance of some

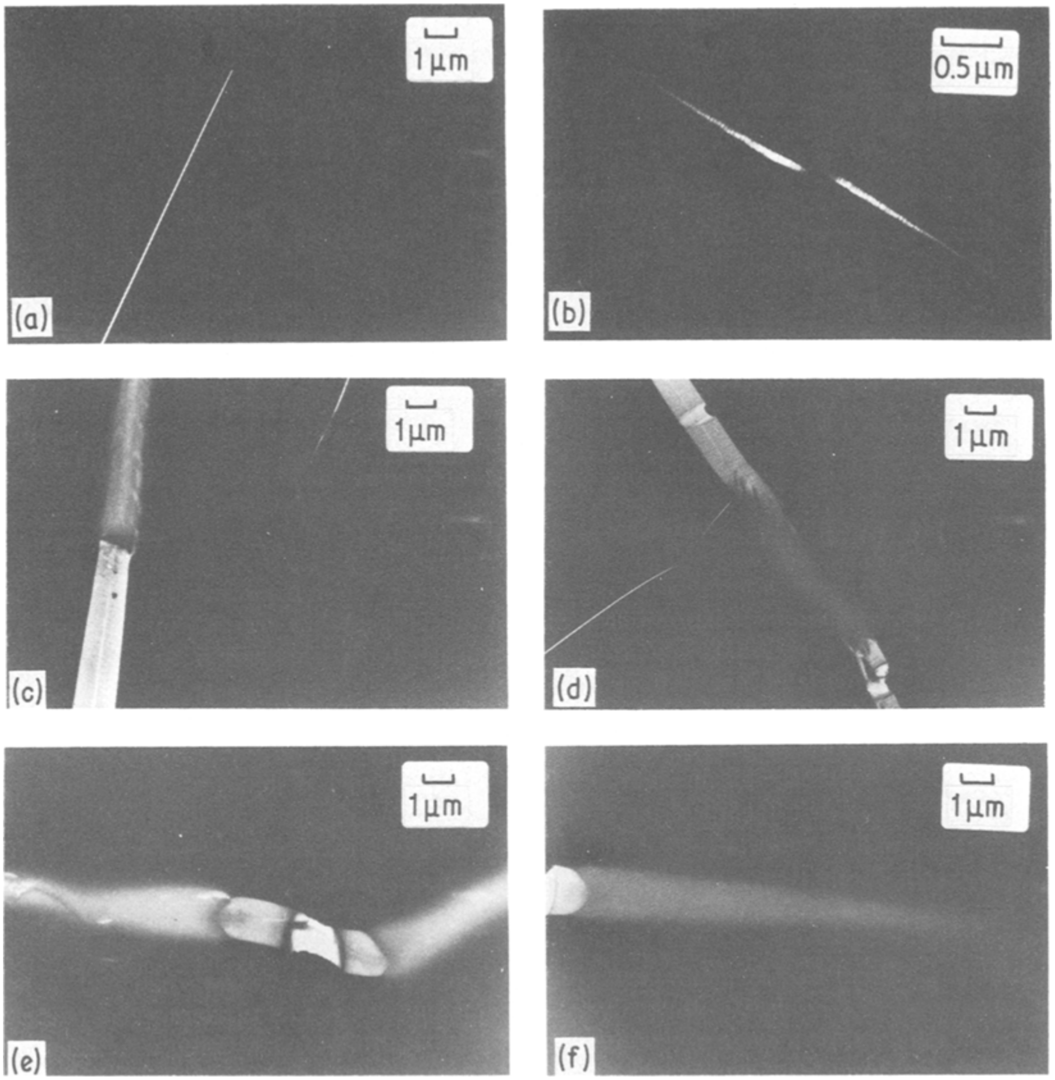
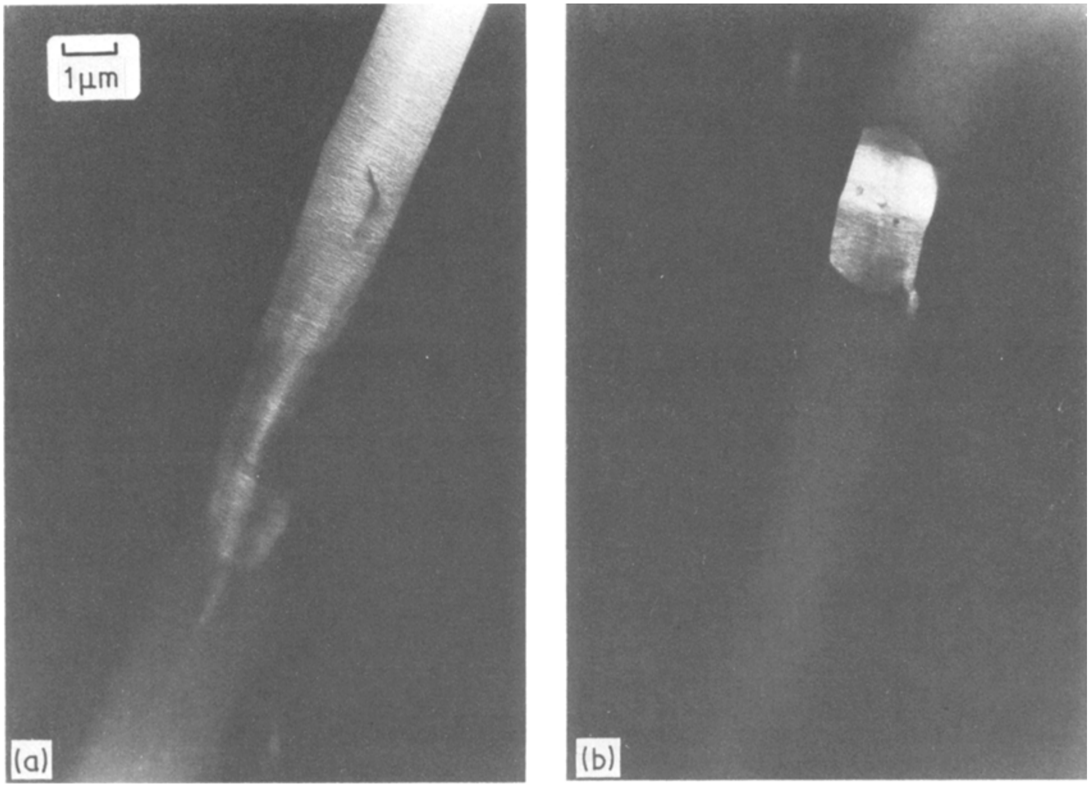


Figure 1 Deformation in MPS 515 under the following conditions: (a) 2.5% at 50° C, (b) 2% at 60° C, (c) 2.5% at 70° C, (d) 2.5% at 80° C, (e) and (f) 2.5% at 90° C.

slight shear occurs in crazes grown at 60° C, but the majority of craze tips still show no shear blunting. At 70° C almost all crazes show some shear blunting at their tips, the shear extending over several microns in some cases. Both high (long, thin) and low ("cigars") aspect ratio crazes form. By 90° C, true deformation zones form, with their characteristic lack of voiding, although these are not as uniform as their counterparts in the room temperature deformation of PC [16].

Unlike the case for crazes in PS at room temperature, it is no longer possible to assign a unique value of λ_{craze} at any given temperature. The experimentally determined value of λ depends on the type of craze under consideration. For instance, at 90° C, some "cigars" still have a relatively low value of ~ 3 to 4, whereas longer crazes have much higher extension ratios (~ 20). By 60° C, however, it seems that the majority of crazes possess extension ratios significantly higher than the room temperature value (~ 4).

Turning now to the high molecular weight sample, MPS 1150, it is found that the strain necessary to induce deformation at 80° C is so high ($> 10\%$) that debonding from the copper grid usually intervenes. Where deformation is found, extensive fibrillation has not occurred as shown in Fig. 2. Instead, the regions of fibril-



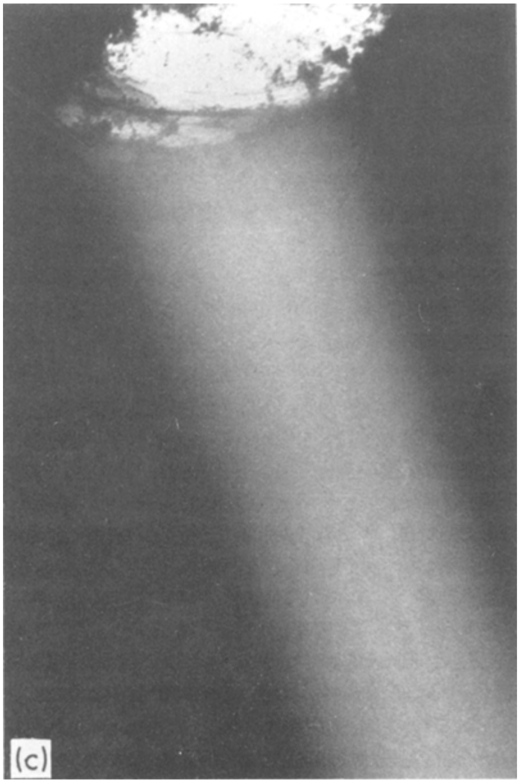


Figure 2 Deformation in MPS 1150 under the following conditions: (a) 4% at 60° C, (b) 5% at 70° C, (c) 6% at 80° C.

lation are short (~ 2 μm long), often terminated by angled shear bands. Unfibrillated shear deformation zones are the more frequent mode of deformation. At 90° C, no deformation has been achieved, indicating that the required strain is outside the possible range of these experiments. As the temperature is dropped, the transition from shear-plus-crazing to crazing alone follows the same pattern as for MPS 515, but with the equivalent mode of deformation occurring at a temperature ~ 10° C lower in the high molecular weight case.

For samples of the two lowest molecular weight specimens, MPS 100 and MPS 350, true deformation zones were never seen at any temperature. At 90° C, MPS 350 showed short crazes with shear at their tips (Fig. 3), but little evidence for any shear whatsoever was seen over the entire temperature range for MPS 100. The strains necessary to induce deformation in MPS 100 were significantly lower than in MPS 515 at the same temperature.

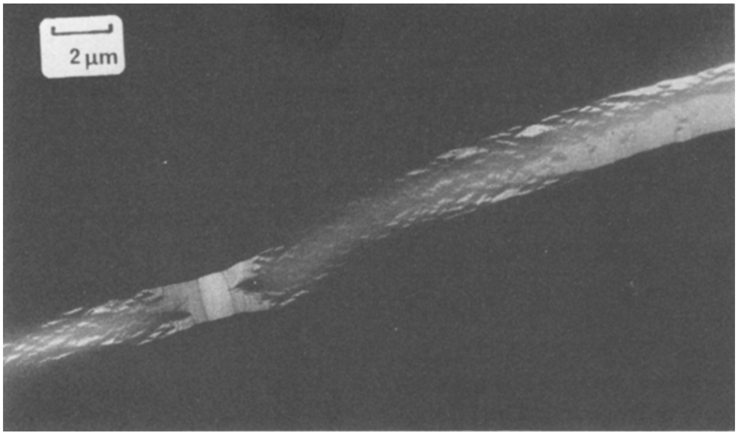


Figure 3 Shear blunting at a craze tip in MPS 350 strained 2.5% at 90° C.

4. Discussion

The results presented in the preceding section show clearly that whereas earlier workers have shown that at room temperature molecular weight has little effect on either the craze stress or microstructure, this is not the case as T_g is approached. It is known (e.g. [17]) that both the crazing stress (σ) and yield stress (Y) drop as the temperature is increased, the latter falling faster than the former for PS. Consequently, an increasing propensity for shear deformation is to be expected as the temperature of straining is increased. However, this TEM study demonstrates that the relative change in σ and Y is molecular weight dependent.

The process of yield is thought to involve segmental processes on a scale much smaller than the entanglement mesh size [18, 19], and hence the total length of a polymer chain involved in yielding will be immaterial. A universal curve for the temperature variation of the yield stress for all molecular weights of PS can, therefore, be assumed (for a given strain rate). The molecular weight dependence must, therefore, lie in the stress for crazing.

As mentioned in Section 1, the required network modification for crazing could occur either via chain scission or disentanglement; it is in the latter mechanism that the molecular weight dependence must reside. Consider a chain disentangling by moving past its neighbours. It will experience a frictive force, F, which will be given by $P\xi_0 v$, where P is the degree of polymerization, ξ_0 the monomeric friction coefficient, and v the velocity of the chain. The monomeric friction coefficient is not tabulated for the glassy state, but a lower bound for F may be obtained by using $\xi_0(T_g)$ which for PS is $0.11\,\mathrm{J\,sec\,m^{-1}}$ [20]. Taking for v a typical craze interface velocity of $0.1\,\mathrm{nm\,sec^{-1}}$, the force required to move a PS chain of degree of polymerization 1000 will be $1.1 \times 10^{-8}\,\mathrm{N}$; for a more slowly growing craze, with v given by $0.01\,\mathrm{nm\,sec^{-1}}$, F is reduced to $1.1 \times 10^{-9}\,\mathrm{N}$. For PS the theoretical bond strength is $3 \times 10^{-9}\,\mathrm{N}$ [21], which implies that scission will intervene before disentanglement can occur for the first example, but for the slower craze growth, disentanglement processes may contribute.

Since the force required to move a given chain past its neighbours, and hence the force associated with disentanglement, is directly proportional to chain length (or equivalently molecular weight), it is clear that disentanglement processes will be of greater importance for short chains, whereas scission is always likely to occur at a lower stress than required for disentanglement for long chains. The stress required for either mechanism to operate is temperature dependent: for disentanglement through ξ_0, and for scission because it is an activated process [21] and the rate of bond breakage will increase with temperature.

These arguments, therefore, not only provide a rationale for the well known decrease in crazing stress as T_g is approached (e.g. [17]), but also explain the observed variation in deformation response with molecular weight. The decrease in crazing stress as the temperature is raised cannot (unlike the yield stress) be represented by a single curve, but rather a family of curves must be drawn with the curve for the lowest molecular

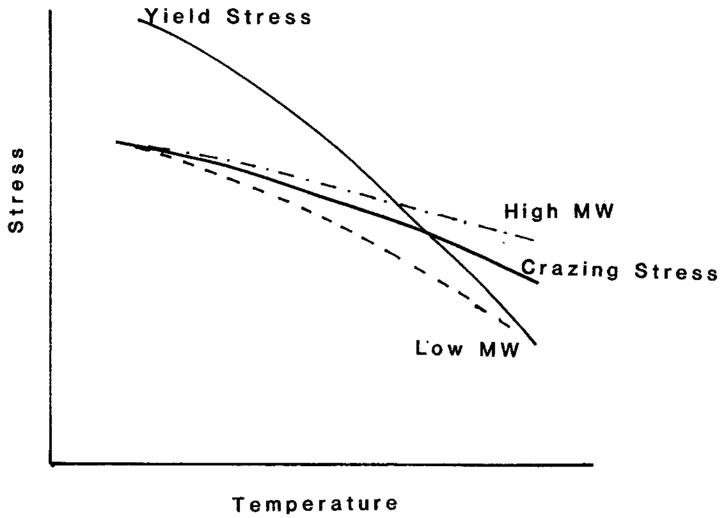


Figure 4 Schematic representation of the temperature dependence of σ and Y. All molecular weights exhibit the same behaviour for Y.

weight sample dropping most steeply. The variation in Y and σ are shown schematically in Fig. 4.

Kramer [9] has suggested the effect of temperature can be accounted for by considering the surface energy Γ required to create the void surface. In the scission dominated regime, the energy of scission contributes $d\nu_E U/4$, where U is the energy to break a primary bond, but the contribution drops as disentanglement processes become important. This consequent decrease in Γ in turn leads to a reduction in the craze tip stress necessary for craze advance. However, this argument is strictly correct only in the limit of infinitely long times, since it neglects the energy cost of disentangling a chain.

For high molecular weight PS, where scission remains the dominant mechanism for network modification at all temperatures, the curves for crazing and yielding in Fig. 4 cross to give a transition temperature, T_{trans}, which experimentally seems to lie at around 60° C (but this value will be strain rate dependent). Because for MPS 100 disentanglement can readily occur, σ drops rapidly for the low MW material pushing the transition temperature up. In practice, it seems that for MPS 100, T_{trans} would actually lie above T_g, so that shear deformation is never observed in these specimens. As the molecular weight is raised, shear processes become important at increasingly low temperatures.

For MPS 1150, the strain necessary to promote any deformation at all at the highest temperatures becomes so high that it cannot be achieved under the current experimental conditions. At 80° C shear processes are dominating to such an extent that regions of fibrillation greater than 1 to 2 μm in length cannot form, and unfibrillated deformation zones are the preferred mode of deformation.

Previously a three-stage model has been proposed for polymers of low l_e strained at room temperature [4, 5]. Initial conditions of high stress/strain rate favour scission, enabling the void structure of a craze to form; as the mean stress drops shear processes start to dominate, and finally, once the strain rate is sufficiently low, disentanglement starts to contribute once again permitting crazing to occur. This model highlights the well-known importance of the strain rate for the observed deformation. In the model proposed here for temperature effects, it must also be recognized that the response of a specimen of a given molecular weight will be altered by strain rate, as clearly shown by the examples given in the calculation of F, so that T_{trans} will be a function of $\dot{\varepsilon}$. This dependence will be most marked for samples of the lowest molecular weight.

Fig. 5 shows that, just as with the low l_e polymers a region of deformation may comprise both voiding and shear deformation. In this case, for MPS 1150 at 70° C, the inner region shows a fibrillated structure whereas the outside exhibits only shear deformation. Such composite effects have not been observed for MPS 100 or MPS 350, presumably because, under the rates of strain used in these experiments, disentanglement can always occur fast enough. Under sufficiently high strain rates,

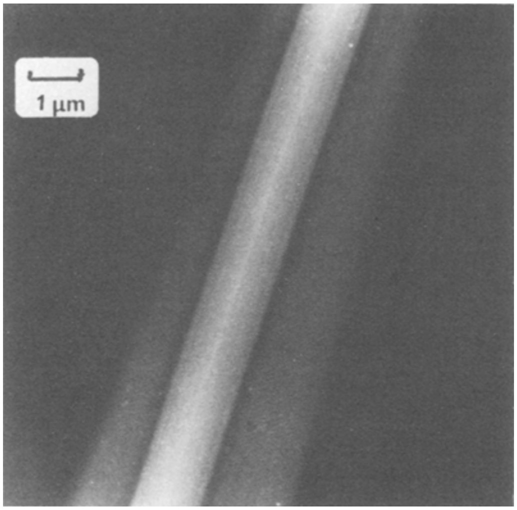


Figure 5 MPS 1150 strained at 70° C. The inner region shows fibrillation, while the outer region exhibits shear deformation only.

however, it should be possible to suppress T_{trans} to the point where shear deformation may be observed even in MPS 100.

In order to make these statements more quantitative, it is necessary to have data for disentanglement rates, i.e. when can the chains move fast enough for the craze interface to move at the observed rates. For a glassy polymer under zero stress, the equilibrium diffusion of the chains by reptation is essentially frozen out; the motion of the chains during crazing can only occur because of the state of stress. No models to describe the ensuing motion currently exist. One speculative way to consider the process by which disentanglement may occur is to utilize the Doi–Edwards model for the melt [8]. Following the application of a step strain, relaxation will occur. In the melt three stages can be recognized: first a local reequilibration without slippage; then retraction of the chain, during which some disentanglement may occur; and finally, recovery of the random coil configuration under Brownian motion. For the glass it may be appropriate to consider the first two stages only, so that disentanglement occurs but the chains remained extended.

Whatever the mechanism, it seems likely that as with reptation in the melt, the mobility (or associated apparent diffusion constant) will be strongly molecular weight dependent, e.g. as M^{-2} as in the case for the diffusion constant for reptation. In this case, a reduction by a factor of 100 arises between MPS 100 and MPS 1150. For a chain of molecular weight 100 000 to disentangle completely during the time available for fibrillation at the craze matrix interface (typically ~ 10 sec), an apparent diffusion constant, D_{app}, of the order of $10^{-11}\,\text{cm}^2\,\text{sec}^{-1}$ is required. This is comparable with values of D measured in the melt. The corresponding figure for chains of molecular weight 1×10^{-6} would need to be $D_{\text{app}} \sim 10^{-9}\,\text{cm}^2\,\text{sec}^{-1}$, a very high figure indeed. Thus, whereas it seems reasonable that the time available is sufficient to permit chains in MPS 100 to disentangle completely, this is not the case for MPS 1150, in line with the experimental observations.

In practice, it may be expected that some degree of scission will always occur, which in turn will reduce the effective molecular weight. A single scission event at the midpoint of a chain of molecular weight 1×10^5 will leave the two remaining chains barely entangled; this is not the case for chains of molecular weight 1×10^6. Thus the occurrence of scission will have a much greater effect on subsequent disentanglement rates for low molecular weight samples than for high. However, only under conditions of extremely low stresses and strain rates is disentanglement likely to be the sole means of network modification for any of the polymers studied here.

It is also of interest to consider how scission and disentanglement separately effect the extension ratio of the craze. For MPS 515 and MPS 1150 above 60° C, a range of craze-types may be observed in any given grid square, and the extension ratio seems to vary significantly from one craze to another. In particular, the short cigar-like crazes with shear at their tips seem to have values of λ close to the room temperature value, whereas the high aspect ratio crazes have values of λ that are much higher. It seems probable that the former grow under conditions of locally high stress/strain rate favouring scission, but as these fall, shear yielding intervenes giving rise to a shear blunted tip. The high aspect ratio crazes, on the other hand, may grow more slowly, via disentanglement, so that T_{trans} is raised to the point such that the condition for yield is never reached. However, it is not clear *a priori* what variations may be expected as scission gives way to disentanglement; both can give rise to the "geometrically

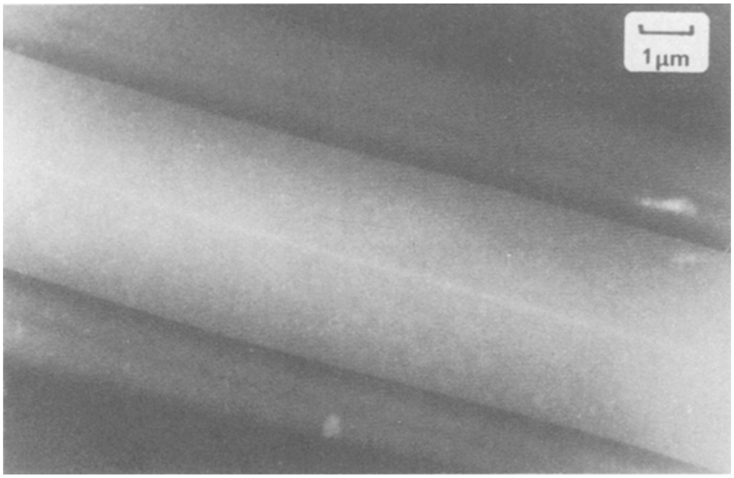


Figure 6 MPS 515 strained 6% within 30 min of preparation (i.e. unaged specimen).

necessary entanglement loss" [9] required for fibril formation.

Furthermore, as indicated above, the act of scission may itself favour subsequent disentanglement, and the process will also be enhanced for molecules lying near a fibril surface by the removal of "tube constraints" [8, 22]. The enhanced mobility of molecules in craze fibrils is also indicated by some recent experiments of Kramer and co-workers [23]. Thus the range of conditions which may promote disentanglement at elevated temperature indicate that a single value of λ_{craze} cannot be assigned to all crazes in a specimen. The experimentally measured value will depend on the precise conditions of stress and strain rate under which that particular craze grew.

Having demonstrated that disentanglement can be an important parameter for crazes grown at elevated temperature in air in PS, it is of interest to consider the implication of the result for other systems. At room temperature, PS represents the opposite end of the spectrum from PS in terms of deformation, exhibiting only shear deformation under the plane stress conditions of the thin films suitable for TEM. However, crazing is promoted at elevated temperatures [4, 24]. In thick samples, where shear is suppressed, it has been shown [25] that the craze stress is strongly molecular weight dependent even below room temperature. This result suggests that disentanglement may always be important for PC. Two factors are of importance in this context: firstly, the energy of scission $d\nu_E U/4$ required for crazing to occur via scission alone is large in this densely entangled polymer, and secondly, typical PC chain lengths are much shorter ($M_w \sim 30\,000$ for commercial grades) than for PS. Although the increased entanglement density over PS may substantially reduce the freedom of the chain to move, the distances over which movement must occur are also greatly reduced. Further work is in progress on this polymer. However, it already seems clear that the corresponding drawing to Fig. 4 must contain an exchange of the positions of the two curves, again with a transition temperature which will be molecular weight dependent. In this case, one would predict that the low molecular weight material should possess a lower transition temperature (shear-to-crazing) than the high molecular weight.

It is also known that various craze parameters are molecular weight dependent in polymethylmethacrylate (PMMA) [26, 27]. Of particular relevance to the present work is the recent observation that high molecular weight PMMA may exhibit substantial ductility at room temperature [23], under conditions of low strain rates. In the present context, the inference is that the transition temperature (crazing to shear) is suppressed to room temperature for sufficiently long chains.

Finally, it is worth considering circumstances under which extensive shear could be observed in PS at room temperature. One possibility is to attempt straining at very low rates which, as mentioned above, has proved feasible for PMMA. A second alternative is to use "unaged" specimens. For materials such as PC, annealing just below T_g or ageing for long times at room temperature are known to lead to an increase in the yield stress [28] and thereby an enhanced propensity for crazing relative to shear deformation. PS is not usually considered to be susceptible to ageing. However, by straining a specimen of MPS 515 at room temperature within 0.5 h of preparing the thin film (but after drying in a vacuum desiccator to ensure removal of solvent), it has proved possible to generate deformation zones (Fig. 6), although containing a fibrillated region at their centre. Measurements of the extension ratio of the DZ yields a value of 2.5 (compared with $\lambda = 4$ at the centre) in good agreement with the predictions of Kramer [9].

5. Conclusions

Whereas at room temperature for PS, scission is the dominant mechanism for the modification of the entanglement network required for crazing, as the temperature is raised, disentanglement processes can become increasingly important. Since the rate at which disentanglement can occur is strongly molecular weight dependent, the stress for crazing itself becomes molecular weight dependent being greatest for high molecular weight materials. As a result, the temperature at which the transition from crazing to shear occurs depends on molecular weight. T_{trans} is lower for long chains than for short. Indeed, for MPS 100 shear processes have never been observed, whereas for MPS 1150, crazes do not form in thin films at temperatures of 80° C or above, all deformation occurring by shear.

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