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The effect of temperature on the transition from crazing to shear deformation in crosslinked polystyrene

LARRY L. BERGER, EDWARD J. KRAMER
Department of Materials Science and Engineering and the Materials Science Center, Cornell University, Ithaca, New York 14853, USA

Thin films ($\approx 0.7\,\mu$m thick) of polystyrene (PS) are bonded to copper grids and crosslinked by exposure to electron irradiation. By controlling the exposure time it is possible to produce samples of PS having a range of network strand densities ν (entangled and crosslinked). After physical ageing at 75° C for 10 to 12 h the PS films are then strained in tension at various temperatures. Transmission electron microscopy is used to characterize the ensuing deformation as well as measure the local extension ratio λ in either a craze or a deformation zone. A transition from crazing to shear deformation is observed to occur with increasing values of ν. At a slow strain rate of $4.1 \times 10^{-6}\,\text{sec}^{-1}$ and a temperature of 23° C this transition in the aged PS occurs at $\nu \approx (10 \text{ to } 14) \times 10^{25}\,\text{strands m}^{-3}$, whereas at the same strain rate and 90° C the transition occurs at $\nu \approx (5.8 \text{ to } 8) \times 10^{25}\,\text{strands m}^{-3}$. The transition from crazing to shear deformation with increasing ν may be rationalized by considering the extra energy required to break more main-chain polymer bonds to form the craze fibril surfaces in the high-ν networks. As the temperature is increased the yield stress σ_y (which is assumed to be independent of ν) decreases almost linearly to zero as T_g is approached. On the other hand the crazing stress may be approximated by $S_c \propto [\sigma_y(T)\nu^{1/2}]^{1/2}$. Thus at higher temperatures the transition from crazing to shear deformation is expected to occur at lower values of ν as observed.

1. Introduction

It now seems clear that the molecular entanglements in the glass play a significant role in determining the mechanisms of plastic deformation for thermoplastic homopolymers [1–6], copolymers [1, 5, 6] and polymer blends [7–9]. For example, highly entangled polymers have been shown to deform primarily by shear deformation whereas less heavily entangled polymers deform primarily by crazing.

The importance of the network strand density ν, where a strand is defined as a portion of a chain bounded by entanglement (or crosslinked points), in determining the mechanism of plastic deformation was further demonstrated by experiments conducted in crosslinked polystyrene PS [10]. These show that PS exhibits a transition from crazing to shear deformation with increasing strand density. In these experiments PS having an intrinsic (entangled) strand density ν_e (which may be determined from melt elasticity measurements just above T_g) was crosslinked with electron irradiation, thus introducing ν_x crosslinks into the polymer glass. The total strand density ν of the polymer is then given by the sum of the intrinsic entanglement density and the crosslink density, i.e.

$$\nu = \nu_e + \nu_x \tag{1}$$

The transition from crazing to shear deformation in PS was observed to occur over the same range of ν where a similar transition was observed in a host of uncrosslinked homopolymers and copolymers [5, 6].

This transition from crazing to shear deformation with increasing ν was rationalized by considering the increase in stress for crazing relative to the stress for shear deformation. During crazing, bulk polymer is converted into small, highly oriented craze fibrils in the active zone, a thin fluid-like region at the craze–bulk interface, via the surface drawing mechanism [11]. In forming the fibril surfaces within a craze a certain fraction of strands must be broken [6, 12] since in crosslinked polymers chain disentanglement cannot occur. The decreased propensity for crazing with increasing ν results from the larger number of strands that must be broken to form a unit area of fibril surface in the molecular networks having higher strand densities.

In this paper we investigate the temperature dependence of the transition strand density ν_t, i.e. the strand density at which the transition from crazing to shear deformation occurs in PS. It is known that the yield stress σ_y decreases almost linearly to zero as T approaches T_g [13, 14]. Since the microscopic events during yielding are believed to involve chain motions over a length scale which is smaller than the length of a strand, increasing ν through crosslinking should have little effect on σ_y, at least at small ν_x. [10, 15–17]. On the other hand the crazing stress S_c may be

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approximated by [5, 6]

$$S_c \propto [\sigma_y(T)(v^{1/2})/h]^{1/2} \qquad (2)$$

where h is the thickness of the strain-softened layer at the craze–bulk interface. For crosslinked PS both h and v are assumed to be independent of temperature. Therefore Equation 2 reveals that S_c should decrease with increasing temperature as the square root of σ_y. By equating S_c and σ_y, v_t may be shown to decrease with T as $[\sigma_y(T)]^{1/2}$. Thus the value of v at which the transition from crazing to shear deformation occurs may be expected to decrease with increasing temperature. We show that this prediction is borne out in the present study.

2. Experimental procedure

A nearly monodisperse PS having a molecular weight $M = 1\,800\,00$ and a polydispersity index $M_w/M_n \leqslant 1.1$ was purchased from the Pressure Chemical Co. and was used throughout this study. Uniform thin films of PS ($\approx 0.7\,\mu$m thick) were produced by drawing glass slides at a constant rate from a solution of PS in methylene chloride. The films were floated off the slides on to the surface of a water bath and picked up on a well-annealed copper grid, the grid bars of which were previously coated with the same polymer [18]. Bonding of the film to the grid was achieved by briefly exposing the film to the vapour of the solvent. Using the intense focused electron beam of a Jeol 733 electron microprobe, starter cracks 100 μm long × 20 μm wide were introduced into the centre of the grid squares [3]. These starter cracks, whose long axes lie normal to the direction of the subsequently applied strain, provide controlled sites for either craze or deformation zone nucleation and growth. It should be noted that this procedure differs slightly from that used by Henkee and Kramer [10] and others [1, 2, 4]. In those experiments dust particles in the film (and not probe holes) were used to nucleate crazes and deformation zones. The presence of the probe holes may be expected to increase the local stress in the film, and thus increase the value of v at which the transition from crazing (which is favoured at higher stresses) to shear deformation (which is favoured at lower stresses) is observed.

The specimens were then exposed to electron irradiation using the electron microprobe operating at a beam current of 1.0×10^{-7} A and an accelerating voltage of 40 kV [10]. The electron beam was defocused to a diameter of 0.4 mm, and rastered across the sample to expose an area of 8.1 mm^2. Each scan had 1000 lines and each line required 0.5 msec to complete. Thus the entire 8.1 mm^2 was irradiated twice a second.

The gel point of the polymer was determined under the identical microprobe irradiation conditions for the 1 800 000 molecular weight PS and another monodisperse PS having a molecular weight of 390 000 and $M_w/M_n \leqslant 1.1$. The gel points determined for these two molecular weights were 10 to 12 sec and 50 to 55 sec, respectively. The crosslinking rate under these conditions [10] has been shown to be linear in time, and thus the ratio of the gel times for these two samples are expected to be given by the inverse ratio of their molecular weights as observed. The gel times determined by using these irradiation conditions are in reasonable agreement with the previously determined gel times for PS under the same conditions [10]. From the crosslinking rate the density of crosslinked strands v_x can be determined for any irradiation time.

One day after irradiation the grids were mounted in a strain frame coupled to a variable-speed motor drive and the strain rig was placed in a controlled-temperature chamber. While in the chamber the samples were physically aged at 75° C for 10 to 12 h (so that thermal equilibrium could be obtained) before straining at the desired temperature. The sample temperature was measured by placing a thermocouple in the centre of one of the grid squares. All the samples were strained at a rate of $4.1 \times 10^{-6}\,\mathrm{sec}^{-1}$ up to a tensile strain of 0.02 to 0.04. Since the copper mesh is deformed plastically during this procedure the strain in the polymer film is maintained even after the grid is removed from the strain rig. Individual grid squares were then cut from the deformed grid and immediately examined in a Jeol 200CX transmission electron microscope operating at 200 kV.

To characterize the extension ratio λ in either a craze or deformation zone (DZ) the method developed by Lauterwasser [18] was used. Using an optical microdensitometer, the optical densities of the locally deformed region (ϕ_c), the undeformed PS film (ϕ_f) and the starter crack (ϕ_h) were measured. For constant-volume plastic deformation the extension ratio is given by

$$\lambda = \left[1 - \frac{\ln(\phi_c/\phi_f)}{\ln(\phi_h/\phi_f)}\right]^{-1} \qquad (3)$$

3. Results

TEM micrographs of the types of plastic deformation observed in PS samples deformed in tension at room temperature are shown in Fig. 1. These films were crosslinked to total strand densities v of 2.0, 3.0, 4.0 and 5.0 times the entangled strand density v_e and were strained at a slow rate of $4.1 \times 10^{6}\,\mathrm{sec}^{-1}$. These micrographs reveal that for $v < 3\,v_e$ crazing is the only mechanism of deformation observed; for $3\,v_e \leqslant v \leqslant 4\,v_e$ both crazing and shear deformation zones are observed, and for $v \geqslant 5\,v_e$ only DZs are observed. Shown in Fig. 2 are TEM micrographs of PS samples crosslinked to strand densities of 1.25, 2.0, 2.25 and $3.0\,v_e$ and then deformed at the same rate of $4.1 \times 10^{-6}\,\mathrm{sec}^{-1}$ at $T = 90°$C. At this temperature only crazes were observed to form for $v \leqslant 1.25\,v_e$, and as v was increased to $2.0\,v_e$ both crazes and DZs formed. As v was increased above $2.25\,v_e$ only shear deformation zones were observed. It appears that the strand density at which shear deformation is first observed in PS decreases with increasing temperature.

Fig. 3 is a schematic map showing the types of plastic deformation observed in the PS films as a function of the total strand density v for samples deformed at temperatures of 23, 60, 75 and 90° C. The data show that the strand density at which shear deformation is first observed is roughly constant with temperature up to 75° C and then decreases rapidly as

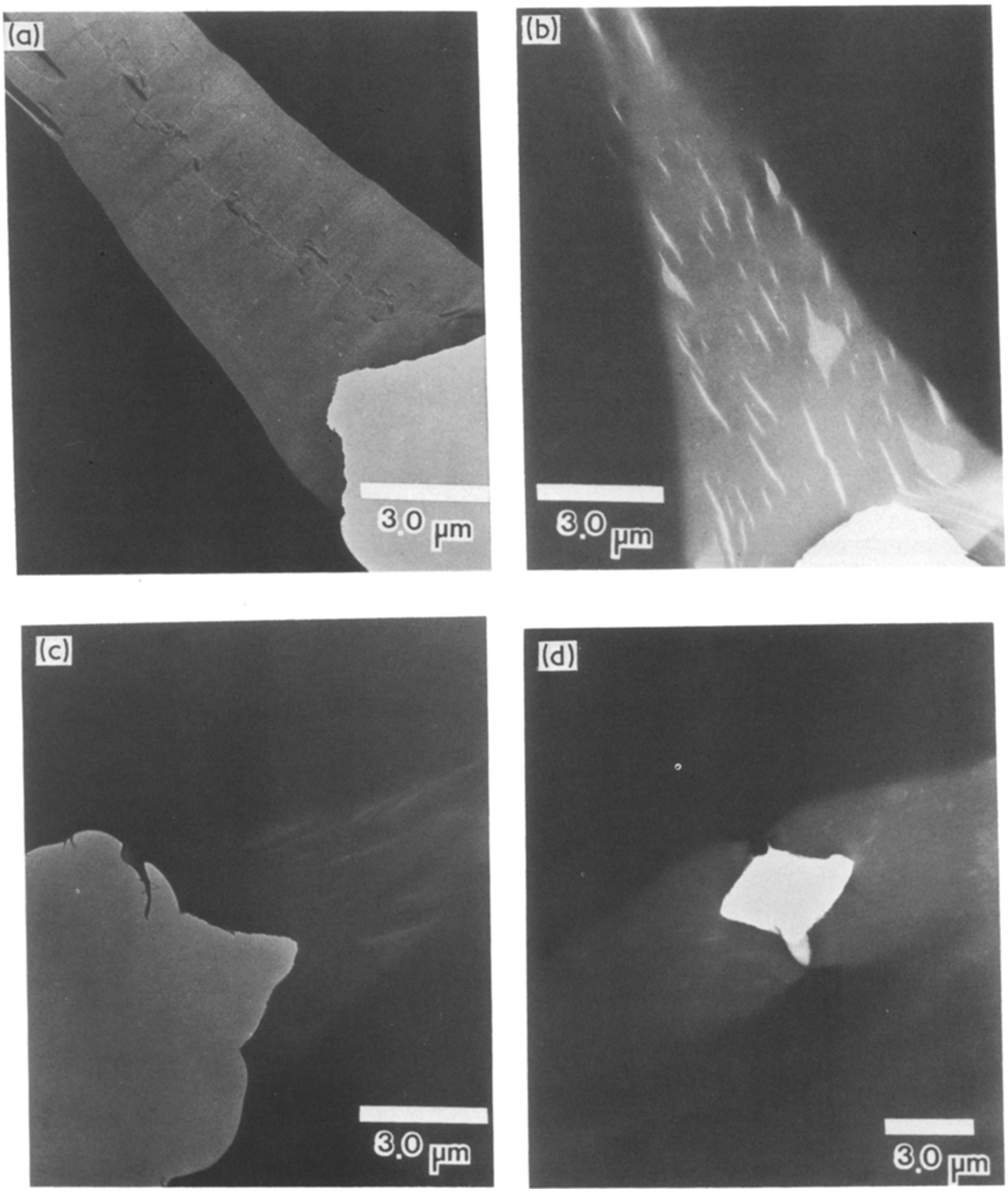

Figure 1 TEM micrographs of the local plastic deformation observed in crosslinked PS films having a strand density of (a) 2.0 ν_e (crazes only), (b) 3.0 ν_e (crazes plus DZs), (c) 4.0 ν_e (crazes plus DZs), (d) 5.0 ν_e (DZs only). All these samples were deformed in tension at a rate of 4.1×10^{-6} sec^{-1} at room temperature.

T is increased to 90° C. A solid line is drawn along the boundary between the unfilled and the half-filled symbols that represents the strand density at which competition between crazing and shear deformation is first observed at each temperature. Similarly another solid line is drawn between the half-filled and filled symbols which represents the lowest value of ν at which shear deformation in the exclusive mode of plastic deformation observed at each temperature.

A plot of the extension ratio in the craze as a function of the temperature at which the samples were deformed is shown in Fig. 4. The solid curves drawn through the data are for samples having a strand density of 1.0, 1.25, 2.0 and 3.0 times ν_e. For the uncrosslinked samples which correspond to a strand density of 1.0 ν_e the temperature dependence of the extension ratio in the craze has been previously measured [19]. In that case it was observed that λ was constant at a value of 4 from room temperature up to 70° C. At higher temperatures λ sharply increased as T approached T_g. In the crosslinked samples a different behaviour is observed. At room temperature the value of the extension ratio in the crazes grown in the crosslinked samples was observed to decrease with increasing strand density to a value of 3.4, 2.8 and 2.2 for samples having ν equal to 1.25 ν_e, 2.0 ν_e and 3.0 ν_e, respectively. Furthermore, in marked contrast to the strongly temperature-dependent λ of crazes in the uncrosslinked samples, in crosslinked samples the value of λ was observed to remain roughly constant with increasing temperature up to 90° C.

A plot of the extension ratio in the DZ (λ_{DZ}) as a function of temperature for samples having strand densities equal to 3.0, 4.0 and 5.0 times ν_e and strained

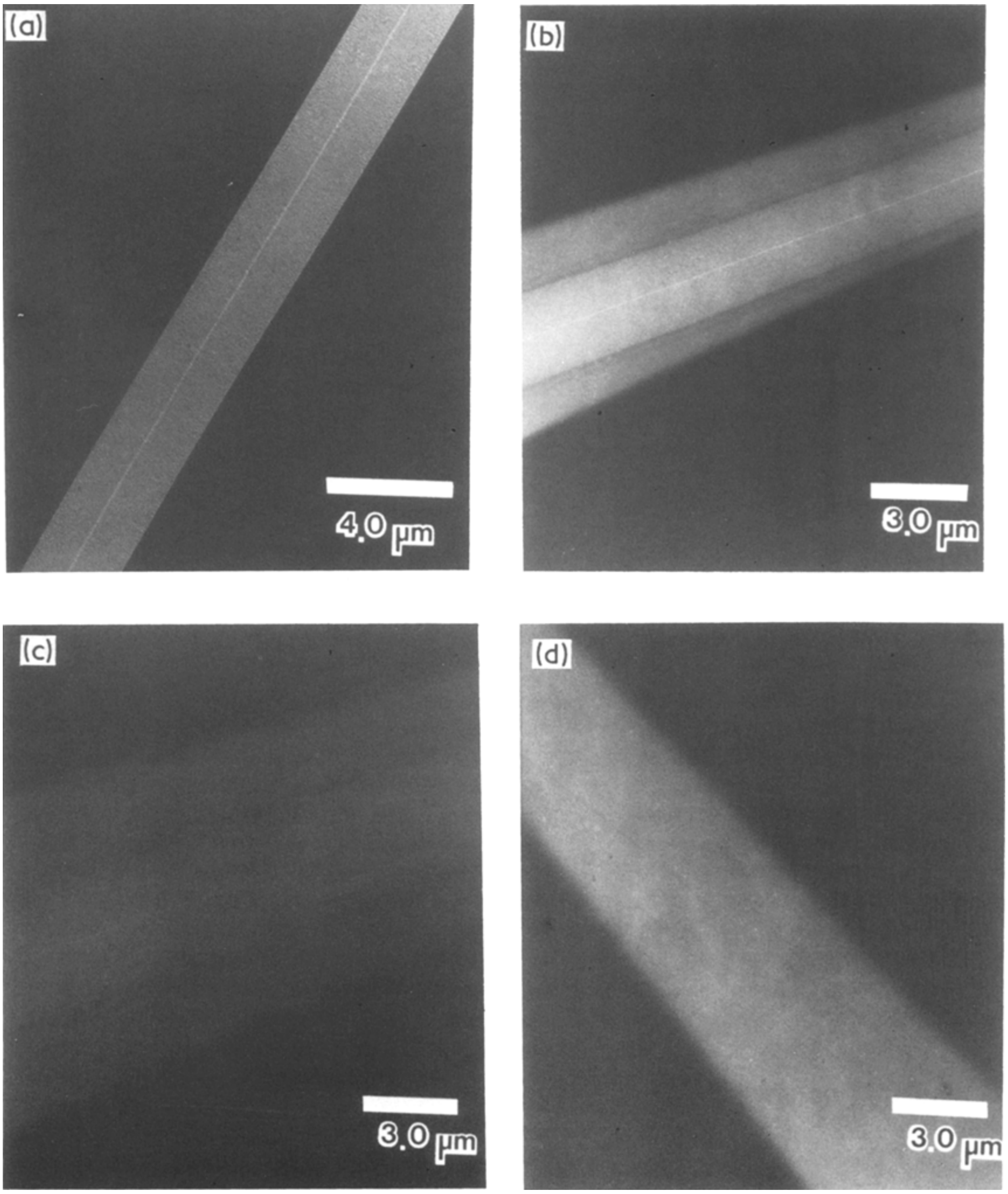

Figure 2 TEM micrographs of the plastic deformation observed in crosslinked PS films having a strand density of (a) 1.25 ν_e (crazes only), (b) 2.0 ν_e (crazes plus DZs), (c) 2.25 ν_e (DZs only), (d) 3.0 ν_e (DZs only). All these samples were deformed in tension at a rate of $4.1 \times 10^{-6}\,\text{sec}^{-1}$ at $T = 90°$C.

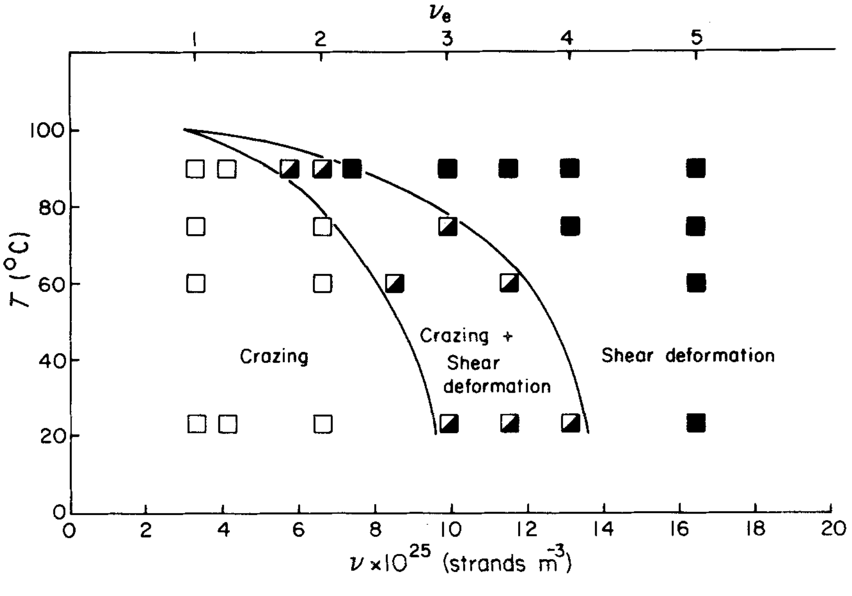

Figure 3 A summary of the dominant mode of plastic deformation observed in crosslinked PS films as a function of the strand density ν and the temperature at which the deformation was carried out: (□) crazing only, (◪) crazing plus shear, (■) shear deformation only. All samples were physically aged at 75°C for 10 to 12 h.

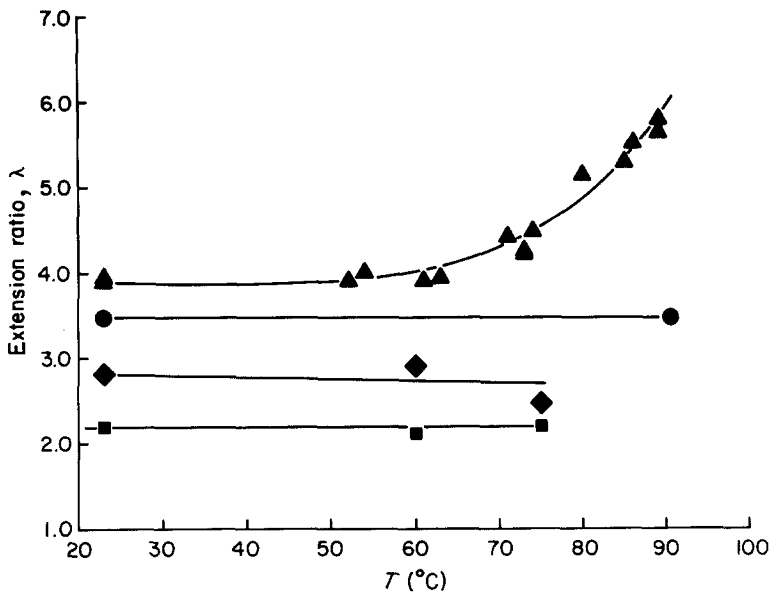

Figure 4 A plot of the extension ratio in the craze as a function of temperature for PS samples strained at a rate of 4.1 × 10^{-6} sec^{-1} for samples having the following values of v: (▲) 1.0 v_e, (●) 1.25 v_e, (◆) 2.0 v_e, (■) 3.0 v_e.

at a rate of 4.1 × 10^{-6} sec^{-1} is shown in Fig. 5. It appears that λ_{DZ} decreases with increasing v. The data also show that for a given strand density λ_{DZ} decreases modestly with increasing temperature.

TEM micrographs of two deformation zones that were grown from crack tips in samples having a strand density of 5.0 v_e at temperatures of 23 and 90° C are shown in Fig. 6. Both of these samples were strained up to a strain $\varepsilon = 0.025$ at a rate of 4.1 × 10^{-6} sec^{-1}. These micrographs reveal that at a given value of v there is a greater degree of strain localization in the DZ grown at the lower temperature. The difference in the strain localization between these two DZs can be made more quantitative by comparing profiles of the extension ratio across the DZ; the strain ε in the DZ is given by $\varepsilon \approx \ln \lambda$. The profiles may be determined from optical microdensitometry of the TEM plates and are shown in Fig. 7. This comparison illustrates the relatively "sharp" shoulder of the DZ grown at 23° C and the diffuse shoulder of the DZ grown at 90° C.

4. Discussion

Fig. 3 clearly shows that the value of v at which shear deformation is first observed in PS decreases slowly from room temperature up to 75° C and then decreases rapidly as T is increased to 90° C. This result may be explained by examining the temperature dependence of both the crazing stress S_c and the yield stress σ_y. The yield stress is known to decrease almost linearly to zero as T approaches T_g [13, 14]. The yielding of a polymer glass is believed to occur via a thermally activated microscopic rearrangement of polymer chains [20]. This cooperative rearrangement may occur by simple bond conformational changes along several polymer backbones. Since the microscopic events during yielding are expected to occur on a length scale which is smaller than the contour length l of chain between entanglement (or crosslinked) points, increasing v through crosslinking should have little effect on σ_y at small values of v_x. On the other hand the crazing stress* may be written as [5, 6]

$$S_c \propto (\sigma_y \Gamma / h)^{1/2} \qquad (4)$$

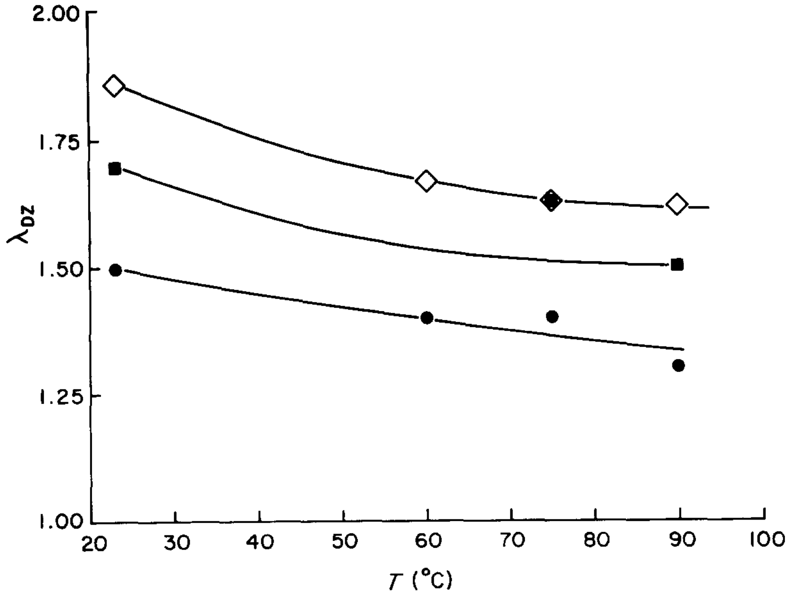

Figure 5 A plot of the extension ratio in the deformation zone as a function of temperature for PS samples strained at a rate of 4.1 × 10^{-6} sec^{-1} for samples having the following values of v: (◇) 3.0 v_e, (■) 4.0 v_e, (●) 5.0 v_e.

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* S_c actually corresponds to the stress required for craze widening via the surface drawing mechanism. The stress to propagate the craze tip (S_t) is higher than S_c and may be written as $S_t \propto \Gamma + (\sigma_y \Gamma / h)^{1/2}$ (see Kramer [5, 6]).

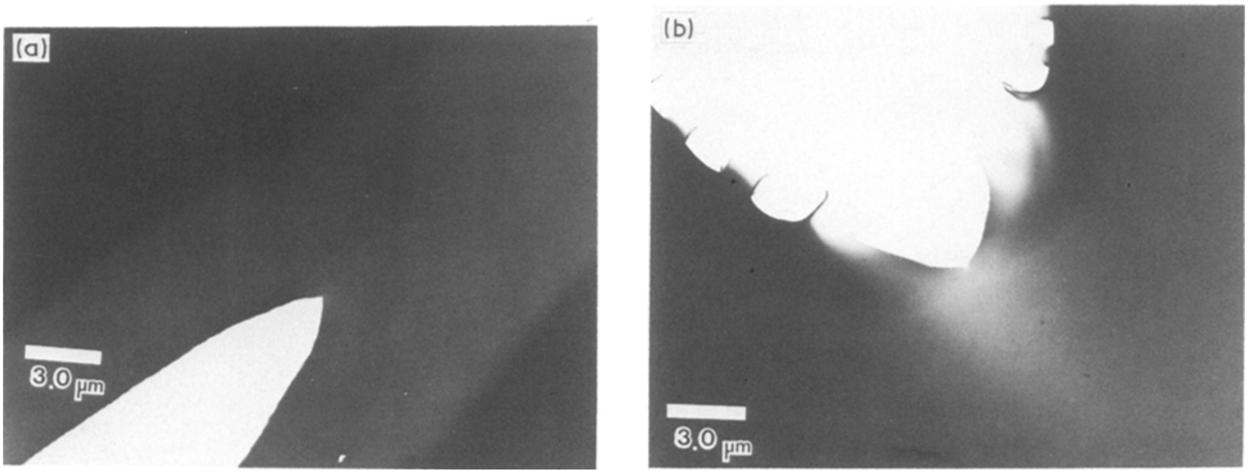

Figure 6 TEM micrographs of deformation zones grown from crack tips in crosslinked PS samples having a strand density of 5.0 ν_e. The samples were strained at a temperature of (a) 23° C and (b) 90° C.

where Γ is the total craze surface energy which in turn may be written as

$$\Gamma = \gamma_s + \tfrac{1}{4} d\nu U_b \qquad (5)$$

where γ_s is the van der Waals intermolecular separation energy, U_b is the energy to break a single covalent bond along the polymer backbone, d is the entanglement mesh size and ν is the total strand density. Since chain disentanglement cannot occur in crosslinked polymers, polymer chains must be broken to create fibril surfaces. Using geometric statistics the number of chains that must break per unit area is $\tfrac{1}{2} d\nu$ [21]. The product $d\nu$ is proportional to $\nu^{1/2}$; therefore increasing ν through crosslinking increases S_c. Now Γ (or ν) is expected to remain constant with increasing temperature (in crosslinked polymers) and thus from Equation 2 one may predict that S_c should be less temperature-dependent than σ_y over the entire temperature range. The temperature dependence of the yield stress at a given strain rate is shown schematically in Fig. 8. Also indicated on this plot are two curves for the crazing stress S_c corresponding to two values of the strand density ν where $\nu_2 > \nu_1$. This figure clearly shows that as ν is increased the curves for the crazing stress and the yield stress intersect at lower temperatures.

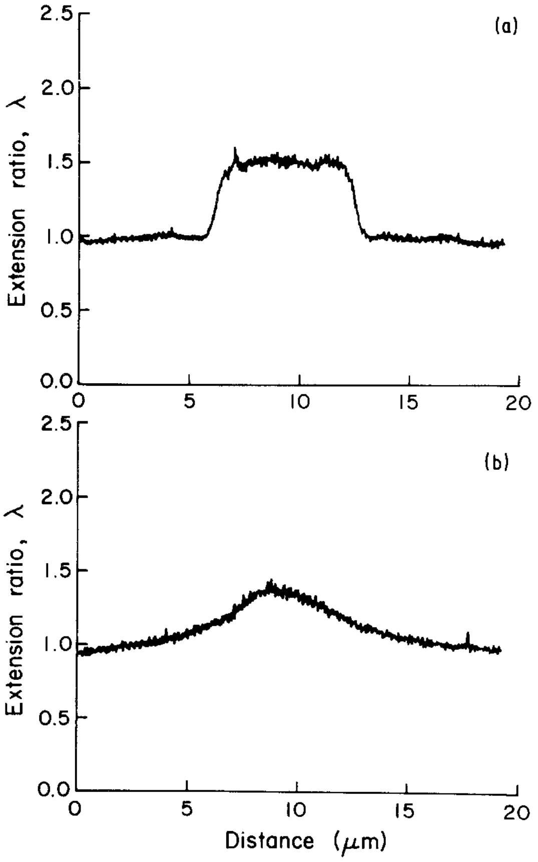

Figure 7 A plot of extension ratio across the DZ for crosslinked PS samples having a strand density of 5.0 ν_e as shown in (a) Fig. 6a and (b) Fig. 6b. The relatively sharp shoulder of the DZ grown at 23° C is evident as compared to the diffuse shoulder in the DZ grown at 90° C.

Using Equation 2 and the previously measured temperature dependence of σ_y in PS [14] one may also predict the temperature dependence of the transition strand density ν_t. This prediction, which assumes that h is independent of temperature, is displayed in Fig. 9. Two curves are shown which denote the boundaries between crazing only and crazing plus shear deformation, and crazing plus shear deformation and shear deformation only. It should be pointed out that these curves were forced to fit the experimentally determined values of ν_t at room temperature by choosing the appropriate constant of proportionality in Equation 2. A comparison of Figs 3 and 9 reveals that Equation 2 only qualitatively predicts the correct temperature dependence of ν_t.

The failure of Equation 2 to quantitatively predict the temperature dependence of ν_t may result from assuming h is constant with T. Clearly this assumption is an oversimplification. In fact recent TEM experiments in uncrosslinked PS suggest that the size of h is an increasing function of temperature [22]. It can be seen from Equation 2 that if h increases with temperature S_c decreases with increasing T more rapidly than $(\sigma_y)^{1/2}$. This increase in h will shift ν_t to higher values of ν (at the higher temperatures) and may explain the discrepancy between the predicted and experimental temperature dependence of ν_t. Further experiments to accurately measure the size of h as a function of T, for example by high-resolution TEM on crazes in gold-decorated thin films [22, 23], are needed to clarify this point.

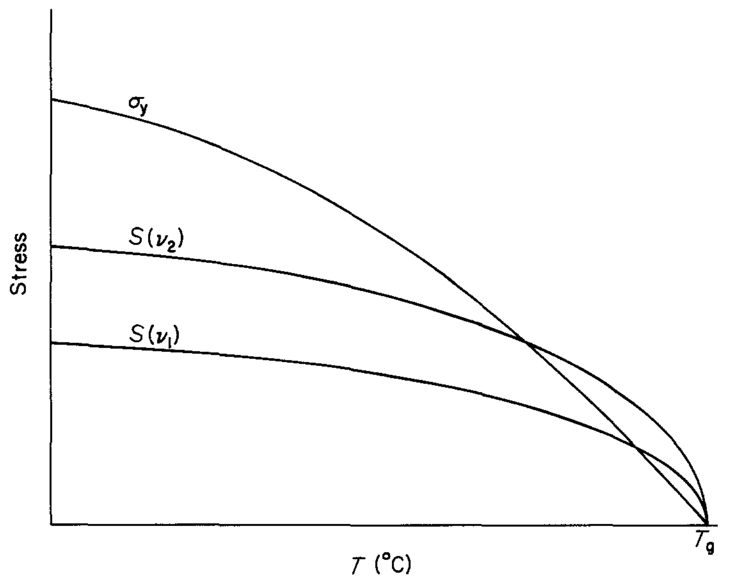

Figure 8 The predicted temperature dependence of the yield stress σ_y and the crazing stress S_c for two values of ν where $\nu_2 > \nu_1$.

The data in Fig. 4 show that the value of λ in the crazes grown at room temperature decreases with increasing strand density. This decrease in λ with increasing ν has been previously observed in a host of homopolymers, copolymers and crosslinked PS and was explained using a simple network model [5, 6, 10]. In an idealized network in which neither chain scission nor chain disentanglement is allowed one may define a maximum extension ratio λ_{max} for a single strand bound between two entanglement (or crosslinked) points.[†] In a real network one may expect the strain-hardening in the craze fibrils (which controls λ) to be correlated with λ_{max}. Henkee and Kramer [10] have shown that such a correlation exists in crosslinked PS (i.e. $\lambda - 1 \approx 0.9(\lambda_{max} - 1)$). The extension ratios determined for the crosslinked samples in Fig. 4 are in good agreement with the values measured by Henkee and Kramer.

The value of λ in crazes formed in the crosslinked samples was observed to remain roughly constant with increasing temperature. This result is in sharp contrast to the temperature dependence of λ for crazes in the uncrosslinked network [19]. For the uncrosslinked samples λ ($= 4$) was observed to remain constant with increasing temperature up to 70° C and then to increase sharply as T approached T_g. Previously we attributed this increase in λ at high temperatures (and slow strain rates) to chain disentanglement during craze formation. In crosslinked samples chain disentanglement cannot occur and thus λ is expected to remain constant with increasing temperature as observed.

The data in Fig. 5 show that λ_{DZ} decreases with increasing strand density. Here too if the simple network model is correct one may expect that the extension ratio in the DZ should correlate with λ_{max}. From the data in Fig. 5 one may determine that $\lambda_{DZ} - 1 \approx C(\lambda_{max} - 1)$ where $C = 0.6$ at room temperature and decreases to $C = 0.45$ at 90° C.

We observed that at higher temperatures the strain within the DZs becomes less localized (Fig. 7). It is interesting to note that a similar decrease in strain localization with increasing temperature has been previously observed in bulk PS samples: Bowden and Raha [24] observed that PS deformed in compression at temperatures below 65° C exhibited a narrow zone of plastic deformation (called microbands), whereas at temperatures above 70° C only diffuse shear zones were formed.

The observed decrease in λ_{DZ} with increasing temperature (C decreases from 0.6 at room temperature to 0.45 at 90° C) may be an artefact that results from the decreased strain localization at the higher temperatures. The DZs grown under these conditions are more diffuse, and in order to quantitatively determine λ_{DZ} using a TEM only relatively narrow DZs ($\sim 10\,\mu$m in width) may be examined. It is possible that in the centre of these narrow DZs the polymer has not been fully extended to its "natural" extension ratio. As can be seen in Fig. 7b, even for the DZs as wide as $10\,\mu$m there is no region in the centre of the DZ over which the extension ratio is constant.

It is also worth noting the importance of physically ageing the samples prior to straining. Physical ageing is known [25–27] to increase σ_y relative to S_c and thus it predisposes the polymer to crazing. This behaviour has been previously observed [1] in polymers having an intermediate strand density (i.e. poly(styrene–acrylonitrile) and poly(phenylene oxide)) that were physically aged and then deformed at room temperature. Similarly, physical ageing may be expected to shift the transition from crazing to shear deformation in PS to higher values of ν. Henkee and Kramer [10] have observed that crosslinked (but unaged) PS deformed at room temperature exhibited a transition from crazing to shear deformation at a strand density of (4 to 8) × 10^{25} strands m^{-3}, whereas in this study the transition was observed to occur at (10 to 14) ×

[†] The value of λ_{max} may be determined from $\lambda_{max} = l/d$ where d is the entanglement mesh size which can be calculated from the Porod–Kratky model of a worm-like chain, i.e. $d = (2al\{1 - (a/l)[1 - \exp(-l/a)]\})^{1/2}$ where a is the persistence length of the chain. For long chains d is asymptotically given by $d = k\langle M_e\rangle^{1/2}$ where M_e is the molecular weight of the chain between entanglement points and k may be determined from the molecular coil dimensions in a theta solvent.

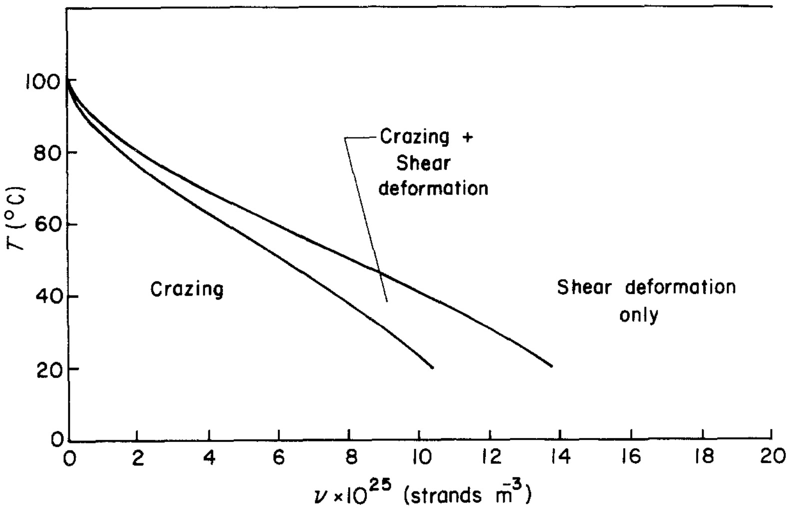

Figure 9 Predicted temperature dependence of the transition strand density (assuming h is constant with temperature). These curves were drawn through the experimentally determined ν_t at room temperature.

10^{25} strands m^{-3}. The higher values of ν required to produce shear deformation in the present study are believed to result in part from the prior physical ageing treatment.‡

5. Conclusions

1. Physically aged PS films crosslinked with electron irradiation exhibit a transition from crazing to shear deformation at a strand density ν of (10 to 14) × 10^{25} strands m^{-3} at room temperature. At higher temperatures this transition occurs at lower values of ν.

2. The extension ratio λ in crazes grown in crosslinked PS decreases with increasing ν. These values of λ are roughly constant with increasing temperature T in contrast to the rapidly increasing $\lambda(T)$ for samples of uncrosslinked PS.

3. The extension ratio in the deformation zones (λ_{DZ}) in crosslinked PS also decreases with increasing ν. Moreover, at a given value of ν, λ_{DZ} decreases modestly with increasing T. TEM reveals that the DZs formed at higher temperatures are more diffuse and have less strain localization than the DZs formed at room temperature.

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‡ It may also be expected that the presence of the probe holes in the film will raise the local stress and shift the transition from crazing to shear deformation to higher values of ν.