Chain Disentanglement during High-Temperature Crazing of Polystyrene†

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ABSTRACT: The formation of small, highly oriented craze fibrils requires a loss of strands in the entanglement network that approaches 50%. At a temperature T well below T_g this loss can occur only by main-chain scission of an entangled strand; consequently the extension ratio λ in the craze is constant with molecular weight M or strain rate $\dot{\epsilon}$. As T approaches T_g chain disentanglement is possible, giving rise to a M and $\dot{\epsilon}$ dependence of λ at sufficiently high temperatures. For polystyrene (PS) with $M = 1\,800\,000$ strained at a high strain rate of $\sim 10^{-2}$ s^{-1} λ is constant up to 90 °C. However, at a slow strain rate of 4.1×10^{-6} s^{-1} λ is constant only up to 70 °C and then sharply increases as T_g is approached. For lower molecular weights this increase begins at lower temperatures or higher strain rates. Disentanglement times τ_d are estimated by measuring the increase in craze interface velocity v_i at elevated T (75 and 90 °C) needed to decrease λ to a prescribed value which is above the natural extension ratio ($\lambda = 4$) at low T. Even though these ambient T's are well below T_g, τ_d scales as $M^{2.9\pm0.5}$, in surprising agreement with the reptation mechanism for disentanglement.

Introduction

The use of polymer glasses for structural applications is limited by their tendency to fail in a brittle manner at small macroscopic strains. In many polymers this failure starts by the formation and breakdown in regions of localized deformation called crazes.[1-6] Crazes are characterized by their interconnected fibril/void structure and, unlike true cracks, are load bearing.

It is now well established that crazes grow in width by the mechanism of surface drawing.[7-9] Here fresh polymer is drawn into the craze fibrils (having diameters in the range of 5–50 nm) from a thin fluidlike active zone approximately 5 nm in thickness at the craze bulk interface. The formation of these small, highly oriented craze fibrils requires an entanglement loss that approaches 50% at room temperature.[10,11] This entanglement loss may occur by either main-chain scission or disentanglement processes in the active zone. The rate of chain scission will depend on the applied stress level but will be independent of the length of the polymer chain (or its molecular weight M). On the other hand the rate of disentanglement processes should be a strongly decreasing function of M. If chain disentanglement occurs by tube relaxation and retraction,[12] the disentanglement time τ_d should increase as M^2 whereas if it occurs by reptation[13,14] τ_d should increase as M^3.

Experiments[15] in our laboratory on lightly cross-linked polystyrene (PS) indicate that at room temperature the primary entanglement loss occurs via chain scission and not disentanglement. However, as the temperature is increased the rate of chain disentanglement is expected to increase faster than the rate of chain scission.[16]

Recently Donald[17] has shown that PS exhibits a transition from crazing to shear deformation as the temperature of deformation is increased. Furthermore she observed that the temperature at which the transition occurred decreased with increasing molecular weight. Donald rationalized these observations by suggesting that chains can disentangle to form fibril surfaces at sufficiently high temperatures. In this paper we demonstrate unequivocally that her hypothesis is correct.

Experimental Procedure

Nearly monodisperse polystyrenes (PS's) having molecular weights M = 50 000, 100 000, 233 000, 390 000, 900 000, 1 800 000, and 3 000 000 were used for these experiments. All of the polymers used were purchased from the Pressure Chemical Co. and had polydispersity indices $M_w/M_n < 1.1$, except the M = 3 000 000, which was purchased from Polysciences Inc. and had $M_w/M_n < 1.3$. Uniform thin films were produced by drawing glass slides at a constant rate from solutions of polystyrene in methylene chloride. In all cases the film thickness, measured by a Zeiss interference microscope, was held constant at 0.7 μm.

The film was floated off on the surface of a water bath and picked up on a well-annealed copper grid previously coated with the same polymer.[18] A short exposure to the methylene chloride vapor served to remove any slack in the film and ensure bonding between the film and the grid. With the intense electron beam of the JEOL 733 microprobe, starter cracks (~100 μm long × 10 μm wide) of known geometry and size were introduced into each grid square.[19] The cracks, whose long axis lies normal to the subsequently applied strain, provide controlled sites for either craze or deformation zone nucleation and growth.

One day after preparation the grids were mounted in a strain frame coupled to a variable-speed motor drive. The entire strain rig as placed in a constant-temperature chamber, and a thermocouple was placed in the center of one of the grid squares. For the high-temperature deformation the samples were heated with an infrared lamp for 12–15 h prior to straining[20] so that thermal equilibrium could be attained. The grids were strained in tension to strains of ~0.025 at a constant rate. Since usually only one craze nucleated and grew from the starter cracks at these rates, wide crazes could be grown and it was possible to measure the craze interface velocity v_i during craze growth using an optical microscope.[21] All such measurements of v_i were made on a region of the craze ~10 μm ahead of the crack tip, i.e., outside of the immediate stress field perturbation of the crack.

To characterize the extension ratio λ in either a craze or deformation zone (DZ) the method developed by Lauterwasser and Kramer[18] was used. With an optical microdensitometer, the optical densities ϕ of the craze 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 simply the reciprocal of the volume fraction v_f, i.e.

$$\lambda = 1/v_f = [1 - \ln (\phi_c/\phi_f)/\ln (\phi_h/\phi_f)]^{-1} \qquad (1)$$

Results

At temperatures well below T_g crazes in air grow in width by the surface-drawing mechanism.[7-9] This mechanism involves transforming bulk polymer into craze fibrils at a thin fluidlike region at the craze bulk interface, the so-called active zone. The active zone lies normal to the direction of the applied strain and has a thickness in the range 5–10 nm. A TEM micrograph of an active zone at the craze bulk interface is shown in Figure 1. The large voids between the fibrils in the craze and the interface which has the appearance of a vaulted cathedral ceiling

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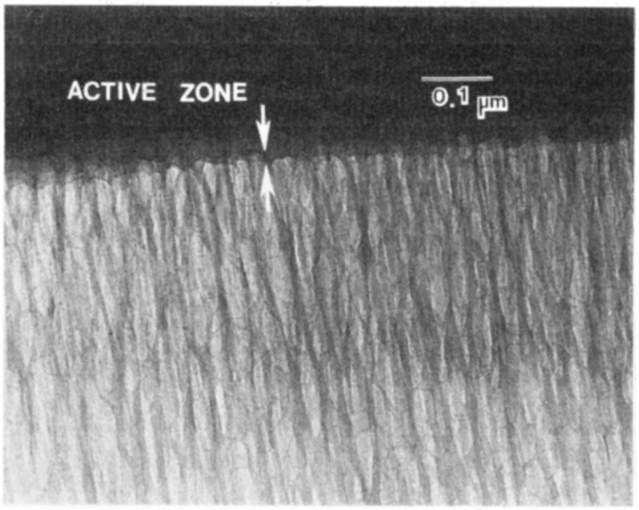

Figure 1. TEM micrograph of an active zone at the craze–bulk interface. The thickness of the active zone is in the range 5–10 nm.

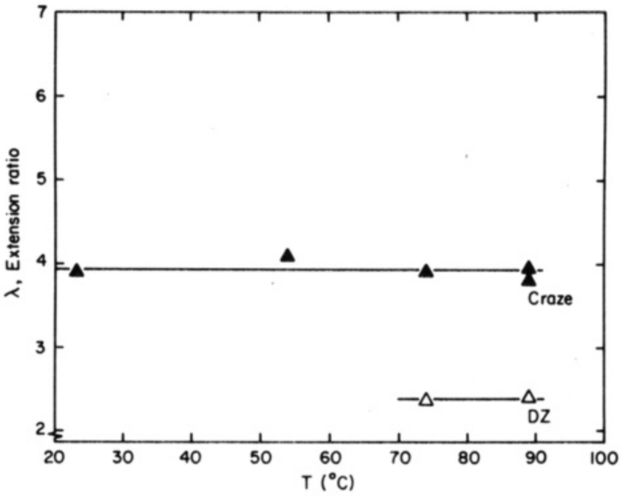

Figure 2. Plot of the extension ratio in the craze vs. temperature for the 1 800 000 molecular weight PS (solid triangles) deformed at a high strain rate of $\sim 10^{-2}$ s^{-1}. Also shown as open triangles are the values of the extension ratio in the deformation zones.

are evident. As the craze grows in width the active zone propagates into the undeformed polymer, converting more material into craze fibrils. This mechanism of craze widening results in a constant λ along the craze except for the material drawn in the near tip region which eventually becomes the craze midrib.[22] The high-temperature crazes also grow in width by surface drawing. The only evidence for craze widening via fibril creep and not surface drawing was observed in the two lowest molecular weights examined, $M = 50\,000$ and $100\,000$ strained at a v_i of 1 nm s^{-1} and at $T \geq 75$ °C. Because fibril creep results in a nonuniform λ across the craze, the results from these two *M*'s under these conditions were not used for quantitative comparisons.

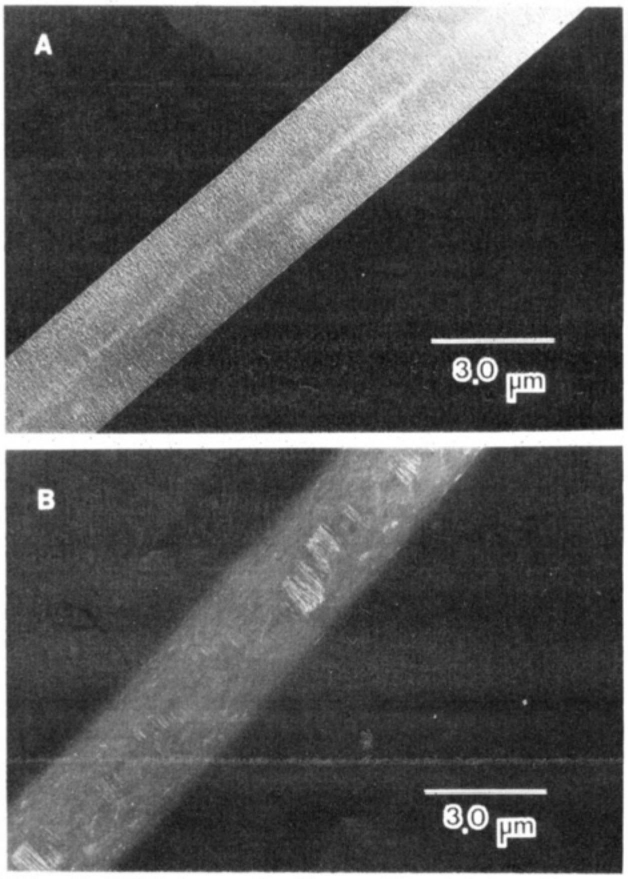

Figure 3. TEM micrographs of a craze (A) and deformation zone (B) grown in a PS sample deformed at $\dot{\epsilon} \cong 10^{-2}$ s^{-1} and $T = 90$ °C.

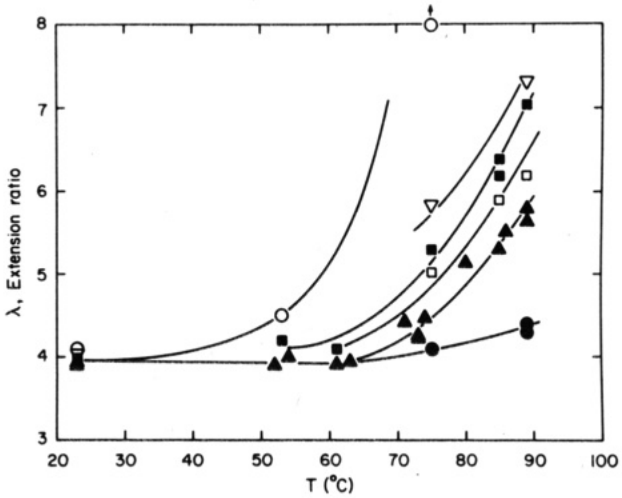

Figure 4. Plot of the extension ratio in the craze vs. temperature for PS samples strained at a slow strain rate of 4.1×10^{-6} s^{-1} for the following molecular weights: (○) $M = 100\,000$, (▽) $M = 233\,000$, (■) $M = 390\,000$, (□) $M = 900\,000$, (▲) $M = 1\,800\,000$, (●) $M = 3\,000\,000$.

Figure 2 shows the extension ratio in the craze (closed triangles) plotted as a function of temperature for the 1 800 000 molecular weight PS deformed at the relatively high strain rate of $\sim 10^{-2}$ s^{-1}. It is apparent that λ in the craze is constant with increasing *T* from room temperature to 90 °C. Furthermore at temperatures above ~70 °C shear deformation zones (DZ's) form in competition with crazes, and both types of deformation may be observed in the same film. Transmission electron microscope (TEM) micrographs of a craze and DZ formed at 90 °C in the 1 800 000 molecular PS strained at a rate of $\sim 10^{-2}$ s^{-1} are shown in Figure 3. The extension ratio λ_{DZ} in these deformation zones is approximately 2.5, and this value is in good agreement with predictions[23] that assume no bond scission or disentanglement accompanies DZ formation. The values of λ_{DZ} appear as the open triangles in Figure 2.

The results for the 1 800 000 molecular weight PS deformed at a much slower strain rate of 4.1×10^{-6} s^{-1} are quite different. The extension ratios in crazes produced

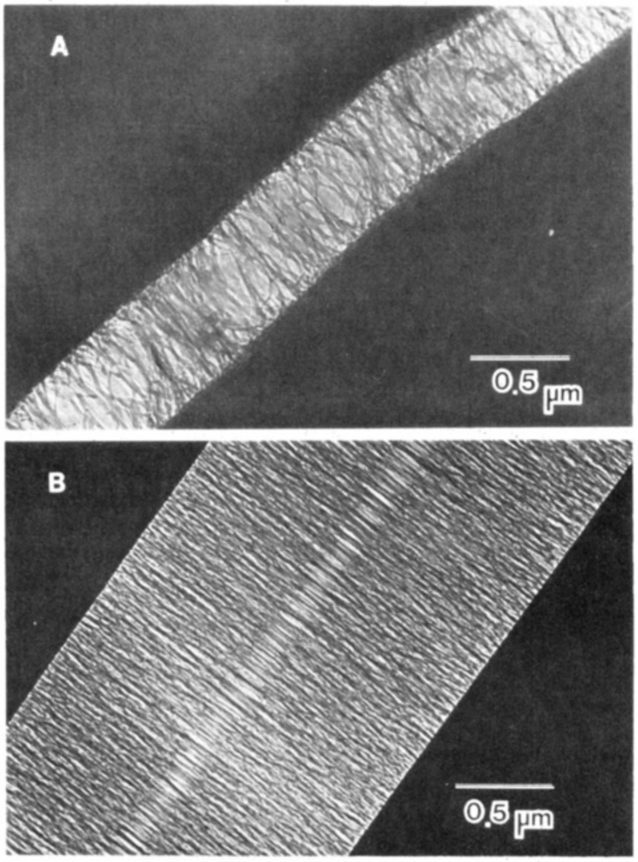

Figure 5. Craze microstructure in the 100 000 (A) and 1 800 000 (B) molecular weight PS crazed at 75 °C using $\dot{\epsilon} = 4.1 \times 10^{-6}$ s^{-1}.

at this strain rate at various temperatures are plotted in Figure 4. At this slow strain rate the extension ratio is 4 at room temperature and is constant with increasing T to 70 °C but then increases sharply as T approaches T_g. Unlike at the high strain rate of $\sim 10^{-2}$ s^{-1}, where both crazes and DZ's were observed at temperatures above 70 °C, at this slow strain rate only crazes formed over the entire temperature range were examined.

Also shown in Figure 4 are the λ vs temperature curves for polystyrene of molecular weight M = 100 000, 233 000, 390 000, 900 000, and 3 000 000 strained at a rate of 4.1×10^{-6} s^{-1}. At this slow strain rate the extension ratio is constant for all molecular weights at about 4 at room temperature. As for the 1 800 000 PS, the λ for the other M's increases sharply with increasing T with this increase beginning at lower T's for lower molecular weights. For the lowest molecular weight PS, 100 000, $\lambda \approx 15$ at 75 °C, whereas at the same slow strain rate, $\lambda = 4.5$ for the 1 800 000 molecular weight PS. The craze microstructures in the 100 000 and 1 800 000 molecular weight PS's crazed at 75 °C at $\dot{\epsilon} = 4.1 \times 10^{-6}$ s^{-1} are shown in Figure 5. These micrographs reveal that the fibril/void structure in the 100 000 molecular weight PS craze is coarser than that in the 1 800 000 molecular weight PS craze.

TEM micrographs of the types of plastic deformation observed in the 3 000 000 molecular weight PS deformed at three different rates at T = 90 °C are shown in Figure 6. At a v_i of 1.0 nm s^{-1} (which corresponded to a $\dot{\epsilon}$ of 4.1×10^{-6} s^{-1}) this molecular weight deformed primarily by shear deformation and not crazing. This is the only molecular weight that exhibited shear deformation at T = 90 °C and this slow v_i. As v_i is decreased from 1.0 to 0.2 nm s^{-1} (from $\dot{\epsilon} = 4.1 \times 10^{-6}$ s^{-1} to $\dot{\epsilon} = 0.7 \times 10^{-6}$ s^{-1}) there is a transition from primarily shear deformation to crazing plus shear deformation to crazing only.

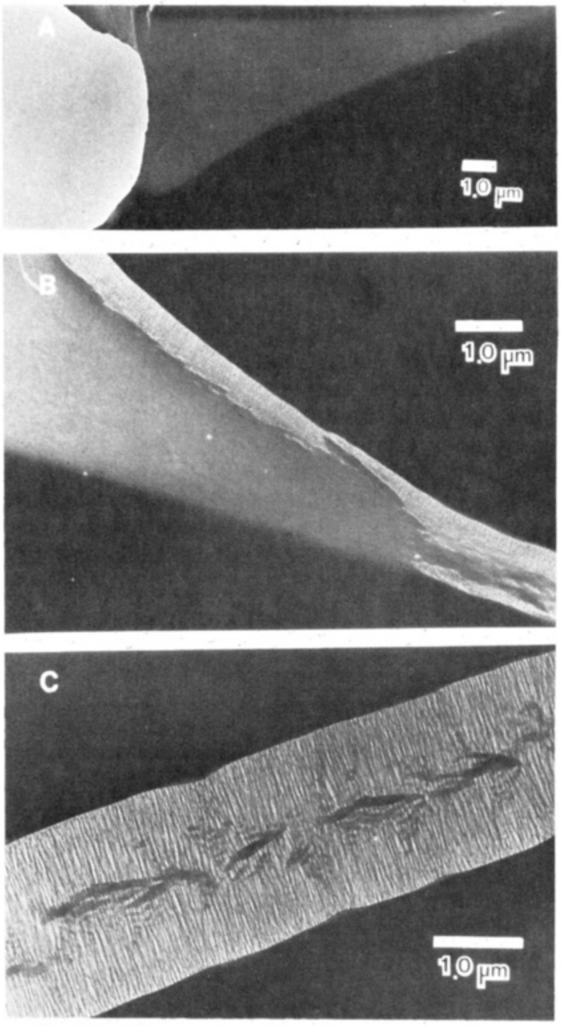

Figure 6. TEM micrographs of the plastic deformation observed in the 3 000 000 molecular weight PS deformed to give three different v_i's: (A) v_i = 1.0 nm s^{-1}, (B) v_i = 0.6 nm s^{-1}, (C) v_i = 0.2 nm s^{-1}.

Recently Donald[17] examined the craze-to-shear transition in monodisperse polystyrenes as a function of temperature and reported that the temperature at which the transition from crazing to shear deformation occurred decreased with increasing molecular weight. Donald observed only shear deformation zones in PS having a molecular weight of 1 115 000 deformed at temperatures above 70 °C. In view of the higher strain rates used by Donald our results are consistent with her observations.

The data in Figure 4 clearly demonstrate that the extension ratio in the craze is dependent on molecular weight at elevated temperatures. Moreover the strain rate dependence of λ at elevated temperatures (cf., Figures 2 and 4) in the 1 800 000 molecular weight PS shows that λ in the craze is strongly dependent on the rate at which the craze is grown. These two results combined suggest that it should be possible to measure for each molecular weight the craze interface velocity required to produce a prescribed value of λ above 4, the natural extension ratio at low temperature. A plot of λ vs. v_i at 90 °C for the 390 000 molecular weight PS is shown as solid squares in Figure 7A. It can be seen that the extension ratio decreases in value from $\lambda \approx 7.0$ at a v_i of 1.0 nm s^{-1} to $\lambda \approx 5.3$ at a v_i of ~ 150 nm s^{-1}. Also shown in Figure 7A is the value of $\lambda \approx 5.8$ (solid triangle) for a craze grown in the 1 800 000 molecular weight PS at a v_i of 1.0 nm s^{-1} and 90 °C. In order to obtain the same extension ratio of 5.8 for these two different molecular weights at a temperature of 90 °C,

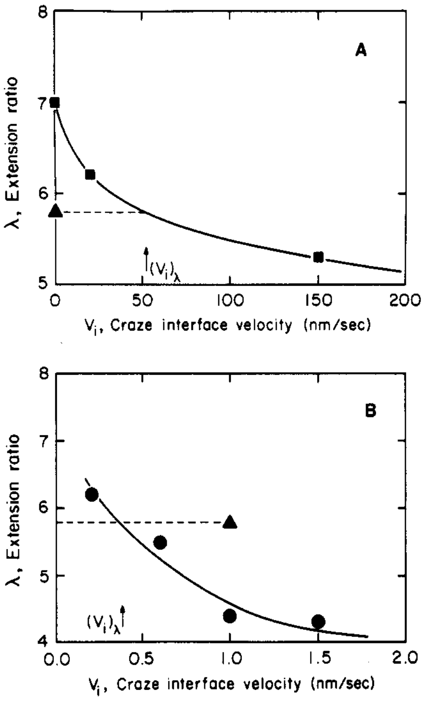

Figure 7. (A) Plot of λ vs. v_i for the 390 000 molecular weight PS (solid squares) deformed at 90 °C. (B) Plot of λ vs. v_i for the 3 000 000 molecular weight PS (solid circles) deformed at 90 °C. Indicated as a closed triangle is the value of λ in the craze for the 1 800 000 molecular weight PS deformed at a v_i of 1.0 nm s^{-1}. Also indicated is the value of v_i $(=(v_i)_\lambda)$ that produces a λ of 5.8 at 90 °C for the 390 000 and 3 000 000 molecular weight, respectively.

v_i for the 390 000 molecular weight PS must be increased to ~60 nm s^{-1}. This value of v_i, which we call $(v_i)_\lambda$, is indicated in Figure 7A. Shown in Figure 7B is a plot of λ vs. v_i for the 3 000 000 molecular weight PS at 90 °C (solid circles). At a v_i of 1.0 nm s^{-1} the extension ratio in the crazed region is 4.3, but this value increases with decreasing v_i. The value of λ in the craze for the 1 800 000 molecular weight PS is also shown as a solid triangle in Figure 7B. For the 3 000 000 molecular weight PS an interface velocity of ~0.3 nm s^{-1} = $(v_i)_\lambda$ is required to increase λ to a value of 5.8.

Similar λ vs. v_i curves were measured for all the molecular weights above 100 000 at temperatures T = 75 and 90 °C.[24] Usually λ was measured at three or four craze interface velocities for each molecular weight and temperature. The $(v_i)_\lambda$'s required to produce an extension ratio of 5.8 at 90 °C and an extension ratio of 4.5 at 75 °C were interpolated from these data. Shown in Figure 8 is a plot of log $(v_i)_\lambda$ vs. log M for λ = 5.8 at 90 °C (solid circles) and for λ = 4.5 at 75 °C (solid squares). From a least-squares fit to both sets of data

$$(v_i)_\lambda \propto M^{-2.4\pm0.5} \tag{2}$$

Discussion

Earlier workers[5] have shown that both the uniaxial strain for crazing and the craze fibril extension ratio are constant in PS for M's ≥ 100 000 at room temperature. These results as well as experiments in our laboratory[15] on lightly cross-linked PS are consistent with chain scission being the predominant mechanism of entanglement loss to form fibril surfaces at temperatures well below T_g. The results for room temperature crazes in PS reported above give added support to this view. At elevated temperatures however the present study demonstrates that the extension ratio is dependent on both molecular weight and strain rate, suggesting that chain disentanglement becomes an important mechanism for entanglement loss under these conditions. To investigate this possibility quantitatively we will estimate the molecular weight dependence of the disentanglement time τ^{d} for an entangled chain in the active zone from the $(v_i)_\lambda$ vs. M data in Figure 8.

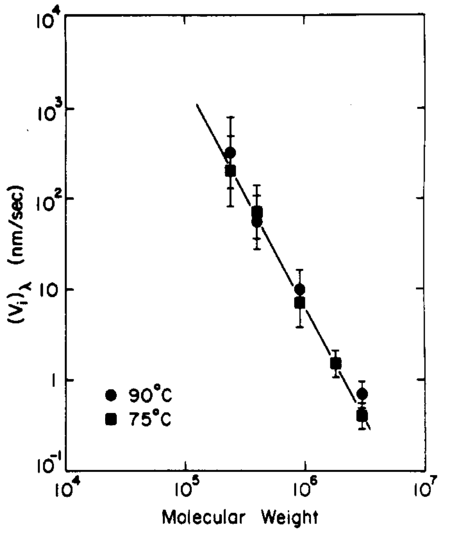

Figure 8. Plot of log $(v_i)_\lambda$ vs. log M, corresponding to λ = 5.8 at 90 °C (solid circles) and to λ = 4.5 at 75 °C (solid squares).

The length of time that an entangled chain resides in the active zone will depend inversely on the craze interface velocity. Thus the residence time t_r for a chain of mass M can be approximated by

$$t_r \approx r(M)/v_i \tag{3}$$

where $r(M)$ is the root-mean-square end-to-end distance of a polymer molecule with mass M. The thickness of the active zone (which from crazing experiments on Au-decorated PS films is typically less than 10 nm[25]) is assumed to be less than $r(M)$. Since r is proportional to $M^{0.5}$, then

$$t_r \propto M^{0.5}/v_i \tag{4}$$

Experimentally the craze interface velocity $(v_i)_\lambda$ scales with M as $M^{-2.4\pm0.5}$ (eq 2). Substitution of eq 2 into eq 4 allows the residence time t_r, at an interface velocity that gives a constant (elevated) λ, to be written

$$t_r \propto M^{2.9\pm0.5} \tag{5}$$

Now for some chain disentanglement to occur in the active zone the residence time of an entangled chain must be comparable to the molecular disentanglement time τ_d, i.e.

$$\tau_d = f t_r \tag{6}$$

where f must be greater than 1. With the assumption that t_r must be a constant fraction $(1/f)$ of τ_d for a constant λ to be obtained at $(v_i)_\lambda$, τ_d must also scale as t_r, i.e.

$$\tau_d \propto M^{2.9\pm0.5} \tag{7}$$

With simple scaling arguments,[26] the reptation model for diffusion in entangled polymers may be used to predict the molecular weight dependence of the disentanglement time. In this model, originally proposed by de Gennes,[13] a given chain is envisioned to be trapped in a network of neighboring chains which form obstacles that allow only translational motion of the chain along its contour. Edwards[27] proposed that the obstacles around a given chain may be thought of as forming a virtual tube. In the reptation model the tube is assumed to remain fixed over a time τ_R known as the reptation time or tube disengagement time. This is the time required for the chain to diffuse a distance such that it loses complete memory of its original tube, and it may be related to the center-of-mass tracer diffusion coefficient D of the polymer chains by[28]

$$\tau_R = \langle r^2 \rangle / (3\pi^2 D) \tag{8}$$

Both theory[13,14,26–28] and experiment[29,30] indicate that $D \propto M^{-2}$, and since $\langle r^2 \rangle \propto M$

$$\tau_R \propto M^3 \tag{9}$$

Thus the experimental dependence of τ_D on M, $\tau_D \propto M^{2.9\pm0.5}$, is consistent with a reptation mechanism for chain disentanglement in the active zone at the craze–bulk polymer interface.

It is also interesting to estimate the magnitude of the disentanglement time using eq 4 and 5 in order to compare it with the magnitude of τ_R in the bulk melt. For a PS chain having a molecular weight of 1 800 000, τ_d can be estimated to be $\sim 10^2$ s in a craze grown at a v_i of 1.0 nm s^{-1} at T = 90 °C. From measurements of the tracer diffusion coefficient for PS[29,30] and eq 8, we estimate[31] the reptation time τ_R to be ~1200 s at a temperature of 174 °C. Thus the τ_d for a chain in the active zone at 90 °C must be an order of magnitude less than the reptation time for a chain in the melt at 174 °C. One may also estimate that a temperature of ~200 °C is required to produce a τ_R of 100 s for the 1 800 000 molecular weight chains in the bulk melt.[31] Thus the rate at which a chain can disentangle in the active zone of the craze 10 °C below T_g is equivalent to the rate of disentanglement of this chain in the bulk melt 100 °C above T_g!

The high mobility of the polymer molecules during fibril formation probably arises from their proximity to the surface of the void in the active zone. The presence of the surface can relax the constraints on segments of the chain, thus enhancing the chain mobility relative to that in the bulk melt. Although no models presently exist to describe molecular motions for polymers near a free surface, it is reasonable to expect that the monomeric friction coefficient ζ_0 which controls the chain mobility would be smaller under these conditions. In the melt ζ_0 is known[32,33] to decrease strongly with increasing temperature. Increased temperature is thought to result in the creation of additional free volume and an increase in the rate of conformational transitions of molecular segments. Thus it seems plausible that the voided surface at the active zone may have a similar effect in decreasing ζ_0 and enhancing chain mobility. Whatever the precise reason for the higher chain mobility may be, the molecular weight scaling of τ_d is identical with that expected for chain disentanglement by reptation.

It is also worth noting other experiments in which a high chain mobility below T_g in craze fibrils has been inferred. Trassaert et al.[34] have argued that craze fibril failure in PMMA occurs via a thermally activated chain disentanglement process. They too attribute the high mobility of the molecules to the large free surface area in the craze. Craze fibril coalescence in PS has been shown[35] to occur at room temperature and is enhanced with increasing temperature. This coalescence requires chain motion over distances of the order of fibril diameters and is driven by the high surface energy Γ associated with the craze fibrils. Thin films of polycarbonate (PC) which deform by shear deformation at room temperature have been observed[36] to craze at elevated temperatures that approach T_g. Crazing in PC at high temperatures is believed to involve chain disentanglement to reduce (at least partially) the scission contribution to the total Γ.

Dettenmaier and Kausch[37,38] have observed that bulk samples of PC deformed at temperatures above $\sim 0.8T_g$ exhibited a second strain-softening mechanism at strains well beyond yield. Moreover the deformed samples were observed to turn opaque at precisely the point at which this strain softening occurred. Scanning electron microscopy and small-angle X-ray scattering revealed at the strain softening was associated with the formation of a unique type of crazing, the so-called type II crazing. The formation of crazes II was observed to occur in samples in which the molecular network was stretched to its maximum extensibility. Dettenmaier and Kausch attributed the formation of crazes II to a stress-activated disentanglement of the polymer chains.

Last, experiments on environmental crazing where the environment is a plasticizer that depresses T_g should have effects similar to increasing T on chain disentanglement during crazing. Yaffe and Kramer[39] observed that λ in PS crazes grown in the vapor of a series of alcohols increased monotonically with decreasing T_g of the plasticized PS. They attributed this increase in λ to a slippage of molecular entanglements that occurred during the drawing of the fibrils from the plasticized active zone.

It is known that both the crazing stress S_c and the yield stress σ_y decrease with increasing temperature,[40,41] the latter falling more rapidly than the former for PS. Thus a transition from crazing to shear deformation is expected as the temperature is increased. This prediction is borne out in the present study and moreover confirms Donald's earlier observation that the temperature at which the transition occurs decreases with increasing molecular weight.

The craze-widening stress S_c may be modeled quantitatively[10,23] by assuming that the polymer fluid in the active zone has a non-Newtonian flow law of the form

$$\sigma = (\dot{\epsilon}/\dot{\epsilon}_y)^{1/n_c}\,\sigma_{yc}(T) \tag{10}$$

where σ and $\dot{\epsilon}$ are the equivalent stress and equivalent strain rate in tension and n_c, $\dot{\epsilon}_y$, and σ_{yc} are material parameters.[42] (If n_c is large σ_{yc} may be considered to be the yield stress of the fluid at a strain rate of $\dot{\epsilon}_y$.) For craze growth via surface drawing, the strain rate in the locally deforming active zone may be taken as proportional to v_i. The crazing stress S_c may then be written as[10,23]

$$S_c \propto (\dot{\epsilon}/\dot{\epsilon}_y)^{1/2n_c}\{\sigma_{yc}(T)\Gamma\}^{1/2} \tag{11}$$

where Γ is the total craze surface energy. At low temperatures or high v_i's Γ consists of two terms:[10,23]

$$\Gamma = \gamma_s + (1/4)d\nu_e U_b \tag{12}$$

The first term γ_s is the van der Waals intermolecular separation energy and the second term is the bond-breaking contribution where ν_e is the entanglement density, U_b is the energy of a primary covalent bond along the polymer backbone, and d is the entanglement mesh size, given as the root-mean-square end-to-end distance of a chain of molecular weight M_e, the entanglement molecular weight.

On the other hand growth of shear deformation zones (DZ's) requires little or no bond scission[43] and thus should occur at a stress S_{DZ}

$$S_{DZ} \propto (\dot{\epsilon}/\dot{\epsilon}_y)^{1/n}\sigma_y(T) \tag{13}$$

which is the shear deformation analogue of eq 10.

Consider first the competition between crazing and shear deformation at low temperatures where chain scission is the only process involved in craze surface formation so we assume that Γ will be independent of v_i and M, $\sigma_y(T) =$

$\sigma_{yc}(T)$,[42] and $n_c = n$. Under these conditions one predicts that S_c is much less dependent on strain rate and temperature than is S_{DZ}. High strain rates and low temperatures should favor crazing, and this behavior is indeed observed in PSAN[44] and lightly cross-linked PS[45] at room temperature. Increasing the temperature should favor shear deformation since the decrease in $\sigma_y(T)$ with T affects S_{DZ} (eq 13) more strongly than S_C (eq 11).

At temperatures and strain rates where disentanglement is possible in the active zone of the craze, this picture must change, since Γ will decrease as M or v_i decreases or as T increases. At high enough v_i's or M's, disentanglement cannot occur and the second term of the right-hand side of eq 12 makes its full contribution to Γ, whereas at lower v_i's or M's disentanglement can occur and consequently Γ, and thus S_c, decreases. Since the amount of disentanglement at a given v_i depends on the molecular weight, S_c itself depends on molecular weight through Γ (and possibly through σ_{yc}[42]). This molecular weight dependence of S_c gives rise to a molecular weight dependence of the temperature at which the craze to shear transition is observed. Moreover at these temperatures lower v_i's, rather than favoring shear deformation, now favor crazing. Chain disentanglement in the active zone may also decrease $\sigma_{yc}(T)$ so that $\sigma_{yc}(T) < \sigma_y(T)$.[42] Thus at high temperatures the DZ's that grow in high M polymers at high v_i's compete with scission-dominated crazes which grow at a high S_C whereas those that attempt to form in lower M polymers at low v_i's must compete with disentanglement-dominated crazes which grow at a much lower S_C.

Conclusions

1. At low temperatures and high strain rates molecular chain scission is the dominant mechanism of entanglement loss to form fibril surfaces.

2. At high temperatures and high strain rates shear DZ's grow in competition with scission-dominated crazing. The extension ratio in these DZ's is ~2.5 and is lower than the extension ratio in the craze.

3. At high temperatures and slow strain rates, chains can disentangle in the active zone at the craze–bulk interface at temperatures well below T_g. The high mobility of the molecules probably results from the proximity of chains to the void surface at this active zone.

4. The disentanglement time for a chain in the active zone scales as $M^{2.9\pm0.5}$, in surprising agreement with the prediction of the reptation model for disentanglement.

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Registry No. PS, 9003-53-6.

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