Roles of Chain Length, Chain Architecture, and Time in the Initiation of Visible Crazes in Polystyrene

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ABSTRACT: Visible craze initiation stress has been measured for a wide range of linear and branched monodisperse polystyrenes (PS) soaked in diethylene glycol. Results show that, for a given time under stress, craze initiation in linear PS is disentanglement-dominated below a critical molar mass and chain scission-dominated above it. Branched monodisperse PS behaves similarly, with the relevant molar mass in this case being the span molar mass. Disentanglement craze initiation stress is found to vary linearly with log molar mass and log time. These observations can be explained in terms of Eyring-type stress acceleration of the process of chain retraction, required to achieve the entanglement loss necessary for creation of craze fibril surfaces. A single effective activation volume of 1.8 nm³ accounts for the dependence of crazing stress on molar mass, time, and temperature under uniaxial tensile stress, both as observed in the present data and in a previous study of rate/temperature dependence.

Introduction

Environmental stress crazing (ESC) is a local deformation phenomenon observed in glassy polymers. It results from the application of a stress with a dilational component, over a period of time in the presence of environmental agents such as organic liquids. The initiation of visible crazes consists of two stages: (1) the nucleation of localized voids about 30 nm in diameter at small inclusions, surface imperfections, or zones of high free volume;^{1,2} (2) the subsequent coalescence of the voids into visible cracklike surfaces spanned by highly oriented fibrils.³ The environment has been shown to facilitate the formation of crazes either by a local plasticization process leading to enhanced molecular mobility or by interfacial tension reduction.⁴ The onset of crazing accounts for a substantial proportion of failures of glassy polymers in service.⁵ In addition, the detailed mechanism of craze formation is a challenging and incompletely understood problem for polymer science. It is not surprising that there has been substantial research in the past four decades on the subject of craze initiation, growth, and failure, and comprehensive reviews are available.^{3,6–8}

Although there is still debate over the exact processes taking place during craze initiation, there is widespread agreement that the extensive formation of free surface in a craze requires breakdown of the entanglement network: the "geometrically necessary entanglement loss" noted by Kramer.³ Entanglement loss can come about as a result of solid-state molecular disentanglement if there is sufficient chain mobility, as provided by a relatively high temperature or the effect of a solvent.⁹ Crazing must be sensitive to chain length if disentanglement is to take place. When chain mobility is reduced, however, such as in dry crazing or at low temperatures, the free surfaces must occur through chain scission,¹⁰ and the craze initiation stress is then expected to be independent of molar mass.

The pioneering work of Fellers and Kee was the first systematic study of the effects of molar mass on the initiation of visible crazes.¹¹ Their study investigated injection-molded bars of different grades of polydisperse polystyrene (PDI > 2.39). Although the breaking stress and fracture elongation were

influenced by molar mass, they could find no measurable changes in craze initiation stress.

The objective of the present work is to develop an understanding of the effects of molecular parameters such as length, architecture, and time on the solid-state mechanical properties of polymers. Much of the previous work on crazing has been carried out on thin films in order to observe the crazes with electron microscopy. The present experiments were carried out on (small) bulk specimens in order to better reflect the triaxial state of stress that is characteristic of visible craze initiation conditions in manufactured polymer products.

In this paper we report measurements of the environmental craze stress for the initiation of visible crazes in isochronal threepoint bending creep experiments on an unusually wide variety of well-characterized samples of atactic polystyrene (PS) with known molecular size and architecture, saturated in diethylene glycol (DEG). A novel miniature crazing test was employed to enable study of materials where only small quantities were available.¹² The results suggest that a remarkably simple model relates molecular parameters to craze initiation stress. The model appears to account well for the measurements reported here and for measurements on PS previously published.

Experimental Section

Materials. The materials used in this study include a range of 14 samples of monodisperse linear atactic PS (PDI = $M_w/M_n < 1.15$) with weight-average molar mass from 68 000 to 967 000 g/mol. Molar mass measurements were performed by size exclusion chromatography (SEC) on a Viscotek TDA 302 with refractive index, viscosity, and light scattering detectors, and results are given in Table 1 with the codes used to refer to the materials in this paper. Material AY was obtained from Pressure Chemicals, material P was obtained from Dow Chemicals, and all other linear materials were synthesized by living anionic polymerization at Durham.

Also included in this study were 10 monodisperse branched atactic PS (PDI = $M_w/M_n < 1.08$) including two 3-arm stars and an H-shape PS obtained from Dow Chemicals and seven symmetric 4-arm stars with a central tetrafunctional silane coupler and varying arm lengths synthesized at Durham.¹³ Molar mass measurements of both arm and star and the corresponding polymer codes are given in Table 1.

Since the available quantity of some of the materials was extremely limited, a technique for the production and testing of miniature prismatic rectangular beams was developed in our Oxford

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 Table 1. Molar Mass Measurements Obtained by Triple

 Detection SEC for the Polystyrene Samples Used in This Study

				architecture	span $M_{\rm s}$
	code	$M_{\rm w}$ (g/mol)	PDI	(functionality f)	(g/mol)
linear	А	68 000	1.03	linear	
	В	75 500	1.03	linear	
	С	94 400	1.05	linear	
	D	108 000	1.04	linear	
	AX	133 000	1.04	linear	
	AY	148 000	1.06	linear	
	E	161 000	1.03	linear	
	BA	206 000	1.08	linear	
	AZ	226 000	1.10	linear	
	F	249 000	1.12	linear	
	AF	262 000	1.05	linear	
	AG	518 000	1.15	linear	
	G	498 000	1.07	linear	
	BB	967 000	1.07	linear	
3-arm stars	AA	201 000	1.05	3-arm asym ^a	180 000
	Z	435 000	1.05	3-arm sym	290 000
4-arm stars	AU	52 800	1.04	4-arm sym	27 400
	(arms)	13 700	1.04	(f = 3.9)	
	AV	102 000	1.06	4-arm sym	54 600
	(arms)	27 300	1.02	(f = 3.7)	
	AW	234 000	1.07	4-arm sym	118 400
	(arms)	59 200	1.04	(f = 4.0)	
	AQ	441 000	1.07	4-arm sym	220 000
	(arms)	110 000	1.03	(f = 4.0)	
	AR	541 000	1.06	4-arm sym	276 000
	(arms)	138 000	1.03	(f = 3.9)	
	AS	822 000	1.03	4-arm sym	386 000
	(arms)	193 000	1.03	(f = 4.2)	
	AT	1 150 000	1.02	4-arm sym	586 000
	(arms)	293 000	1.05	(f = 3.9)	
H-shape	AB	310 000	1.05	H-shape ^b	240 000

^{*a*} Asymmetric trifunctional star has nominally 2 arms 90 000 g/mol and 1 arm 20 000 g/mol. ^{*b*} H-shape has nominally a central span 100 000 g/mol connected to trifunctional units with 1 arm 35 000 g/mol and 1 arm 70 000 g/mol on both sides.

laboratory. It has been described elsewhere, so only a brief account will be given here.¹² Small PS plates 0.5 mm in thickness were compression-molded using rectangular molds in a hand-operated hydraulic press with heated platens. The top and bottom surfaces of the mold were lined each time with a fresh sheet of 0.15 mm thick soft temper 1200 aluminum foil obtained from Multifoil Ltd. Care was taken to align the rolling direction of the foil with the long axis of the beams in order to provide a repeatable surface texture on the molded polymer, as this is known to affect craze initiation.¹⁴ The mold was held at 170 °C for 15 min and cooled to room temperature at a rate of 15 °C/min. Miniature rectangular beam specimens typically 0.5 mm × 2 mm × 7 mm in size were cut from the plates using a custom-made jig with parallel single-beveled blades. The brittleness of samples AU and AV, however, prevented satisfactory samples from being cut from these materials.

Miniature Creep Experiments. A miniature three-point bend creep testing rig was constructed in our laboratory in order to craze the miniature beam specimens. The technique for measurement of visible craze initiation stress in the miniature specimens, and its use and validation against results for larger specimens, was described in the previous publication.¹² Specimens were soaked in analytical reagent grade diethylene glycol (DEG) for a minimum of 1 day prior to testing, after which no further solvent uptake could be measured. DEG is a mild crazing agent for PS and was used in order to ensure the growth of fine, stable crazes required in the miniature specimens and to avoid premature brittle fracture as seen frequently in monodisperse specimens crazed in air. Each test consisted of subjecting the beam specimen, simply supported at its ends and still soaked in DEG, to a constant central load for a specified loading time. During this time the beam exhibited creep under the load. Given a sufficiently large stress, crazes formed perpendicular to the beam axis, initiating at the location of the



Figure 1. Isochronal measurements of craze initiation stress (t = 300 s) as a function of molar mass *M* (linear samples) or span molar mass *M*_s (branched samples). The lines indicate linear regression through the low molar mass data and an average constant value through the high molar mass data (linear PS only).

maximum tensile stress (the surface of the beam). After unloading, the beam was removed from the loading rig, and the surface was wiped prior to its placement on an angled support under a low power optical microscope. Transmitted light inclined at a small angle (e.g., 10°) to the specimen surface normal was then used to make the crazes visible, and within 1 h of crazing, five measurements of the length of the crazed region were taken across the width and averaged to obtain the mean length l_c . At least five specimens were tested for each polymer under each condition, although further repetitions were performed where sufficient material was available. In the present work, all crazing tests were carried out at room temperature (~20 °C).

Evaluation of Visible Craze Initiation Stress. The elementary theory of bending of slender beams was employed to calculate the axial tensile stress at the surface of the beam at the extremities of the crazed region, i.e., at the points where crazes were just initiated³⁶ under the conditions of the experiment:

$$\sigma_{\rm c} = \frac{3P(l-l_{\rm c})}{2bd^2} \tag{1}$$

where *P* is the applied load, *l* the support spacing, *b* the breadth, and *d* the depth of the beam. In the results that follow, the mean values of σ_c are plotted, together with standard deviations, for each PS sample under each condition.

Results

Linear Polymers. Craze initiation stress measured on the linear polymers in isochronal (t = 300 s) creep tests is plotted against molar mass M in Figure 1. It was not possible to generate visible stable crazes in the lowest molar mass PS, sample A ($M_w = 68\ 000\ g/mol$), without fracture during the creep time. A number of authors have reported difficulties in growing crazes in monodisperse polymers of molar mass close to $2M_e$,^{10,15} where the entanglement molar mass $M_e = 18\ 000\ g/mol$ for PS.¹⁶ For sample A we give instead approximate values for the lower bound for the stress at no craze formation and upper bound for the stress at which unstable craze propagation leads to fracture.

The results in Figure 1 (filled symbols) clearly reveal two regimes. For the shortest molecules the craze initiation stress increases with M, as would be expected if disentanglement were the rate-limiting step in formation of a craze. But at a critical molar mass of approximately 140 000 g/mol, there is a transition



Figure 2. Measurements of craze initiation stress for linear PS as a function of molar mass M for various creep times.

in behavior and the craze stress becomes independent of M, consistent with chain scission being rate-determining. A quantitative interpretation of these two regimes is given below in terms of a simplified model of craze formation.

Branched Polymers. Craze initiation stress measured on the branched polymers in isochronal (t = 300 s) creep tests is also included in Figure 1. The relevant molar mass in these cases is taken to be the span value M_s (see the discussion below for an explanation of the use of M_s). In the 4-arm star polymers $M_s =$ $2M_{\rm a}$, where $M_{\rm a}$ is the molar mass of the arm, obtained from direct SEC measurement. In the 3-arm stars and H-shape sample nominal values are used as molar mass was not measured separately on the arms. The values used are given in Table 1. It was not possible to cut specimens from samples AU and AV $(M_s = 27\ 400\ \text{and}\ 54\ 600\ \text{g/mol},\ \text{respectively})$ because of their extreme brittleness. The data in Figure 1 (open symbols) are consistent with the craze stress for a branched polymer agreeing approximately with that for a linear polymer with corresponding *M*. However, this result is not conclusive, as there is only one branched polymer that could be tested that falls in the "disentanglement" region of the graph. Moreover, in the "scission" region there is evidence for the values of craze stress for branched polymers exceeding those for linear polymers by 2-3 MPa.

Time Dependence in Linear Polymers. Craze initiation stress was measured for four creep times t = 12, 60, 300, and 1800 s in the linear polymers, and the values are plotted versus molar mass *M* in Figure 2. It was not possible to initiate stable crazes in all materials at all creep times. For instance, although it was possible to grow stable crazes in 300 s experiments in sample B, it proved impossible to do so at 12, 60, and 1800 s. The growth of stable crazes in a given creep time requires a stress small enough that it does not fracture the sample (by catastrophic craze growth) but large enough that crazes are initiated. Individual measurements of craze initiation stress at different creep times are shown for four representative polymers in Figure 3.

It was found that the appearance of the crazes evolved with time under load. Using a technique similar to that used for the measurement of the crazes,¹² micrographs of the crazed specimens were produced, under angled transmitted light. The images were processed by subtracting the equivalent image obtained in normal reflected light, and then inverting the image, to highlight the positions of the crazes and enhance the contrast

of the inverted image. Figure 4 shows four such micrographs for polymer AX at t = 12, 60, 300, and 1800 s.

Although it is difficult to discern specific differences in craze morphology at the craze initiation boundary, it is apparent that longer times result in wider, more developed craze patterns. It is particularly evident that in Figure 4a, in the t = 12 s image, crazes throughout the specimen are very short relative to the width of the sample and thus more difficult to see. Similar patterns have been recorded in the other polymers.

Discussion

A Simple Model of Craze Initiation. The results given above can be explained quantitatively in terms of the formation of free surface being the rate-limiting step in craze initiation, as observed in the present study. In the present work we refer to craze *initiation* as the entire process by which a craze nucleates and then grows to a size where it is visible in our particular experimental method. A schematic sketch is given in Figure 5, showing (a) the location where the craze *will* initiate and (b) the same location after the craze *has* initiated.

The local tensile stress normal to the craze is σ when initiation occurs. The initiation process involves creation and stretching of, say, $n_{\rm f}$ craze fibrils per unit area of craze. However, the fibrils form within an entangled network of molecules. Hence, the new free surface surrounding each fibril (dotted lines in Figure 5) is crossed initially by, say, $n_{\rm r}$ molecular strands, which therefore must disentangle or break to form the new surface. Indeed, by consideration of chain statistics, Kramer and co-workers have established that the formation of craze fibrils by disentanglement requires a loss of somewhere in the order of 50% of the original entanglements.¹⁷ The formation of the voids is accompanied by elongation of the fibrils. Thus, opposing faces of the craze move apart, and there is a displacement Δ normal to the craze plane. Consequently, work $\sigma \Delta / n_f n_r$ per surface-crossing strand is provided by the applied stress. In addition, an area A_0 of new surface per surface-crossing strand is created, with a free energy cost of γA_0 , where γ is the specific surface energy of the fibril. This parameter is likely to be higher than the van der Waals surface tension of the equilibrium surface of the polymer in the melt. The nature of a new surface created in the solid state, and hence its energy, will be sensitive to the mode of its creation (e.g., chain disentanglement or scission).

Disentanglement Crazing. Consider first the situation in which surface-crossing molecules disentangle to form the fibril surfaces. As each new surface forms (the side surfaces of a craze fibril), surface-crossing molecules gradually retract within their entanglement "tubes", losing entanglements at their ends and allowing formation of the free surface of a craze fibril. As the fibril is released from lateral constraints, it stretches uniaxially under the stress σ .¹⁸ In this picture of events, the rate-limiting step in disentanglement is chain retraction, which normally occurs on the time scale of the longest Rouse time $\tau_{\rm R}$. This is related to chain length (via molar mass *M*), temperature *T*, and the monomeric friction coefficient ζ :¹⁹

$$\tau_{\rm R} = \frac{\beta \xi M^2}{T} \tag{2}$$

where β is a monomer-specific constant. Deep in the glassy state in the absence of stress, τ_R is, of course, effectively infinite, and chain retraction does not occur. However, the polymer chains in close proximity to the forming craze nucleus benefit from increased mobility. Sufficiently high stress in this region shortens relaxation times of Rouse modes, normally associated with the melt, to the experimental time scale. The reason is that, for surface-crossing strands during fibril formation, their diffusional hops along the tube occur in the presence of a macroscopic free energy gradient. For a surface-crossing strand,



Figure 3. Individual measurements of craze initiation stress as a function of time for linear PS polymers: C: $M_w = 94400 \text{ g/mol}$ (a), D: $M_w = 108000 \text{ g/mol}$ (b), AX: $M_w = 133000 \text{ g/mol}$ (c), and AF: $M_w = 262000 \text{ g/mol}$ (d), with linear regression lines through the data sets.



Figure 4. Enhanced micrographs of crazes in miniature test specimens of polymer AX at t = 12 s (a), 60 s (b), 300 s (c), and 1200 s (d), showing the coarsening of the craze pattern with time.

when the work done by the applied stress exceeds the energy required to form new surface $(\sigma\Delta/n_f n_r > \gamma A_0)$ a hop in the direction of disentanglement will reduce the free energy of the system.³⁷ In the present state of knowledge, it is uncertain how the overall free energy reduction should be apportioned among the many hops constituting chain retraction in the glassy state.³⁸ Here, therefore, we invoke the simplest hypothesis: the reduction in free energy per hop is $\sigma V_c - \gamma A_c$, where $A_c \propto A_0$ and $V_c \propto \Delta/n_f n_r$, independent of molar mass. Thus, the free energy barrier is lowered for forward hops, and the time scale for craze initiation τ_c is reduced from τ_R to

$$\tau_{\rm c} = \frac{\beta \zeta M^2}{T} \exp\left(\frac{\gamma A_{\rm c} - \sigma V_{\rm c}}{2k_{\rm B}T}\right) \tag{3}$$

assuming a symmetric barrier. Clearly, the monomer-specific constant V_c plays the role of an Eyring activation volume for craze initiation. The present proposal is similar to the suggestion by Berger and Kramer,²⁰ that proximity to the active crazing



Figure 5. Development of a craze from a craze precursor site (a) to a visible craze with displacement Δ under the action of an applied stress σ (b).

zone has the effect of reducing the monomer friction coefficient, leading to a reduction in crazing time scales.

Application to Crazing under Three-Point Bending. Consider a creep test of duration *t*. According to the argument above, crazes will initiate (i.e., become visible) at all locations where

$$\frac{t}{\tau_{\rm c}} \ge 1 \tag{4}$$

Equation 3 then allows us to calculate the minimum required stress. But craze initiation sites normally lie on the specimen surface, at microscopic stress concentrations resulting from surface roughness. Here the local stress σ exceeds the far field stress σ_c by a stress concentration factor *f*

$$\sigma = f\sigma_c \tag{5}$$

The importance of surface roughness has been investigated previously by the experiments of Argon and Hannoosh¹⁴ and discussed in the context of a new criterion for craze initiation recently proposed by Bucknall.² However, for experiments in which specimen surfaces have reproducible roughness, the stress concentration factor will be constant. Thus, combining eqs 3–5, the boundary of the observed crazed region will occur where

$$\sigma_{\rm c} = \frac{2k_{\rm B}T}{fV_{\rm c}} [\ln \zeta + 2\ln M - \ln T - \ln t + \ln \beta] + \frac{\gamma A_{\rm c}}{fV_{\rm c}} \quad (6)$$

We may recognize the square bracket to be simply $\ln(\tau_{\rm R}/t)$.

Linear Polymers. Equation 6 predicts the craze initiation stress to be linear in both ln *t* and ln *M*, as supported by the experimental data in Figures 1 (low *M* region) and 3. For a quantitative fit of the model to data in Figure 1, we performed linear regression through craze initiation measurements on polymers B, C, D, and AX, where the dependence on molar mass is most evident. The fit gave $\sigma_c = a_0 + a_1 \ln M$, with parameters $a_0 = -93 \pm 20$ MPa (the \pm indicates standard error) and $a_1 = 9.2 \pm 1.8$ MPa. The linear regression line (with correlation coefficient 0.73) is shown in Figure 1. From eq 6, the effective activation volume obtained from these data for T = 20 °C is $fV_c = 1.8 \pm 0.3$ nm³.

Branched Polymers. In branched chains with a single branch point, the molar mass associated with chain retraction is the span molar mass $M_{\rm s}$.¹⁶ Where $M_{\rm s}$ is only a small number of entanglement lengths there may be differences between $\tau_{\rm R}$ for a branched chain of $M_{\rm s}$ compared with a linear chain of length $M = M_{\rm s}$ since the branch point effectively pins the center of mass of the branched chain. However, when the equivalent linear

chain is long, the random nature of the fluctuations along the tube effectively pins its midpoint in the same way as a branch point. The shortest equivalent chain for the branched polymers crazed in this study contains \sim 7 entanglements.

Polymers AU, AV, and AW have a span molar mass M_s which is sufficiently small to expect disentanglement crazing, but AU and AV were too brittle to cut and thus unable to be tested. But Polymer AW gave good agreement with the disentanglement craze initiation stress expected from the linear regression for linear polymers, when evaluated at its span molar mass M_s .

Low Molar Mass Samples. Extrapolation of the disentanglement crazing regression line to zero craze initiation stress predicts that this occurs at M = 24200 g/mol. Such a value may be compared with the value of 51 000 g/mol obtained by Bersted et al. for the minimum length of polymer contributing to tensile strength.²¹ In addition, Lainchbury et al. found that the transition between brittle glasslike fracture and crazecontrolled fracture occurs between 20 000 and 51 000 g/mol.²² Although molecules shorter than $2M_e$ are thought to be uncoupled to the entanglement network, the fracture toughness of PS of $2M_e$ is still an order of magnitude bigger than the ideal brittle value of 2γ where γ is the surface energy.²³ Kramer suggests that these short molecules form small crazes whose span is shorter than the wavelength of light. Yang et al.²⁴ have shown that polymers with $M < 2M_e$ are unable to sustain stable craze growth and that the stability of craze growth increases with molar mass. These previous observations are consistent with the difficulties encountered in growing stable crazes in sample A ($M_w = 68\ 000\ g/mol$) and in cutting samples AU and AV $(M_s = 27400 \text{ and } 54600 \text{ g/mol, respectively})$, while polymers with longer chains could be tested and crazed satisfactorily.

Chain Scission Crazing. If the local stress acting on an individual molecule that is required for disentanglement exceeds the stress required to break the C-C backbone, the molecule will preferentially split into two shorter parts. Such chain scission provides another route to entanglement loss. Clearly, this will occur in the present context only where there is great local stress concentration. The local stress to fracture a C-Cbond exceeds the stresses applied macroscopically in the present work by about 3 orders of magnitude. Nevertheless, such concentration may occur at the tip of an expanding void. Thus, for a given set of time, temperature, and structure conditions, there will be a length of molecule $M_{\rm crit}$ where the stress for disentanglement in the experimental time window t becomes equal to the stress for chain scission σ_{∞} . For all polymers with $M > M_{\rm crit}$, chain scission will be the mechanism by which new surfaces are formed. Craze initiation stress is then expected to become independent of molar mass.

The isochronal t = 300 s craze initiation data for linear polymers BA, AZ, F, AF, G, AG, and BB, shown in Figure 1, show no apparent dependence on molar mass. This was confirmed by fitting a function of the form $\sigma_c = b_0 + b_1 \ln M$ to these data, giving parameters $b_0 = 11.8 \pm 5.6$ MPa and b_1 $= 0.32 \pm 0.43$ MPa. The hypothesis that b_1 is not significantly different from zero cannot be rejected with significance at the 5% level since the Student's t-test on the experimental data yields $t_0 = 0.744$ and $t_{0.025,39} = 1.68$. We therefore conclude that in this region the data take the form of $\sigma = \sigma_{\infty}$ (craze initiation stress is independent of molar mass) and find $\sigma_{\infty} =$ 16.1 ± 1.4 MPa, which is included as the horizontal full line in Figure 1. The crossover between the two regression lines occurs at $M_{\rm crit} = 140\ 400\ {\rm g/mol}$. In the branched samples there is also a range of molar mass in which the craze initiation stress appears insensitive to molar mass. Statistical analysis of isochronal t =300 s craze initiation measurements on branched polymers AB,



Figure 6. Rate of change of craze initiation stress with log time as a function of molar mass for materials C, D, AX, AY, BA, AF, AG, and BB, with bars showing standard errors. Also shown (dashed line) is the prediction for the rate dependence of disentanglement crazing obtained from eq 6 and (solid line) the rate dependence for scission obtained from linear regression on the high molar mass samples.

AG, Z, AR, AS, and AT, shown in Figure 1, yields $t_0 = 1.07$, and since $t_{0.025,22} = 1.71$, the hypothesis of zero molar mass sensitivity cannot be rejected with significance at the 5% level. We can again deduce that there is a region in which the data takes the form of $\sigma_c = \sigma_b^{\text{th}}$ and find $\sigma_b^{\text{th}} = 18.1 \pm 1.3$ MPa.

We can also compare linear and branched polymers in the chain scission region and can reject the hypothesis that $\sigma_{\infty} = \sigma_{\infty}^{b}$, for which we obtain $t_0 = 2.37$ and $t_{0.025,63} = 1.67$. Thus, we conclude that for $M > M_{crit}$ the craze initiation stress in branched PS is higher than in linear PS with significance at the 5% level. This could arise from the more pronounced strain stiffening expected in a branched polymer delaying the onset of entanglement loss. Recent data from the authors' laboratory show that an increase in strain stiffening as a result of process-induced molecular orientation can result in a significant increase in craze initiation stress.²⁵

Kinetics of Craze Initiation. The rate of change of craze initiation stress with respect to $\ln t$ has been estimated through linear regression on materials C, D, AX, AY, BA, AF, AG, and BB from the data in Figure 2 (and shown for four polymers in Figure 3) and is plotted in Figure 6.

There is greatest time dependence in low molar mass samples, decreasing to a constant value with increasing molar mass. In the region where disentanglement crazing is the dominant mechanism, using eq 6 and the effective activation volume found from isochronal measurements through varying molar mass $fV_c = 1.8 \pm 0.3 \text{ nm}^3$, we expect a value of $d\sigma_c/d \ln t = -4.6 \pm 0.9$ MPa. The lowest molar mass sample where the time dependence could be measured (sample C) gave a value of $d\sigma_c/d \ln t = -5.2 \pm 0.8$ MPa, which is in reasonable agreement with the value calculated from the activation volume obtained from the molar mass dependence.

In the region where scission crazing is the dominant mechanism, at high molar mass, the average value of $d\sigma_c/d \ln t$ found from the data was -1.7 ± 0.3 MPa. The origin of this time dependence is unclear. However, it may result from craze growth rather than initiation. The optical technique used to measure craze initiation relies on crazes growing to a visible size in the given experimental time window, and it is possible that crazes have initiated in samples in creep for, say, 12 s but have not been able to grow to a visible size. Tervoort and Govaert measured the kinetics of craze initiation in a brittle grade of polydisperse PS, and their findings lead to an activation volume for craze initiation of $fV_c = 1.8 \text{ mm}^{3.26}$. The use of a brittle grade of PS implies a low molar mass and hence increased likelihood that the craze initiation process will be disentanglement-dominated. The activation volume found from their data is equal to the value obtained from our experiments in the disentanglement regime to within experimental accuracy.

Application to Crazing under Uniaxial Tension at Constant Strain Rate. To compare the present model for disentanglement crazing with other data available, consider a uniaxial tension test at constant strain rate $\dot{\varepsilon}$ where crazing occurs at a small strain $\varepsilon_c = \dot{\varepsilon} t_{\text{tens}}$ at time t_{tens} . Assume the polymer is linear elastic prior to crazing. τ_c is a function of stress, which in this test is a linear function of the experiment time, $\sigma(t) = E\dot{\varepsilon}t$, where *E* is the tensile modulus. Extending the argument used above to predict crazing during creep, crazes will now initiate at all locations where

$$\int_0^{t_{\text{tens}}} \frac{\mathrm{d}t}{\tau_{\rm c}} \ge 1 \tag{7}$$

Using the expression for τ_c given in eq 3 and integrating eq 7 gives

$$\tau_{\rm R} = \frac{2k_{\rm B}T}{fV_{\rm c}E\dot{\varepsilon}} \left(\exp\left(\frac{fV_{\rm c}E\dot{\varepsilon}t_{\rm tens}}{2k_{\rm B}T}\right) - 1 \right) \exp\left(-\frac{\gamma A_{\rm c}}{2k_{\rm B}T}\right)$$
(8)

Again, the local stress σ is assumed to exceed the far field stress σ_c^{tens} by a stress concentration factor f as in eq 5. For $\exp(fV_c E\dot{\epsilon}t_{\text{tens}}/2k_B T) \gg 1$ (the value is at least $\exp(8.5f)$ for the data to which this applied below) we can write

$$\sigma_{\rm c}^{\rm tens} = E \dot{\varepsilon} t_{\rm tens} = \frac{2k_{\rm B}T}{fV_{\rm c}} \left[\ln \zeta + 2 \ln M - 2 \ln T + \ln \dot{\varepsilon} + \ln \left(\frac{fV_{\rm c}E\beta}{2k_{\rm B}}\right) \right] + \frac{\gamma A_{\rm c}}{fV_{\rm c}}$$
(9)

Alternatively, we can obtain an expression for the equivalent creep time t_{creep}^* at which crazing would occur if subjected to the constant stress $\sigma_c = E \hat{\epsilon} t_{tens}$

$$t_{\text{creep}}^{*} = \frac{2k_{\text{B}}T}{fV_{\text{c}}E\dot{\varepsilon}} \left(\frac{\exp\left(\frac{fV_{\text{c}}E\dot{\varepsilon}t_{\text{tens}}}{2k_{\text{B}}T}\right) - 1}{\exp\left(\frac{fV_{\text{c}}E\dot{\varepsilon}t_{\text{tens}}}{2k_{\text{B}}T}\right)} \right) \approx \frac{2k_{\text{B}}T}{fV_{\text{c}}E\dot{\varepsilon}}$$
(10)

and apply the values to eq 6.

Han et al. measured craze initiation strain in thin films of monodisperse linear PS with $M_n = 110\ 000\ \text{g/mol}$ and PDI = 1.04 stretched at constant strain rates of $\dot{\varepsilon} = 10^{-3}$ and $10^{-4}\ \text{s}^{-1}$ over a range of temperatures 20–80 °C.¹⁸ Here the monomeric friction coefficient ζ is not constant across the series of tests, as the temperature is varied. It is, however, proportional to the viscosity according to Stokes' law and hence can be described by an equation of Macedo–Litovitz form.²⁷ The validity of this approach, as applied to glassy polymers, was demonstrated in our Oxford laboratory in constitutive modeling of glassy polymers.²⁸ Hence, at a given temperature *T* and glass structure, defined by the fictive temperature T_f (at which the polymer would have the same structure if it were in equilibrium), the monomeric friction coefficient is given by

$$\zeta = \zeta^* \exp\left(\frac{\Delta H}{RT^*} - \frac{\Delta H}{RT}\right) \exp\left(\frac{C}{T_f^* - T_\infty} - \frac{C}{T_f - T_\infty}\right) \quad (11)$$

where ζ^* is a known value of the friction coefficient at a reference temperature T^* and structure, defined by the fictive temperature T_f^* , ΔH is the enthalpic contribution to the free energy barrier, *C* is the Cohen–Turnbull constant, T_{∞} is the Vogel temperature,²⁹ and *R* is the gas constant. The reference



Figure 7. Experimental measurements of craze initiation stress obtained in constant strain-rate tensile tests at various temperatures and strain rates, on a monodisperse linear PS, by Han et al.¹⁸ This graph shows a fit to eq 9 in the disentanglement crazing region (hollow points, with dashed line) and the deviation to chain scission crazing (solid points).

value may calculated from the equation proposed by Majesté et al.³⁰ and is equal to $\zeta^* = 1.852 \times 10^{-5}$ g/s at $T^* = T_f^* = 170$ °C.

Han et al. specify that the same cooling history was applied to all samples, and we can therefore assume that they are isostructural. We use values of $\Delta H = 162$ kJ/mol, C = 222 K, $T_{\infty} = 85$ °C, and a fictive temperature $T_{\rm f} = 95.3$ °C obtained in our laboratory on PS below the glass transition with a similar temperature history.³¹ Also, we neglect variations in surface energy with temperature and molar mass and assume γ to be constant over this range. A value of E = 3.51 GPa was used throughout. We now replot the data of Han et al. in the form described by eq 9 as $\sigma_c^{\text{tens}}/2T$ vs ln $\zeta + 2 \ln M - 2 \ln T + \ln M$ $\dot{\varepsilon}$, in Figure 7. Linear regression through the disentanglement crazing part of the data (shown in Figure 7 as hollow points) yields a mean value of the effective craze activation volume of $fV_c = 1.8 \pm 0.4$ nm³. This shows remarkable agreement with the value (1.8 \pm 0.3 nm³) obtained for creep experiments in DEG in the present work.

Direct Comparison of Data Sets from Creep and Tensile Tests. In order to compare directly the data set presented in this paper for 300 s creep in DEG with the data set obtained in constant rate tension in air by Han et al.,¹⁸ we convert the latter measurements to equivalent creep times at the craze initiation stress through eq 10. Results are plotted in Figure 8 as $\sigma_c/2T$ vs ln $\zeta - \ln T + 2 \ln M - \ln t$ for both data sets. We have shown in a previous study that there is no measurable difference in the glass transition temperature between dry PS and PS saturated in DEG.¹² Therefore, the monomeric friction coefficient was assumed to be unaffected by the presence of DEG in plotting the present data in Figure 8.

The two regimes are clearly visible in both cases. In the disentanglement region, the two data sets show the same gradient, reflecting the common activation volume in the two cases, noted above. It is clear that the effect of the different crazing environment is merely to cause a vertical shift in the curves. This may be attributed to the solvent reducing the interfacial tension of the polymer, and hence the value of the surface energy γ , and would result in a vertical offset of ($\gamma_{PS-air} - \gamma_{PS-DEG}$) A_c/fV_c between the two data sets, according to eq 6. Although we could not find a measurement of the van der Waals



Figure 8. Experimental measurements of craze initiation stress in monodisperse PS: (a) data for varying molar mass polymers in 300 s creep in DEG (this paper, circles); (b) data for varying temperature and strain rate in constant rate tension tests, dry, from Han et al.¹⁸ converted to equivalent creep times (diamonds and squares). In both cases the two regimes are visible: disentanglement crazing (hollow symbols) and chain scission crazing (filled symbols).

surface energy of PS in DEG in the literature, it is interesting to note that for PS in air at room temperature the van der Waals surface energy is $\gamma_{PS/air} = 33 \text{ mN/m}$, and in *n*-pentane it is $\gamma_{PS/}$ *n*-pentane = 16 mN/m.³² A more thorough treatment would need to account for variations in surface energy with temperature and with molar mass, although below T_g and for entangled molecules $(M > 2M_e)$ these effects are small.^{33,34}

Transition from Disentanglement to Chain Scission Crazing. The transition from disentanglement crazing to chain scission crazing is clearly apparent in Figure 8 for both data sets. In the present data it occurs at a value of $\ln \zeta - \ln T + 2$ $\ln M - \ln t \approx 3.6$, and in the data of Han et al. at a very similar value of $\ln \zeta - \ln T + 2 \ln M - \ln t \approx 3.7$, as obtained from the intercept of linear regression lines on the different regions of the data. The near equality of these two figures is remarkable. It implies that the transition occurs at a constant value of $\tau_{\rm R}/t$, irrespective of the presence of the DEG causing a change in surface energy. The physical reason for this is unclear. It requires the DEG-induced vertical shift of the chain scission data to equal that of the disentanglement data. Of course, because of the vertical shift, the stress at the transition is substantially different in the two experiments: $\sigma_c/2T = 26 \times 10^3 \text{ Pa/K}$ in the data obtained in DEG, and $\sigma_c/2T = 77 \times 10^3$ Pa/K in the data in dry PS.

Comparison with Other Literature Data. The earliest analysis of the effects of molar mass on craze initiation was by Fellers and Kee.¹¹ Through room-temperature tensile tests they performed visible craze initiation experiments on a range of dry polydisperse PS with PDI between 2.39 and 3.51 injection-molded into dog-bone specimens. The crazing stresses found were of around 30 MPa, lower than the value of 40 MPa found in our dry crazing measurements.¹² They were also unable to discern any molar mass dependence. Although it is not clear how to extrapolate the craze criterion to a polydisperse material, the data of Fellers and Kee lie significantly to the right of the disentanglement-scission transition in Figure 8, with values of ln $\zeta - \ln T + 2 \ln M - \ln t > 7$, irrespective of which mass average is used. Hence, the lack of molar mass dependence is consistent with the present findings.

The work of Plummer and Donald³⁵ consisted of tensile stretching of monodisperse PS films of two molar masses bonded to copper grids, in a similar manner to that of Han et al.,¹⁸ but with significantly increased scatter in the experimental measurements. The regions of disentanglement and scission are visible, but the exact transition point is difficult to discern with precision.

Multiaxial Stress States. It should be noted that, in general, the free energy barrier to molecular diffusion during craze formation is independently modified by the work done by the mean stress σ_m in both the forward and the reverse directions as well as by the work done in fibril stretching by σ . It is well-known, for instance, that the presence of a hydrostatic compressive stress suppresses crazing and that crazes are difficult to form in a state of pure shear. Expressed as a multiaxial craze initiation criterion, the time scale for craze initiation would be

$$\tau_{\rm c} = \frac{\beta \zeta M^2}{T} \exp\left(\frac{\gamma A_{\rm c} - \sigma V'_{\rm c} - \sigma_{\rm m} V_{\rm p}}{2k_{\rm B}T}\right) \tag{12}$$

where $V'_{\rm c}$ is the activation volume truly associated with craze fibril extension and $V_{\rm p}$ is the pressure activation volume. However, both the present experiments in three-point bending and those of Han et al.¹⁸ in uniaxial tension subject the polymer to a uniaxial remote stress state, and hence a fixed ratio of σ to $\sigma_{\rm m}$, and cannot distinguish between the relative contributions of the activation volumes $V'_{\rm c}$ and $V_{\rm p}$ to craze initiation. In addition, the presence of a growing craze void influences the relationship between the local stress state at the craze tip and the far-field externally applied stresses.

Conclusions

This study has investigated experimentally the effects of chain length, chain architecture, and time on visible environmental stress craze initiation in miniature isochronal creep tests on PS soaked in DEG, in a wider range of well-characterized polystyrenes than were available hitherto. The results indicate that, in linear monodisperse PS in 300 s creep at room temperature in DEG, there are two regions of behavior: solidstate disentanglement for $M < 140\ 000\ g/mol$ and chain scission for $M > 140\ 000\ g/mol$. In the chain scission region craze initiation stress is independent of M. Branched PS follows the same pattern of behavior as linear PS provided that the span molar mass M_s is used in place of M, and shows a slight increase in craze initiation stress in the chain scission region compared with the linear PS.

In the disentanglement region craze initiation can be expressed as an Eyring stress-accelerated flow process with an effective molecular activation volume $fV_c = 1.8 \pm 0.3 \text{ nm}^3$ in which the rate-limiting step is chain retraction that provides the necessary entanglement loss for crazes to form. The same activation volume also accounts for previous measurements of temperature and rate dependence of the tensile craze stress in linear PS tested dry.

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- (36) From this point we use the term "initiated" to mean crazes just became visible under the conditions of the experiment.
- (37) Here we do not consider the entropic changes arising due to stretch of the fibrils since we are concerned with the early stages of craze initiation in isotropic materials. Entropy changes may become significant during craze growth or during initiation in preoriented materials.
- (38) With increasing molar mass, retraction of each chain involves an increasing number of hops, but fewer molecules are required to retract to form one fibril.

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