

A simple viscoelastic model for fatigue crack propagation in polymers as a function of molecular weight

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A simple theory is presented to explain the strong influence of molecular weight (M) on rates of fatigue crack propagation (FCP) in amorphous polymers. It is proposed that the equation describing FCP rates may be expressed as the product of two functions, one involving the stress intensity factor (ΔK), and the other characterizing the relaxation process occurring in the plastic zone. To provide a physical network in the plastic zone that can sustain fatigue loading, it is proposed that one needs a sufficient fraction of molecular fibrils per unit area (W^*) whose lengths are greater than M_c , the critical value of M required for entanglement. This effect can be summarized as a generalized rate process (confined at the plastic zone) expressed by $A \exp(B\sigma)$ where σ is a stress and A and B are constants (B including the volume of activation). It is deduced that M influences the activation volume through the values of W^* and W , the weight fraction of molecules whose $M > M_c$. Using the equation developed it was possible to correlate FCP data of PVC and PMMA as a function of M with a high degree of confidence. Also, the value of activation volumes obtained compared favourably with those in the literature for static tests. The complementary value of W^* for these polymers was also seen to approximate closely to the void fraction in a craze. Extension to other cases such as semi-crystalline materials also seems possible.

(Keywords: fatigue crack propagation; molecular weight; molecular weight distribution; plastic zone; entanglement; rate process; volume of activation)

INTRODUCTION

Molecular weight (M) and its distribution have long been known to be important in determining the flow behaviour and mechanical response of polymers¹⁻⁴. For example, as molecular weight is increased from a low value, a critical value is found beyond which the dependence on M of melt viscosity (ref. 3, ch. 3), strength⁴⁻⁶, and fracture energy^{7,8} increases markedly; eventually the strength and fracture energy begin to level off. Also, a pronounced plateau in compliance begins to appear at long relaxation times (ref. 3, ch. 9). The enhanced resistance to deformation and flow above some such critical value, M_c , has generally been attributed to the ability to form an effective entanglement network; M_c is usually taken to approximately equal $2M_e$, where M_e is conventionally defined as the average molecular weight spacing between entanglements (ref. 1, ch. 10). While the term 'entanglement' is sometimes taken to imply the existence of discrete loci of coupling, no particular topology of coupling is assumed in this paper; M_c and M_e are still useful measures of the extent of coupling between molecules, whatever the precise nature of the interaction.

Examination of the intensity of M dependences reveals a wide variation from property to property. Whereas melt viscosity depends on approximately the 3.4th power of M (for $M > M_c$) (ref. 1, ch. 10), viscoelastic processes, and also the first and second normal stress differences in the melt⁹, show dependences to higher powers, even to the 12th power. Strong effects of M have also been noted on the times to failure by stress-cracking¹⁰⁻¹², and on the stability of crazes⁴⁻⁶. Thus, the strong increase in fracture

energy and tensile strength with increasing M in polystyrene and poly(methyl methacrylate) has been related to the increased stability and strength of crazes as M increases $M_c^{4-6,8,14}$ (see also ref. 13, ch. 9); in contrast, the initiation of crazing is much less dependent on $M^{6,16}$. Interestingly, the introduction of even a small concentration of high- M polystyrene in a matrix containing molecules whose $M (< M_c)$ is too low to give stable crazes, can result in the formation of fibrils effective in spanning the craze faces¹⁵.

Molecular weight and fatigue behaviour

Striking effects of M on fatigue life in unnotched specimens have also been noted for several polymers^{16,17}; (for reviews, see refs. 18 and 19). Even though values of M were high enough that static properties had reached nearly asymptotic values, an order of magnitude difference in M resulted in up to a 3-orders-of-magnitude difference in the number of cycles to failure over a wide range of cyclic stress; the higher M , the greater the lifetime. At about the same time, we reported similar strong dependences of fatigue crack propagation (FCP) rates in poly(methyl methacrylate) (PMMA)²⁰ and poly(vinyl chloride) (PVC)²¹. Consistent with the study of unnotched specimens, large decreases in FCP rates were observed with increasing M , even though values of static fracture toughness varied little over the same range of M . Also, small concentrations of high- M PMMA were found²² to stabilize crack growth in very brittle, low- M PMMA's¹⁵. In any case, it was proposed that at least up to a point, the higher the M , the greater the resistance to

disentanglement under long-term cyclic loading and unloading¹⁹⁻²². In this respect, the effect of fatigue is analogous to that of slow creep or stress relaxation in which high values of M are reflected in a very much delayed response, even above T_g (ref. 3, ch. 9).

In our studies (just cited), it was found that the curves of da/dN , (the crack growth rate per cycle), could be related to the range in the stress intensity factor, ΔK , reasonably well by the Paris equation²³:

$$\frac{da}{dN} = A\Delta K^n \quad (1)$$

In equation (1), $\Delta K = Y\Delta\sigma\sqrt{a}$, where Y is a geometrical factor depending on the specimen design, $\Delta\sigma$ is the range in applied stress, and a the crack length. By comparing values of da/dN at constant ΔK , the following empirical expression was found to relate da/dN at constant ΔK to M^{20-24} (see Figure 1):

$$\left[\frac{da}{dN}\right]_{\Delta K} = A_f e^{B_f/M_x} \quad (2)$$

where M_x is an average M (typically the weight-average M) and A_f and B_f are constants (the subscript f referring to fatigue). Since then, these findings of exceptional enhancement of FCP resistance in high- M polymers have been confirmed here and elsewhere in PVC²⁴ and in many other polymers: high-density polyethylene²⁵, polyacetal²⁶, polyamides²⁶, polycarbonate²⁷ and poly(ethylene terephthalate)²⁸. Indeed, equation (2) holds well in general as long as values of the exponent n in equation (1) are reasonably close to each other. Alternately, one may compare ΔK at a given da/dN . Combination of equations (1) and (2) yields an equation similar to (2):

$$(\Delta K)_{da/dN} = C_f e^{(-D/M_x)} \quad (2a)$$

Of course, when n is constant A_f is proportional to ΔK^n .

In ref. 22 it was shown that FCP rates in PMMA were very much dependent on W , the weight fraction of species having $M > M_c$, where M_c is the critical value of M for entanglement. [It may be noted that Platonov *et al.*²⁹ also recommend the use of W rather than M_x when correlating mechanical response with M .] Based in part on this observation, a simple viscoelastic model is proposed to account for the dependence of FCP rates on M in glassy polymers having unimodal distributions of M , and possible extensions to other systems are suggested. The model leads to good predictions of FCP behaviour in PMMA and PVC, justifying equation (2), (at least within the range of M considered here) and, by analogy, the model fits some other viscoelastic responses as well. This paper revises preliminary results presented earlier³⁰, and presents a more complete analysis. (For discussion of an alternate approach, see Appendix 1.)

EXPERIMENTAL

For this study, PVC and PMMA were selected, FCP data were taken from refs. 20 and 24, and distributions of M (MD) were re-examined using a Waters gel permeation chromatograph (g.p.c.), model 200A. The data were analysed to obtain several molecular weight averages (M_n ,

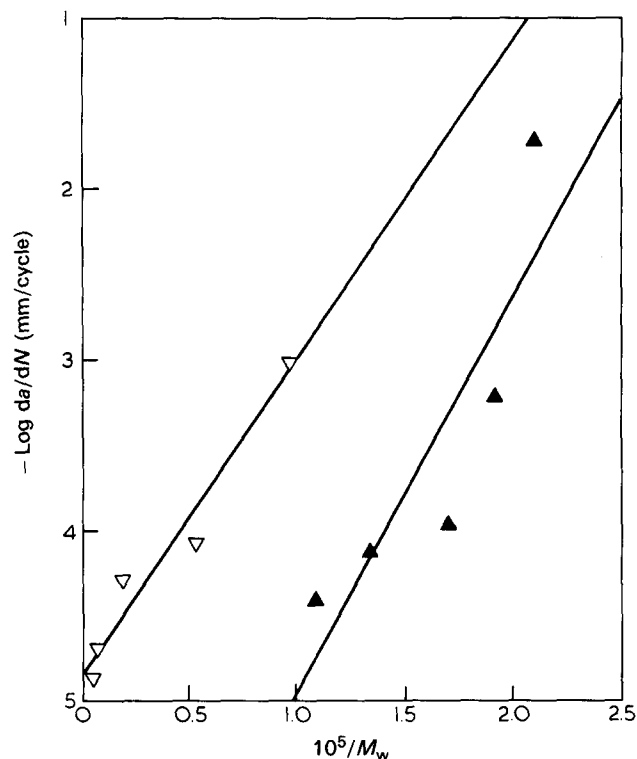


Figure 1 Log FCP rate vs. $10^5/M_w$ (\blacktriangle) PVC and (∇) PMMA FCP data from refs. 24 and 20 respectively

M_w , M_z), and integral distributions were obtained by a Simpson procedure. Values of the cumulative weight fraction I_w and I_z fraction were also evaluated by interpolation (using Lagrange polynomials) at assumed values of M_c .

W , the weight fraction of molecules having $M > M_c$, is equal to $(1 - I_w)$; the values of W were also estimated using equation (3a) for PVC:

$$W = \exp\left[-1.46\left(\frac{M_c}{M_w}\right)^{1.946}\right] \quad (3a)$$

With PVC, a correlation factor of 0.99 was found, assuming $M_c = 22000$ (a value justified below). For PMMA a similar expression is valid for our low-to-medium- M specimens ($M < 6 \times 10^5$), for an M_c of 30000:

$$W = \exp\left[-0.038 \exp\left(\frac{+5.143M_c}{M_w}\right)\right] \quad (3b)$$

A comparison of W values is given in Table 1, along with values of M_w , which gave the best correlations with the various parameters discussed below. W^* , the critical value of W required to sustain plastic deformation, was estimated by plotting the relative fracture surface energy, γ/γ_∞ (where γ_∞ is the value of γ in the limit of very high M) vs. W , and locating the intercept on the x-axis (see below). The molecular weight corresponding to W^* , M^* , was then estimated using equations (3a) and (3b) for PVC and PMMA, respectively.

It should be noted that a universal calibration method³¹ including the Ptitsyn correction for non-Gaussian swelling³² was used to take into account the fact that g.p.c. screens with respect to hydrodynamic volume, not M . The values for the Mark-Houwink constants (K and a) are reported in Table 1 together with molecular weight

Table 1 Characteristics of polymers used

PMMA ⁽²⁰⁾ $M_c = 30,000$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$W(\text{g.p.c.})$	$W(\text{Eqn. 3b})$
$\Phi 0$	2.96	17.7	0.991	—
$\Phi 1$	3.73	13.4	0.996	—
$\Phi 2$	5.37	12.4	1.00	—
$\Phi 3$	1.19	5.07	0.949	0.950
$\Phi 4$	0.74	1.92	0.919	0.919
$\Phi 5$	0.50	1.05	0.857	0.848
$\Phi 6$	0.34	0.75	0.734	0.744
PVC ⁽²⁴⁾ $M_c = 22,000$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$W(\text{g.p.c.})$	$W(\text{Eqn. 3a})$
131.1	1.87	4.79	0.704	0.724
132.1	2.46	5.26	0.776	0.764
133.1	2.88	5.93	0.816	0.808
134.1	3.50	7.51	0.880	0.874
135.1	4.14	9.2	0.909	0.910

Mark-Houwink Constants Used (THF, 25°C, $[\eta]$ in dl/g)				
Polymer		$K \times 10^4$	a	Ref.
PS	$M > 10^4$	1.45	0.7	69
	$M < 10^4$	9.0	0.5	
PMMA	$M > 31,000$	1.04	0.697	70
	$M < 31,000$	21.1	0.406	
PVC	—	1.63	0.766	70

information. No corrections for broadening or skewing were applied. Although the lack of such calibration in earlier results^{20,22,24,67} does not affect the qualitative conclusions discussed above, such correction is obligatory for quantitative discussions.

On the choice of M_c . Operationally, M_c is usually taken to be the value of M at which the dependence of melt viscosity on M changes from the first to 3.4-th power. As noted in the introduction, M_c is often related to $2M_c$. However, there are major exceptions (for example, PMMA) in which the proportionality factor may be as high as 3. Also, in terms of a limiting molecular weight at which the entanglement network starts to manifest itself in mechanical properties, controversy also exists. For example, a 'zero' tensile strength (no plastic deformation) was observed by Gent and Thomas⁵ to appear for $M_n \approx 2M_c$ (although the zero strength for PMMA is approached for a value of M_n of about 25 000 in the range of M_c). Kusy and Turner suggested⁸ a critical M for PMMA of 10^5 , past which plastic deformation would occur ($\sim 3M_c$). Also the limit of tensile strength for small films¹⁵ is invariably achieved at a lower M than with a thicker sample^{5,6}. Therefore values of W and Z were evaluated at different values of M_c ; justification for the M_c values preferred is given below (see Discussion: The role of molecular weight).

RESULTS AND DISCUSSION

First let us assume that the mechanism of failure is dominated by a viscoelastic relaxation process, e.g. creep or stress relaxation¹⁰. This assumption is surely reasonable for an amorphous polymer in which most of the specific fracture energy reflects plastic deformation rather than bond rupture. To wit, healing experiments conducted on broken specimens of PMMA and PMMA-SAN show that the original fracture toughness of the

virgin specimen can be restored if sufficient time is allowed for healing of the crack past T_g^{33} . Since disentanglement is inherently reversible while primary bond rupture is essentially irreversible³⁴, a significant amount of molecular fracture would be reflected in a drop in the maximum recoverable fracture toughness. In any case, the formalism developed below should not be affected by the occurrence of some bond rupture (see below).

Bringing in the accelerating affect of the driving force implicit in ΔK , we then consider that da/dN can be expressed as the quotient of two terms, one a function of ΔK and the other an M -dependent characteristic time, τ_f , that reflects the resistance to chain disentanglement:

$$\frac{da}{dN} = f(\Delta K) \cdot \frac{1}{\tau_f} \quad (4)$$

Thus, the test parameter $f(\Delta K)$ reflects the effect of applied force *per se*; the material parameters τ_f reflects the response of the molecular network involved and thus depends both on M and on the loading conditions.

Now the question is: How is τ_f related to M ? Experience suggests some kind of exponential dependence; indeed Rudd¹⁰ described the relaxation behaviour of PS to failure as:

$$\tau_s = A_s e^{B_s M_w} \quad (5)$$

where τ_s in this case is the time to failure, and A_s and B_s are constants (the subscript s referring to static loading). However better agreement with Rudd's data is achieved by use of the following equation, especially when $M_w/M_n > 2$:

$$\tau_s = A_s e^{-B_s/M_w} \quad (6)$$

Equation (6) also leads to values of τ_s that are more physically realistic when M is infinite or very small. We suggest, therefore, the following general relationship

between τ and M :

$$\tau = A e^{-B/M_x} \quad (7)$$

where M_x may be, for example, M_n , M_w or M_z .

Another interesting precedent exists for an exponential dependence of τ on M ; a digression illustrates the usefulness of such a relationship. In a detailed study of relaxation in the melt, Prest and Porter³⁵ analysed the behaviour of blends of narrow-MD PS. They considered that $\eta_0 \cdot J_e^0$ (the product of the zero-shear viscosity, η_0 , and the equilibrium compliance, J_e^0) could be taken as a measure of the time-scale of relaxation of the high- M components ($\eta_0 \cdot J_e^0$ has, of course, the dimension of time).

Now taking $\eta_0 \cdot J_e^0$ as τ_v and constants A and B in equation (7) as A_v and B_v (the subscript v referring to viscous flow), a plot of the data following equation (7) was found to give an excellent fit, especially when M_z was used (Figure 2). If we assume that η_0 can be related to M_w by the expression³ $\eta_0 = A' M_w^D$ (where A' is a constant and $D \approx 3.4$), substituting for η_0 in equation (7), and taking logarithms, we obtain:

$$\ln J_e^0 = C - D \ln M_w - B_v/M_z \quad (8)$$

where the constants can also be determined by multilinear regression analysis.

A plot using equation (8), (Figure 3a) gives better agreement with experimental results than several other treatments³⁶⁻³⁹ and fits as well as the sophisticated treatment of Soong *et al.*⁴⁰ (not shown). The data of Akovali for PS⁴¹ were also found to follow equation (8), (Figure 3b).

Since J_e^0 is difficult to describe analytically in terms of

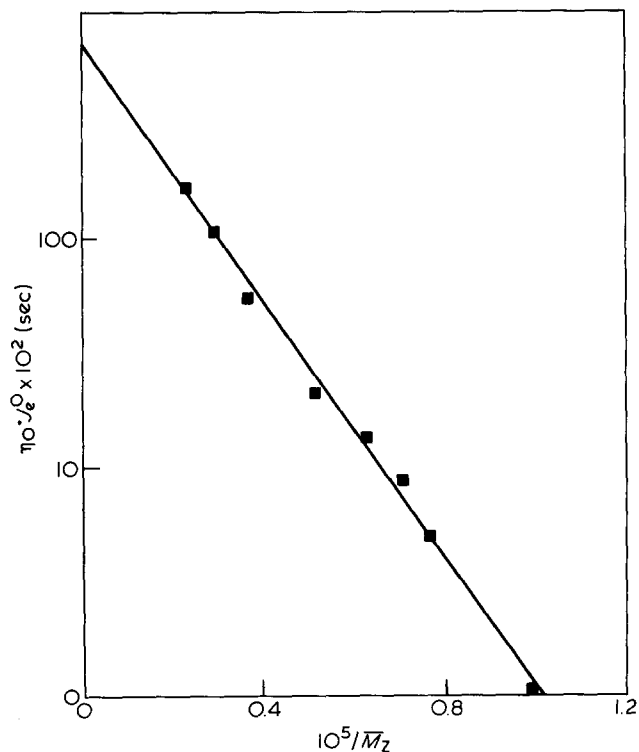


Figure 2 Steady-state melt relaxation time $\tau_v (=J_e^0 \cdot \eta_0)$ vs. $1/M_z$ for bimodal blends of PS at 192°C. Experimental data from Prest and Porter (■)³⁵. $A_v=6.542$, $B_v=6.433 \times 10^5$

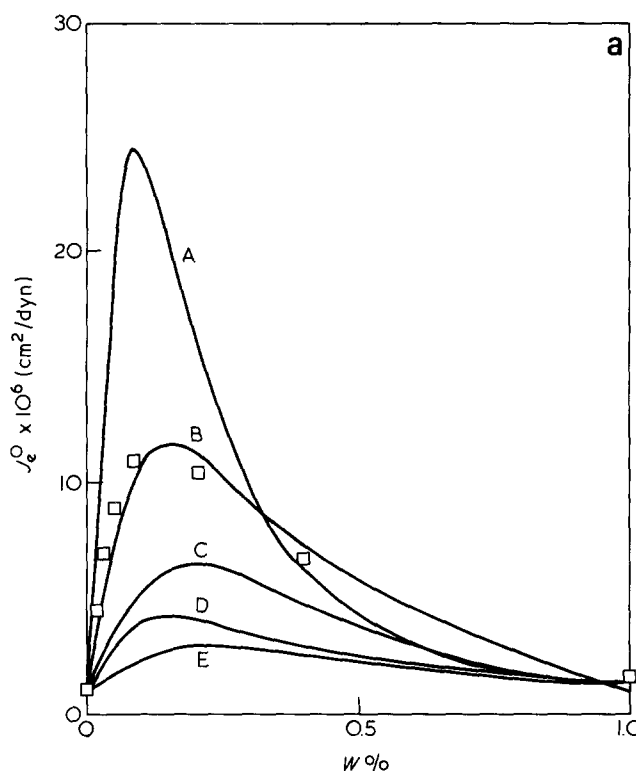


Figure 3a Steady-state shear compliance, J_e^0 vs. weight fraction of the high- M component for bimodal blends at 192°C. Experimental data (■) from Prest and Porter³⁵. Curves A, C, D and E use approaches from refs. 37, 38, 36 and 39, respectively. Curve B, based on equation (8) of this paper is also approximated closely by the treatment of Soong *et al.*⁴⁰ $C=45.843$, $D=3.414$, $B_v=6.433 \times 10^5$ or $C=44.813$, $D=3.327$, $B_v=6.349 \times 10^5$ (multilinear regression)

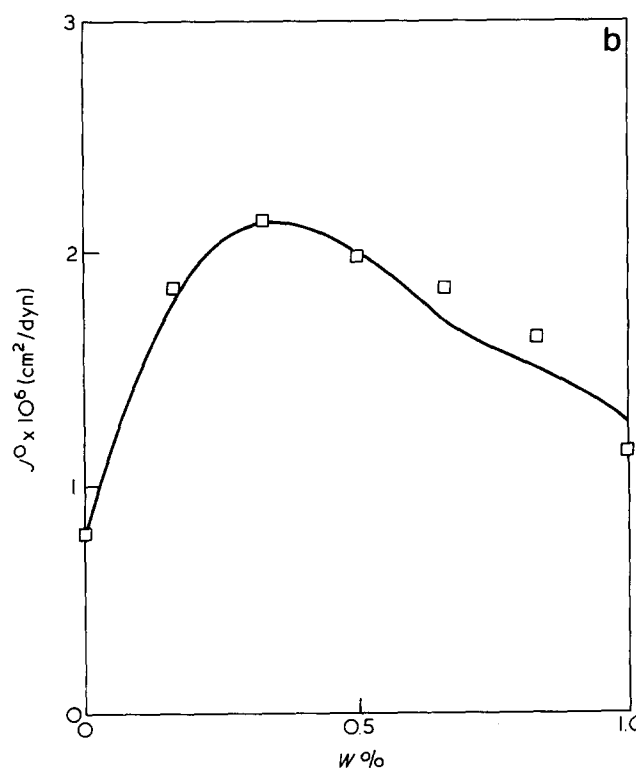


Figure 3b Steady-state shear compliance, J_e^0 vs. weight fraction of the high- M component for bimodal blends of PS at 129°C. Experimental data (■) from Akovali⁴¹. $C=40.39$, $D=3.032$, $B_v=6.317 \times 10^5$ (multilinear regression)

M^{40} , the suitability of equation (8) is gratifying, at least in the range of M covered. To be sure, equation (8) cannot hold for extremely high values of M . This is because equation (7) predicts an asymptotic limit for τ so that after reaching a maximum, J_c^0 will decrease rather than level off as reported in literature¹.

Considering the flow behaviour of the polymer in the melt as analogous to the relaxation behaviour in the plastic zone ahead of the growing fatigue crack, we note that the value for B_v of 6.43×10^5 is within the range for B_f found in fatigue— $(5-8) \times 10^5$. Thus the effect of M on the fatigue process appears to be analogous to that observed in static relaxation or viscoelastic processes in the melt.

Fatigue as a rate process

Many failure processes involving either bond breakage or plastic deformation can be expressed (see refs. 13, ch. 3; and 42) in a form of the Zhurkov equation⁴³:

$$\tau = \tau_0 \exp[(U_0 - V\sigma)/RT] \quad (9)$$

where U_0 is the energy of activation for the failure process, V a characteristic volume (often termed γ , the 'activation volume'), σ the applied stress, and τ_0 a constant. In the case of failure by crack propagation (which is preceded by formation of a plastic zone ahead of the crack), τ is envisioned as a time related to the life-time of a given plastic zone. [Although τ may be biased by the influence of K or ΔK , the time of formation of the plastic zone (typically a craze) is negligible compared to its lifetime⁴⁴, so that equation (9) should still be followed. The initiation of crazes is independent of M , while their propagation is strongly dependent¹⁶.]

For sinusoidal loading ($\sigma = \sigma_m + \Delta\sigma \sin \omega t$), the lifetime τ_f (or an unnotched specimen) has been expressed in terms of the mean stress, σ_m , and stress range, $\Delta\sigma$, as^{45,46}:

$$\tau_f = \tau_0 \frac{\exp(E_a/RT) \cdot \exp(-V\sigma_m/RT)}{I_0(V\Delta\sigma/RT)} \quad (10)$$

where E_a is the apparent energy of activation, τ_0 and V are defined as in equation (9), and I_0 is a zero-order modified Bessel function⁴⁵. For a wide range of σ (up to $0.9 \times \sigma_y$, the yield stress), fitting shows⁴⁷ that equation (10) can be expressed as the following analogue to equation (9):

$$\tau_f = A' \exp(-V'\sigma_m/RT) \quad (11)$$

where V' is an apparent activation volume. For data on PMMA^{46,48} and PVC⁴⁹, equation (11) was found to hold at a high level of confidence (≈ 0.99).

Now V' must depend on the stress-wave characteristics, though we do not know how the stress wave is translated into the stress sensed in the plastic zone. In fact, the Bailey criterion (equivalent to Miner's rule for the accumulation of damage during cycling) may not hold very well⁴⁶. For the present purposes, we have assumed that the applied mean stress acting on the plastic zone is reflected in a localized quasi-static stress $\sigma_{m,y}$ defined as $\sigma_{m,y} = \sigma_y X(1+R)/2$, R being the ratio of minimum to maximum load. (For use of $\sigma_{m,y}$, see below.) Here it is understood that $\sigma_{m,y}$ and the state of the plastic zone are independent of ΔK , as should be the case if negligible hysteretic heating occurs at the crack tip and if the increase in strain rate associated with an increase in ΔK

has a negligible effect on the state of the plastic zone. However, A' must depend on ΔK to account for the dependence of τ_f on the applied stress and hence on ΔK .

Combining equations (11) and (4) and replacing σ_m by $\sigma_{m,y}$, we then have

$$\frac{da}{dN} = f'(\Delta K) \exp(V'\sigma_{m,y}/RT) \quad (12)$$

where $f'(\Delta K) = f(\Delta K)/A'$. Equation (12) relates the FCP rate to the activation volume and parameters that characterize local and remote stresses. [For a discussion of an alternate approach in terms of an activation surface, see Appendix 2.]

The role of molecular weight

One may expect that the effect of M on da/dN should be manifested through the activation volume, V' ; the larger M , the lower V' should be, since the molecules effective in resisting crack growth should be packed more effectively (see the discussion below). If V'_∞ is the limiting activation volume for very large values of M , we may define V' as $V'_\infty/\psi(M)$, where $\psi(M)$ reflects the fraction of molecules that can form effective entanglements under the load concerned (a quantitative expression for $\psi(M)$ is deduced below). Assuming that σ_m is independent of ΔK , and that σ_m is translated into the average effective stress $\sigma_{m,y}$ in the plastic zone, equation (12) then becomes:

$$da/dN = f'(\Delta K) \exp[\sigma_{m,y} V'_\infty / RT \psi(M)] \quad (12a)$$

$$= f'(\Delta K) \exp[C_f / \psi(M)] \quad (12b)$$

where C_f is a constant at a given temperature, strain rate and frequency.

To relate $\psi(M)$ to the distribution of molecular weight, it is convenient to consider the effect of the distribution on the activation volume. For flow and fracture processes, Eyring and Tobolsky^{50,51} have defined V in terms of N_0 , the number of bonds per stressed unit area, and λ , the distance between equilibrium positions of a bond in the initial and stressed states. Thus $V = \lambda/2N_0$, where $\lambda/2$ is the distance along the reaction coordinate to the peak of the potential-energy barrier. For the purpose of this study, N_0 is taken as the number of molecular strands from these molecules having $M > M_c$ that intersect a unit area prior to stressing. A strand consists of a number of mers (two to three) which participate actively in the entanglement. The ratio of the number of entanglements formed to the number of possible active sites is equal to p and is independent of M . It is a function of the molecular structure in particular the cross-sectional area of the mer; p is also equal to the ratio of one active area to the area of one entanglement spacing. Hence $N_0 p$ represents the number of entanglements formed by the molecules whose length is in principle sufficient to transmit the stress experienced in the plastic zone, i.e. experienced during yielding. The state of the system may be assumed to be that encountered at the T_g ⁵², or even above T_g (by analogy with the strong effect of M on, for example, stress relaxation at long times).

However, if plastic deformation is to be sustained, it is reasonable to consider that a minimum value exists for N_0 ; this minimum value may be termed N^* , which is expected to be a function of T and strain rate. This

concept has been previously expressed by Bokshitskii⁵³, and by Scanlan⁵⁴ in discussions of chemorheological behaviour involving the rupture of primary bonds. Hence the number of strands that are actually effective becomes $(N_0 - N^*)$, and below the threshold value N^* , catastrophic rupture may be expected. Also, in general N_0 will be less than N_∞ , the maximum number of potentially load-bearing strands that can be accommodated per unit area. Thus the maximum possible number of effective strands becomes $(N_\infty - N^*)$. As we shall see, both V' and $\psi(M)$ can be related very simply to the magnitudes of N_0 , N^* and N_∞ . In terms of the unit area, then the area defined by $1/N_\infty$ is the minimum area per load-bearing strand.

We may now define V' (or actually V'_M , the value of V' for a given M) in terms of the proportion of *actually effective* load-bearing strands, i.e., those that not only can take part in entanglements but also are effective in resisting the load:

$$V'_M = \frac{\lambda}{2(N_0 - N^*)} = \frac{\lambda}{2(N_0 - N^*)} \cdot \frac{(N_\infty - N^*)}{(N_\infty - N^*)} \quad (13a)$$

and

$$V'_\infty = \frac{\lambda}{2(N_\infty - N^*)} \quad (13b)$$

Following our earlier definition of $V'_M = V'/\psi(M)$, then

$$\psi(M) = \frac{N_0 - N^*}{N_\infty - N^*} \quad (14)$$

Thus $\psi(M)$ adjusts the activation volume to reflect the proportion of molecules that can actually participate in effective entanglement networks and in resisting deformation and failure.

Of course it is convenient to work with such accessible quantities as the weight fraction. The actual number of entanglements per unit area $N_0\rho$, is equal to $N_\infty\rho$, its maximum possible value, multiplied by a dilution factor resulting from the fact that only those molecules greater than M_c share the load in the plastic zone. Since it is now established⁵⁵ that in the bulk we are in a state of association of molecules similar to the one of a θ -solvent the area occupied by one molecule is equal to $k_0 M_i^2$, (k_0 in $\text{nm g}^{-1/2} \text{ mole}^{1/2}$) and here we neglect the change of the first power dependency on M to around 1.2 occurring at very low M . We can thus relate $N_0\rho$ to $N_\infty\rho$ as follows:

$$N_0\rho = N_\infty\rho \left(\frac{\sum_{M_i > M_c} n_i k_0 M_i^2}{\sum_{i=0}^{\infty} n_i k_0 M_i^2} \right) \quad (15)$$

This can in turn be written approximately as

$$N_0 = N_\infty W \quad (16)$$

Because N_∞ is fixed by the polymer chemistry, a unique value of W , W^* , corresponds to N^* . The complementary value of W^* , $1 - W^*$, can be related to the number-average of the areas which do not carry load under post-yielding conditions and is in effect the void fraction if crazing is going on. Equation (14) then becomes:

$$\psi(M) = \frac{W - W^*}{1 - W^*} \quad (17)$$

In effect we take all entanglements to be equivalent dissipators of energy. This means that perfectly monodis-

perse samples having $M > M_c$ should behave similarly in FCP or impact tests, regardless of M . The effect is the same as if a single relaxation time governs the disentanglement process. Experiments on narrow-MD polystyrene in progress should allow us to test this assumption. Each quantity in equation (17) can be determined experimentally: $(1 - W)$ by g.p.c. or from equation (3); as shown below, W^* is found by extrapolating values of fracture surface energy, γ , vs. W to $\gamma = 0$.

Thus $\psi(M)$ may also be taken to be the variable that governs the variation of the fracture surface energy γ with M . Kusy and Turner⁸ have related γ to the Griffith fracture energy, γ_0 , as follows:

$$\gamma = \gamma_0 + W\gamma_\infty \quad (18)$$

where γ_∞ is for the limiting case of $M \rightarrow \infty$ or $W = 1$. We suggest using $\psi(M)$ instead of W , so that

$$\gamma = \gamma_0 + \psi(M)\gamma_\infty \quad \text{and} \quad (19)$$

$$\gamma \approx \psi(M)\gamma_\infty$$

for high values of M . In equation (19), $\gamma = \gamma_0$ at a value of M , M^* , corresponding to W^* ; Kusy and Turner in effect took W^* to equal zero whereas we take W^* to be finite. It must be recognized that γ_0 is not a finite constant, but varies with M albeit slowly as revealed by the experimental work of Robertson⁵⁶ and in the theoretical treatment of Kramer⁵⁷ or Kusy and Katz⁵⁸. However, at $M = M^*$, γ is around $0.01\gamma_\infty$, the extrapolation procedure is then justified and gives us an estimate of M^* , the M at which cooperative energy dissipation due to entanglements becomes possible.

Combining equations (12b) and (17), we obtain the following

$$\frac{da}{dN} = f(\Delta K) \exp \left[C_r \frac{(1 - W^*)}{(W - W^*)} \right] \quad (20)$$

which expresses the FCP rate in terms of a function of the applied stress and a function of the fraction of molecules that can form entanglements that are effective in resisting cyclic loads. Of course, the choice of M_c will bear on W^* . We believe that $(1 - W^*)$ should compare with the void fraction in a range under similar conditions as reported in the literature. Table 2 summarizes different values of W^* and Z^* obtained using equation (19) with W or Z , the Z fraction of molecules greater than M_c , respectively together with published void contents. The use of W stems

Table 2 On the choice of M_c (isotropic polymer)

2a. PMMA void content (reported: 0.4)⁽⁶⁶⁾

$M_c \times 10^{-4}$	3	4	6	8	10
$1 - W^*$	0.34	0.5	0.73	—	—
$1 - Z^*$	—	—	0.30	0.45	0.6

2b. PVC void content (reported: 0.56 to 0.64)⁽⁶⁸⁾

$M_c \times 10^{-4}$	1	2	2.2	2.6	3
$1 - W^*$	0.21	0.53	0.59	0.71	0.82
$1 - Z^*$	0.03	0.14	0.17	0.24	0.32

from this comparison and the use of $M_c = 22\,000$ for PVC and $M_c = 30\,000$ for PMMA seems plausible.

While the value of 30 000 for the M_c for PMMA agrees well with values from literature (ref. 1, p. 378; and ref. 59) unequivocal values for the M_c of PVC are apparently not available. Recently values of 7500⁶⁰ and 5800⁶¹ have been used, but the former is calculated (and subject to possibly large error) and the source of the latter is not given. From the review of Porter and Johnson⁶² one can infer an M_c of around 6250 from experiments in dilute solution (6.5% PVC in cyclohexanone). However, values could be much higher. For example using Van Krevelen's correlation (ref. 63, pp. 259 and 246) one can calculate an M_c of 12 500 for PVC. Also Kaelble⁶⁴ gives an M_c of 6500 (no source) which implies an M_c of from 13 000 to possibly 19 500. Finally, from a study of Edwards and Collins⁶⁵ on the viscosity of PVC melts vs. \bar{M}_w at different shear rates, an M_c close to 20 000 can be inferred.

Thus, although the critical molecular weight necessary for the onset of cooperative dissipation due to entanglements in the plastic zone in FCP under tension-tension loading is not necessarily equal to the M_c derived from viscosity measurement in shear vs. \bar{M}_w , the values are not far apart.

Tests of the model

Values of W and W^* . As shown in Table 1, values of W determined from the g.p.c. data agree well with values determined using equation (3). Since values of γ for PMMA could be estimated from data in ref. 20, W^* was determined for PMMA by expressing $\psi(M)$ as $[-W^*/(1-W^*)] + [W/(1-W^*)]$. Assuming that γ_0 is negligible in comparison to γ_∞ , a plot of γ/γ_∞ vs. W was used to verify the validity of equation (19), i.e., whether or not W^* is in fact a finite quantity. Using a value of 2.6×10^2 J/m² for γ_∞ ²⁰, the following relationship was obtained (Figure 4):

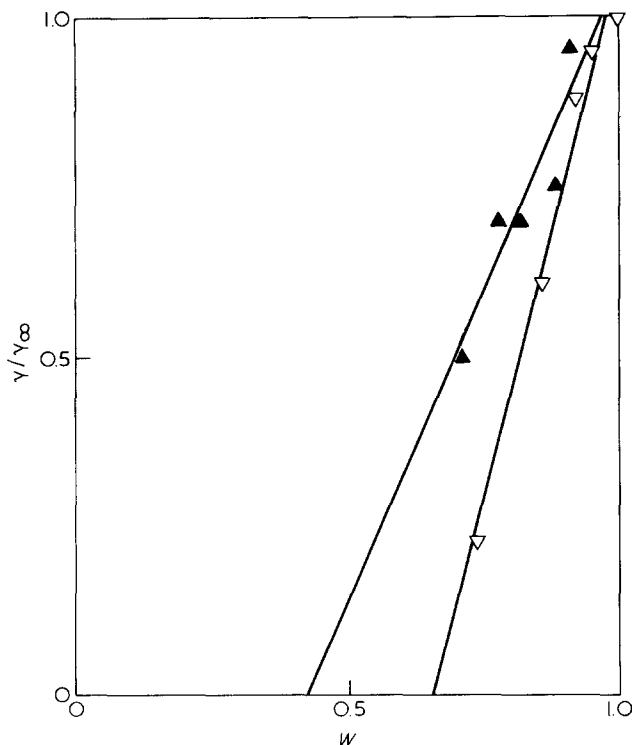


Figure 4 Relative fracture energy, γ/γ_∞ , vs. wt. fraction species having $M > M_c$; (\blacktriangle) PVC and (∇) PMMA

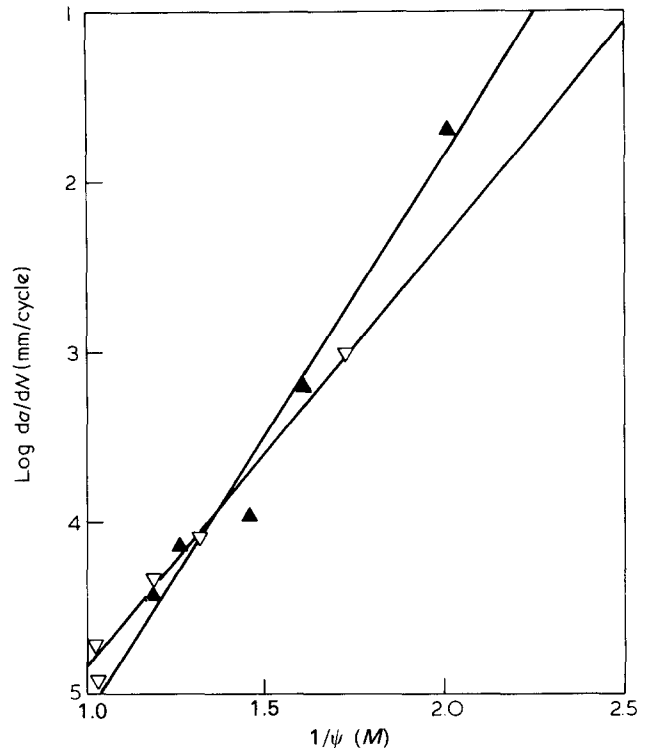


Figure 5 Log FCP rate vs. $1/\psi(M)$; (\blacktriangle) PVC and (∇) PMMA; $1/\psi(M)$ from equation (23)

$$\gamma/\gamma_\infty(\text{PMMA}) = (-2.01) + (3.08W) \quad (21)$$

The fact that the intercept is negative $[-W^*/(1-W^*)]$ confirms that W^* is a positive number, as proposed. The value of W^* itself may be obtained from the intercept, from the slope, or by setting $\gamma = 0$; the average of all three values is $0.66 (\pm 0.01)$. This value seems quite reasonable, for the corresponding value of M_w , 6.5×10^4 , is close to the minimum M_w required to effectively bear a load, as judged by the minimum M_w required to achieve machinability of a specimen²². Also, the value of $(1-W^*)$ 0.34 agrees well with the estimate of 0.40 for the void fraction in a typical PMMA craze⁶⁶.

In the case of PVC, accurate values of γ over a wide range of M were not available; the data in refs. 21 and 24 are believed to be too high, due to delamination during testing, and insufficient data are found in other literature. An estimate of 0.5 for γ/γ_∞ was therefore taken for the lowest- M sample studies by analogy with relative impact strengths from ref. 67. Figure 4 then yields the following relationship:

$$\gamma/\gamma_\infty = -0.74 + 1.8W \quad (22)$$

The value found for W^* is 0.41; its complementary value 0.59 falls in the range of the value reported by Ishikawa *et al.*⁶⁸ for a PVC range at 303 K (0.56 to 0.64), it corresponds to a M_w^* of 28 000 with this assumed MD.

Fitting of fatigue data. Taking FCP data^{20,21,24} for PMMA and PVC [at $\Delta K = 0.6$ and 0.8 MPa \sqrt{m} , respectively], and fitting to equation (12b) ($C_I = B_I'$) we have (see Figure 5):

$$\ln(da/dN) = A_I' + B_I'/\psi(M) \quad (23)$$

As is evident from Table 3, the fit is excellent. Now we may work backwards to see if we can obtain the empirical

equation (2) by determining $\psi(M)$ as a function of M_w and substituting for $\psi(M)$ in equation (23). In fact the following equation holds well (see Table 4 and Figure 6) for the range in M considered:

$$1/\psi(M) = A'' + B''/M_w \quad (24)$$

Substituting equation (24) in equation (23), we obtain:

$$\ln(da/dN) = A_f'' + B_f''/M_w \quad (25)$$

The coefficients in equation (2) and (25) are compared in

Table 3 Coefficients for FCP rates as a function of $\psi(M)$ ^a

Polymer	A_f'	B_f'	Confidence level
PMMA ($M_c=30000$)	-16.70	5.70	0.99
PVC ($M_c=22000$)	-19.33	7.52	0.98

^aFollowing equation(23)

Table 4 Coefficients for $1/\psi(M)$ as a function of $1/M_w$

Polymer	A''	B''	Confidence level
PMMA	0.979	7.45×10^4	0.99 ^a
PVC	0.254	7.69×10^4	0.94

^aCorrelation excludes sample $\Phi 6$, which was too brittle to test

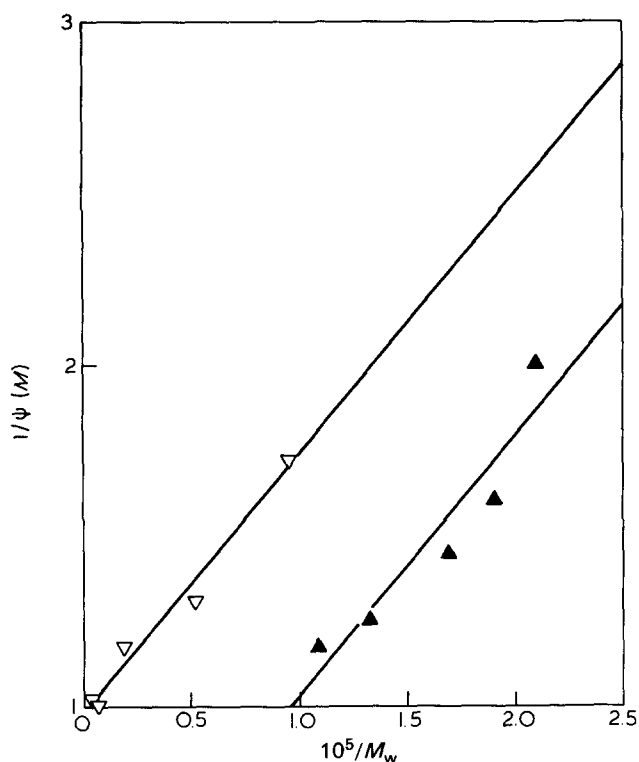


Figure 6 Relationship between $1/\psi(M)$ and $10^5/M_w$; (\blacktriangle) PVC and (∇) PMMA

Table 5 Comparison of coefficients in fatigue crack propagation equations (2) and (24)

Polymer	A_f'' (Eqn (25))	$\ln A_f$ (Eqn (2))	B_f''	B_f (Eqn (2))	Confidence Level (Eqn (2))
PMMA	-11.20	-11.24	4.25×10^5	4.48×10^5	0.97
PVC	-17.42	-16.90	5.78×10^5	5.46×10^5	0.87*

* The fit is better when \bar{M}_n is used ($r = 0.975$)

Table 5. The good agreement not only verifies self-consistency but also supports the interpretation of the empirical equation (2) in terms of the molecular weight distribution relative to the requirements for stable entanglement networks. [It should also be noted that equation (23) gives more realistic predictions at very low M than equation (2). For example, with $\bar{M}_w = 50000$ and the same MWD as the series ϕ , equation (2) predicts a finite value for da/dN , while equation (23) predicts catastrophic rupture, as is found.]

Finally, we can observe from the values of ψ achieved by the highest M of PMMA (ϕ_0) and PVC 135.1, that while the FCP resistance for high M PMMA has been saturated the FCP resistance for PVC can still be increased (up to threefold) over the highest M reported here.

Activation volumes. Additional support for the interpretation proposed in equation (20) may be obtained by examining values found for the activation volume. While one should not expect values of activation volume to necessarily be equal in static and cyclic experiments, one might suppose that they would have the same order of magnitude. If we consider equation (12) \equiv equation (12b), we can calculate values of V' and compare them with values of V from static experiments or V' assuming sine wave loading (see equation (11)). The calculated values in Table 6 are based on the use of the stress defined above as $\sigma_{m,y}$. The values of V and V' from FCP are within a factor of 2, and the assumption of quasi-static stress seems to be better than the sine-wave assumption. Note also that each value of V' is higher for PVC than for PMMA — as is found for V . Thus the use of quasi-static stress in calculations based on cyclic loading gives values of activation volume that are close to those for static loading. It should be emphasized again that the values of the constants in equations (2), (23), (24), (25) are only valid for the experimental conditions of refs. 20, 21, 22, 24, 67 — namely, frequency of 10 Hz, room temperature, sinusoidal loading and $R = 0.1$ (ratio of minimum to maximum load).

Possible extensions. While the treatment proposed is developed for amorphous polymers having unimodal distributions of M , it should be possible to extend it to other cases such as bimodal distributions as in homopolymer blends²² and crystalline polymers. With the latter, a major effect of M may be manifest through the stability of the tie sequences between crystallites. Indeed preliminary calculations that take account of the crystalline morphology suggest that extending to the crystalline case is possible⁴⁷. Also consideration of the influence of the external variables (frequency, ΔK , temperature, stress wave function) would be very informative.

CONCLUSIONS

Several conclusions may be drawn:

Table 6 Comparison of activation volumes in fatigue and static deformation

Polymer	v^a	v^b	$V' (\sigma_m, v)^c$
PMMA ($M_w = 2.10^5$)	574	—	—
$\sigma_y = 81$ MPa	673	1180	420
PVC ($M_w = 6 \times 10^4$)	1740	3040	900
$\sigma_y = 55$ MPa			

^a The values given in descending order in the column are from refs. 48, 46 and 49, respectively; units in $m^3/g\text{-mole} \times 10^6$ under static loading

^b From the values of column 1, using equation (11)

^c By identification of equation (12a) and (12b)

(1) The empirical dependence of FCP rates on $\exp(B/M)$ in PMMA and PVC can be interpreted in terms of W , the fraction of molecules whose $M > M_c$, and W^* , the minimum fraction of such molecules required to form a crack-resisting network, the value of $1 - W^*$ comparing favourably with the void fraction in a craze.

Specifically, $(da/dN)_{\Delta K}$, the crack growth rate per cycle, can be related to these parameters as follows: $(da/dN)_{\Delta K} = A_f \exp[B_f/\psi(M)]$, where $\psi(M) = (W - W^*)/(1 - W^*)$.

(2) The function $\psi(M)$ also appears to control the activation volume in fatigue and the fracture surface energy.

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 70 ASTM Standard Method D3593.77, Table X3

APPENDIX 1

In a recent dimensional analysis^{A1} of the relations existing between healing, fracture, self-diffusion and fatigue of random-coil polymer, R. P. Wool proposes that da/dN is merely proportional to the quotient of the distance of interpenetration X to the time, t_∞ , necessary for complete diffusion of the molecules for complete interpenetration. Since X is proportional to $M^{0.5}$ and t_∞ is proportional to M^3 (if a reptation model is assumed), then Wool suggests that da/dN is proportional to $M^{-2.5}$. However, analysis of FCP data reported in this paper according to this model, gives always poorer fitting.

- A1 Wool, R. P. *Polymer Prepr.* 1982, **23**(2), 62

APPENDIX 2

Pollet and Burns^{B1,B2} have suggested that static stable crack propagation can be explained in terms of an

activation process whose characteristic parameter is a surface (area) that is inversely proportional to G , the strain energy release rate. The surface would then be inversely proportional to K^2 (in general, $G \propto K^2/E$)

$$\frac{da}{dt} = v_0 \left(\frac{G}{G_{ic}} \right)^{\frac{C(T)}{kT}} \simeq v_0 \left(\frac{K}{K_{ic}} \right)^{\frac{2C(T)}{kT}} \quad (B1)$$

where v_0 = maximum possible crack speed at temperature T , G_{ic} is the critical strain energy release rate (for the opening mode), and $C(T)/G$ is the activation area.

This equation resembles the Paris law, but effectively normalizes da/dt with respect to the static fracture toughness, K_{ic} . However, the slope implied in a plot of $\ln da/dt$ vs. $\ln \Delta K$ [i.e., $2C(T)/kT$] would be very sensitive to M for both activation volume and activation area must be sensitive to the defect concentration and hence to the concentration of chain ends of non-entangled species. In fact this prediction does not agree with experimental findings²⁴; the slopes are not very dependent on M . Thus our assumption that the activation volume is independent of ΔK appears to be reasonable, at least with the experiments discussed in this paper. Also in our case the activation process is explicitly confined in the plastic zone.

- B1 Pollet, J. C. and Burns, S. J. *Int. J. Fracture* 1977, **13**, 667
 B2 Pollet, J. C. and Burns, S. J. *Int. J. Fracture* 1977, **13**, 775