By inserting relation 10 in the relation $s \sim c\xi^2$, the sedimentation coefficient should be independent of concentration. Perhaps this theoretical prediction is reflected in the plateau-like regime in *Figure 1b*.

Sedimentation experiments with the aim of more systematically studying the influence of molecular weight are in progress.

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Correlation between crack growth rate and fracture mode transitions in low density polyethylene

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The fatigue crack propagation (*FCP*) behaviour of low density polyethylene (LDPE) has been described by Andrews and Walker[1] and by Hertzberg et al.[2]. The results published by the former authors showed a discontinuity in the *FCP* behaviour of this material at a crack growth rate of $\sim 10^{-3}$ mm/cycle; no such discontinuity in fatigue reponse was reported in the latter study. We have since re-examined the *FCP* behaviour at 10 Hz of compact-tension specimens of LDPE as a function of ΔK, over a wider range of ΔK (*Figure 1*). These data show a decrease in crack growth rates (da/dN) with increasing ΔK between $\Delta K = 0.4$ MPa m$^{1/2}$ and 0.6 MPa m$^{1/2}$, followed by an increase in da/dN with ΔK above 0.6 MPa m$^{1/2}$; the solid lines shown in *Figure 1* represent the data reported in ref 2. Thus the absence of any discontinuity in *FCP* behaviour for LDPE reported in the earlier study[2] can be traced to the fact that the entire ΔK test range was above the transition range identified in the present investigation.

Since Andrews and Walker evaluated *FCP* rates as a function of $\mathscr{F}$, an elastic-plastic surface work parameter, while Hertzberg et al. measured crack growth rates as a function of the elastic stress intensity factor range, ΔK, these results cannot be compared directly. Nevertheless, it is interesting to note that the crack growth rate corresponding to the transition at A (da/dN $\sim 10^{-3}$ mm/cycle) agrees closely with the *FCP* rate at the discontinuity reported by Andrews and Walker[1]. Thus, a phenomenological similarity is apparent between the LDPE data reported by Andrews and Walker and the present results which must reflect an equivalent intensity of the stress–strain field at the advancing crack tip.

An examination of the fracture morphology of LDPE revealed a marked change in the fracture surface ap

pearance at the da/dN–ΔK transition at location B (*Figure 1*). Below $\Delta K = 0.6$ MPa m$^{1/2}$, the fracture surface exhibited a tufted appearance consisting of small voids, while large voids dominated the fracture topography at higher ΔK levels (*Figures 2a* and *2b*). This contrast in appearance is striking, considering the difference in magnification between *Figures 2a* and *2b* (~ 700x and 20x,
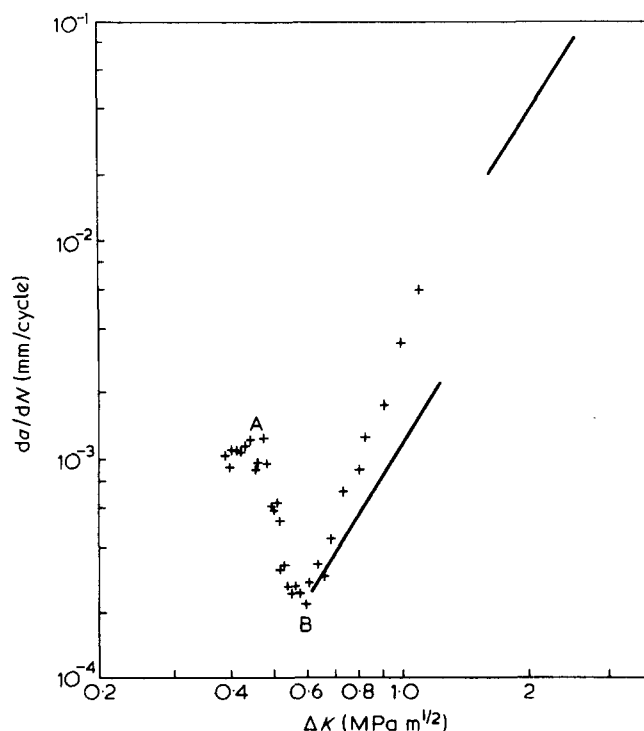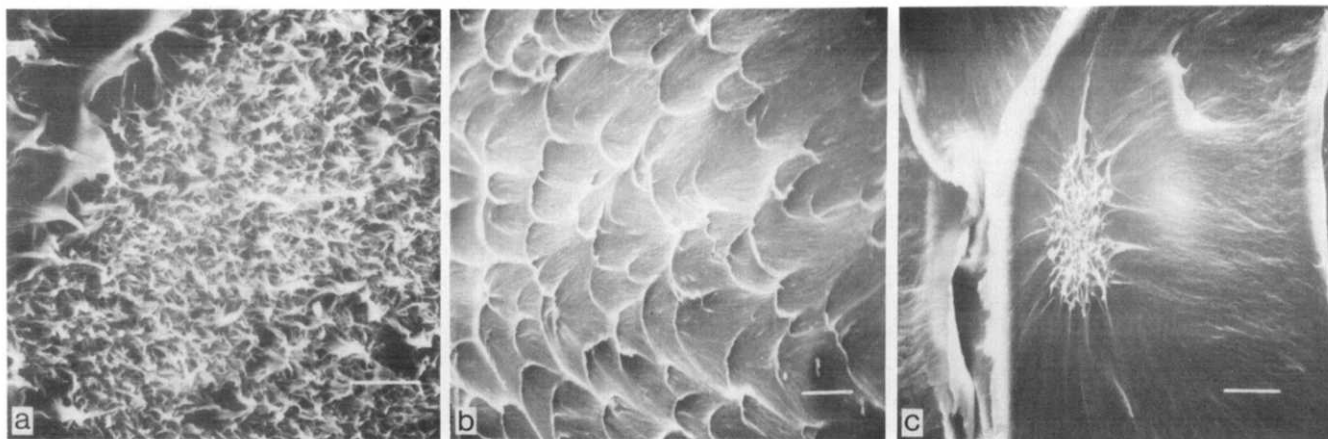

Figure 1 Fatigue crack growth rates at 10 Hz as a function of ΔK in LDPE. Note the decrease in da/dN with increasing ΔK between A and B. Solid lines represent *FCP* data for LDPE from ref 2

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Figure 2 Void coalescence mechanism in LDPE: (a) very fine voids at ΔK = 0.45 MPa m$^{1/2}$, scale bar = 20 μm; (b) coarse voids at ΔK = 1.0 MPa m$^{1/2}$, scale bar = 0.5 mm; (c) centre of coarse void showing texture similar to that shown in (a), scale bar = 30 μm. Crack propagation direction from left to right; frequency, 10 Hz

respectively). It is believed that both of these fracture surfaces were produced by a void growth mechanism. Above ΔK = 0.6 MPa m$^{1/2}$, though, there seems to have been a dramatic decrease in the nucleation rate of these voids and an enhanced opportunity for pronounced void growth. Curiously, these large voids appear to have been nucleated by local void clusters whose appearance was quite similar to the smaller voids seen at low ΔK levels (*Figure 2c*). The discontinuity in *FCP* behaviour reported by Andrews and Walker also was accompanied by a change in fracture morphology but was described differently, based on alternative microscopic techniques. Nevertheless, the phenomenological similarity of the two studies is confirmed. Unfortunately, while the correlation between crack growth rate behaviour and fracture mode transition in LDPE is striking, the fundamental reason for this behaviour remains unknown.

It is not clear why LDPE exhibits *FCP* discontinuities and high density polyethylene (HDPE) does not[3]. In the latter study, fatigue crack growth rates increased continuously with increasing ΔK values for several molecular weights and thermal histories. Additional complexities become apparent when comparisons are made with regard to fracture surface markings. For example, ultra-high molecular weight polyethylene[4] and HDPE[3] reveal various groupings of parallel fatigue fracture surface lines. Though White and Teh[5] reported similar features in LDPE, none were identified in this investigation. Clearly, much additional research on the fatigue behaviour of polyethylene is needed.

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A comment on the histogram method in photon correlation spectroscopy applied to dilute polymer solutions

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Photon-correlation spectroscopy[1] is now routinely used to measure diffusion coefficients of macromolecules in dilute solution since rapid and accurate determinations can be made. It is usual to measure the diffusion coefficient D as a function of the solute concentration c, principally to obtain D_0, the value of D at infinite dilution, from an extrapolation of the data. Thus, although the main purpose of these investigations is often to determine D_0, it is also possible to study the concentration dependence, and this has been a popular area of investigation in the study of dilute polymer solutions.

For an ideally monodisperse polymer sample in dilute solution, D varies linearly with c:

$$D(M,c) = D_0(M)(1 + k_D(M)c) \quad \text{(monodisperse)} \quad (1)$$

(The M-dependence has been indicated for completeness.) The coefficient k_D depends on the particular system and is