Effect of molecular weight on the fracture morphology of poly(methylmethacrylate) in cleavage

In previous work [1,2] the fracture surface energy (γ) of poly(methylmethacrylate) (PMMA) has been shown to be strongly dependent upon molecular weight ($\bar{M}_v$). These values have ranged from $\gamma \sim 1 \times 10^5$ erg cm^{-2} for an $\bar{M}_v \gtrsim 1 \times 10^5$ down to $\gamma \sim 5 \times 10^2$ erg cm^{-2} for $\bar{M}_v \sim 2 \times 10^4$. The large magnitude of γ at high $\bar{M}_v$ has been attributed to the vast amount of plastic deformation which occurs immediately ahead of the crack tip, while the latter result has been ascribed to the energy required to essentially separate two planes of atoms. The present note confirms this viewpoint by the appearance of the fractured surface.

A series of parallel cleavage bars was prepared from Plexiglas G (Rohm and Haas Co) and irradiated using ^{60}Co gamma-irradiation to reduce the molecular weight in a controlled manner. After the slow degassing of radiation by-products was complete, the bars were pulled in an Instron testing machine ($T = 295$ K) at crosshead extension rates ranging from 6×10^{-5} to 5×10^{-1} cm min^{-1}. Because of the radiation source geometry a radiation gradient, and hence a molecular weight gradient, resulted longitudinally across each specimen. In the present sample (Fig. 1) the viscosity average molecular weight ($\bar{M}_v$) ranged from a high of 2.2 $\times 10^5$ (at $L = 0$ in.) to a low of 1.9×10^4 (at $L =$ 7 in.). $\bar{M}_v$ was determined from the limiting viscosity relation, $[\eta] = K\bar{M}_v^{\alpha}$, in which $K = 5.5 \times 10^{-5}$ dl g^{-1} and $\alpha = 0.76$ (benzene at 25° C) [3].

While the testing of parallel cleavage bars with varying molecular weights is greatly simplified by the constant modulus ($E = 3.8 \times 10^{10}$ dyn cm^{-2}) and cantilever beam constant ($n = 2.67$), the problem of unstable fast crack propagation is ever present. Although conceptually a solution to this problem is obvious – to propagate the crack in the direction of increasing γ (i.e $\bar{M}_v$) -- nevertheless, certain useful information may be gleaned from the propagation of an uncontrolled crack. To illustrate this point a series of photomicrographs (Zeiss Universal Microscope) was taken in zones corresponding to the γ, $\bar{M}_v$, and length of specimen (L) indicated (Fig. 1). In agreement with earlier investigators [4, 5], a surface replete with interference colours and plastic deformation patterns is shown in the area of continuous *stable* slow crack growth (Fig. 1a, $\gamma \sim 0.9 \times 10^5$ erg cm^{-2}, $\bar{M}_v \sim 1.3 \times 10^5$, and $L = 1.5$ in.). Here the dark bands or steps which run parallel to the direction of crack propagation represent small changes in elevation between fracture planes. These are caused by the different degrees of elastic distortion of the material that result from local variations in crack velocity or crack front displacement. Fainter vertical striations represent points of crack hesitation. While the photomicrograph shown is typical of the stable fracture region in which γ is relatively insensitive to changes in molecular weight ($\bar{M}_v \gtrsim 10^5$), the bands or steps gradually give way to a mirror smooth surface as $\bar{M}_v \ll 10^5$ [6].

As the molecular weight decreases, *unstable* fracture abruptly occurs as seen by the boundary between stable and unstable crack growth (Fig. 1b). Now ribs perpendicular to the fracture direction are formed which are more like those seen in polystyrene [5, 7], and the interference colours shift to lower wavelengths. Recently Döll [8] has observed these same ". . . . coarse-structured features immediately at the onset of fast crack propagation ($\sim$200 m sec^{-1}) which (were) rib-like in appearance . . . . " in single-edge-notched plate specimens of PMMA ($110\,000 < \bar{M}_w < 163\,000$). Moreover, at crack velocities much greater than his reported "molecular weight dependent fracture transition", similar rib spacings ($\sim 100\,\mu$m) were found for $\bar{M}_w = 110\,000$ [8] versus $\bar{M}_v = 98\,000$ (Fig. 1b). In the region in which $\bar{M}_v$ and γ are decreasing then (Fig. 1b to g), it is reasonable to deduce that the fracture velocity will increase. That this is the case is shown by a series of sharp lines (schematic) in which the ribs on the side distant from the propagating crack tip are somewhat larger than on the proximate side. These sharp lines and the correspondingly large decrease in $\bar{M}_v$ and γ suggest that each of these marks represents a sudden acceleration of the crack front. By (c) the ribs decrease in size (c.f. Benbow on polystyrene [7]) taking on a slightly different appearance and showing less evidence of plastic deformation, as exemplified by the "shatter-cone"* failure regions (x) [9]. Upon further crack growth the rib spacing continues to

* In geology, the term "shatter-cone" refers to a distinctively striated conical fragment of rock formed by shock waves generated by meteorite impact.

decrease, as evidenced by the progressively lighter shading in the schematic illustration, and the area covered by the "shatter-cone" failure increases (c.f. Fig. 1d and e); note that a linear relationship has been suggested between $\gamma^{1/2}$ and $\log_{10}$ rib periodicity, [10]. At this point $\gamma \sim 1 \times 10^3$ erg cm^{-2} and $\bar{M}_v \sim 2.4 \times 10^4$.

As the crack front progresses and lower γ and $\bar{M}_v$ values are encountered, the brittle nature of the material predominates (Fig. 1f) until Wallner lines [11] are faintly resolvable, the intersections of which cause the periodic, stippled banding (Fig. 1g and schematic drawing). At $L = 6$ in., $\gamma \sim 400$ erg cm^{-2} ($\bar{M}_v \sim 1.9 \times 10^4$) and a featureless sur-

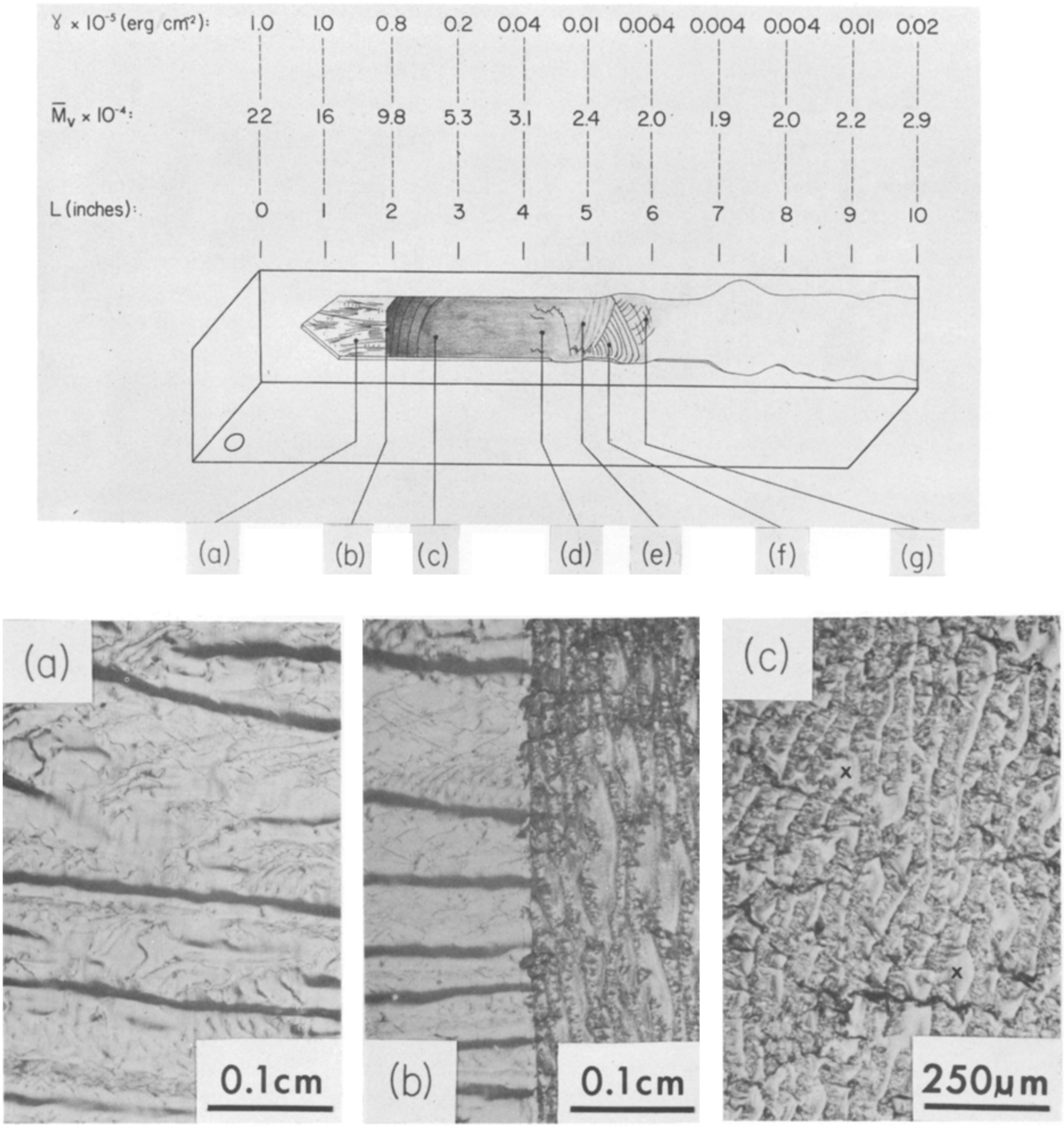

Figure 1 Relationship of fracture morphology to γ as a function of $\bar{M}_v$ on a parallel cleavage bar (type a, test 32, Table I of [2]; fracture initiated at left).

face results. Not only is the surface absent of any interference colours (true for $\bar{M}_v \lesssim 0.9 \times 10^5$), but the fracture becomes as transparent as a plate of glass. Note that the crack apparently continues to accelerate, since it tries with increasing success to run out of the groove, and that the return to higher $\bar{M}_v$ (c.f. $L = 5$ in. and $L = 9$ in. where $\bar{M}_v$ are similar) does not affect the featureless appearance. Similarly, in the stable slow crack propagation of low molecular weight PMMA (type b, test 38, Table I of [2] $\bar{M}_v \sim 2.5 \times 10^4$, cross-head extension rate $= 0.5\,\mathrm{cm\,min^{-1}}$), a featureless surface was formed in which the sporadic departure from the groove was commonplace [6]. This observation reinforces the fact that these morphological features are primarily due to changes in $\bar{M}_v$ and not to changes in velocity.

For some time the γ of many "glassy" polymers have been known to be orders of magnitude greater than those which theoretical calculations would

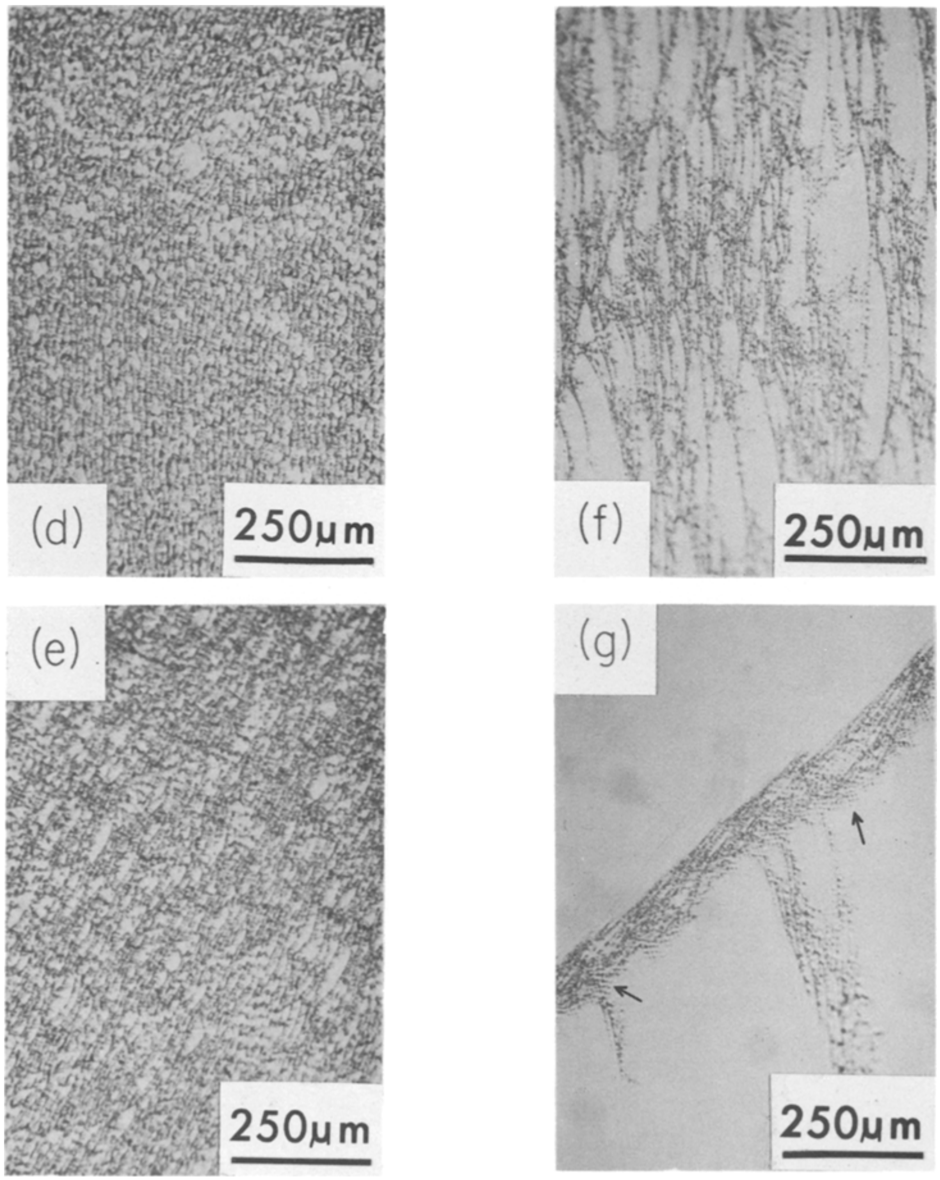

Figure 2 continued.

predict. The photomicrographs shown demonstrate that the fracture morphology takes on an increasingly brittle character until at $\bar{M}_v \sim 2 \times 10^4$ the surface appears featureless. While the rate of crack propagation may influence the precise $\bar{M}_v$ at which a featureless fracture appearance results, nevertheless, the indication that low molecular weight PMMA ($\bar{M}_v < 2.5 \times 10^4$) approaches a truly glassy state is corroborated.

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