

## Properties of Ultra-high Modulus Linear Polyethylenes

We have recently been studying the effect of molecular weight and molecular weight distribution on the cold drawing behaviour of linear polyethylene. Some of the results seem to be sufficiently unusual to warrant reporting at this stage.

Figure 1 shows the extensional moduli of two selected samples (sample 1:  $\bar{M}_n=6,180$ ,  $\bar{M}_w=101,450$ ; sample 2:  $\bar{M}_n=13,350$ ,  $\bar{M}_w=67,800$ ) as a function of the natural draw ratio. The extensional moduli were calculated from the 10 s isochronal stress-strain curves obtained from the creep response in a dead loading creep experiment at room temperature. The different natural draw ratios were obtained by varying the morphology of the initial material by adopting different initial quenching conditions. The details of the preparation are the subject of a patent application (Br. Pat. Appl. 10746/73 (filed 6.3.73)).

In agreement with previous work<sup>1</sup>, it is clear that the

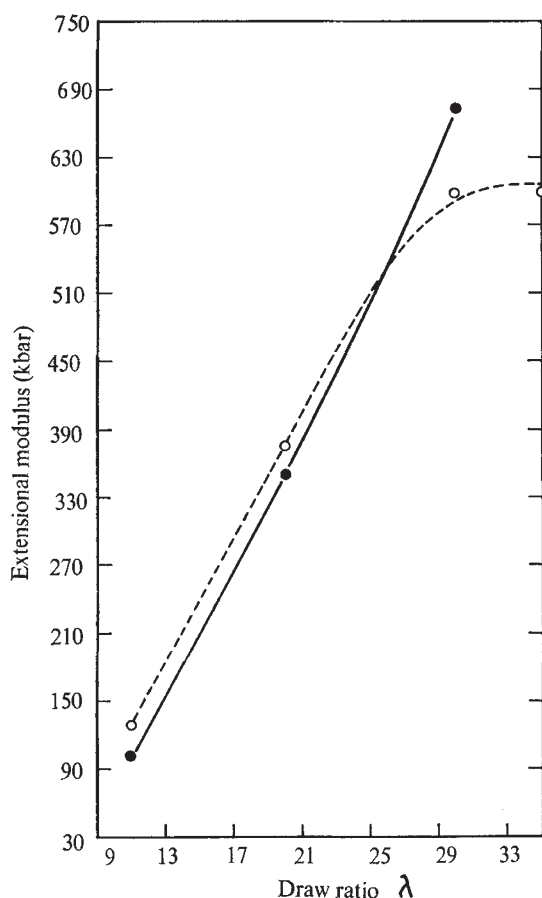


Fig. 1 Extensional moduli at two samples. ●—●,  $\bar{M}_n=6,180$  and  $\bar{M}_w=101,450$ ; ○---○,  $\bar{M}_n=13,350$  and  $\bar{M}_w=67,800$ .

extensional modulus is strongly dependent on the natural draw ratio. At the highest draw ratios the extensional moduli are by far the highest ever recorded for this polymer ( $\sim 7 \times 10^{10}$  N m<sup>-2</sup>) and almost approach the range of the theoretical moduli for fully extended polyethylene chains ( $2.4 \times 10^{11}$  N m<sup>-2</sup>, according to ref. 2). It also seems that up to draw ratio 30 the effects of molecular weight and molecular weight distribution on modulus are very small.

Differences in molecular weight and distribution do, however, give rise to structural differences between the samples which are revealed by their melting behaviour. The melting curves were measured on a Du Pont Thermal Analyser with a differential scanning calorimeter (DSC) cell and operated in

a DSC heat mode. The results are shown in Fig. 2. Sample 1 shows a melting peak at about 137° C, which is typical of oriented linear polyethylenes in the lower draw ratio range hitherto examined<sup>3</sup>. Sample 2, on the other hand, shows a melting peak at 138.5° C, corresponding to the presence of extended chain material conventionally defined as extended chain crystallites (ref. 4 and D. C. Bassett, private communication).

It therefore seems from the results of the thermal analysis that extended chain crystallites can be produced by cold drawing, provided that polymers of suitable molecular weight and molecular weight distribution are chosen. It is also evident from the mechanical data that the presence of extended chain crystallization *per se* is not a necessary requirement for the production of high modulus material. We believe that this is because oriented non-crystalline extended chain molecules (tie molecules)<sup>1,5</sup> are just as effective in contributing to the overall stiffness.

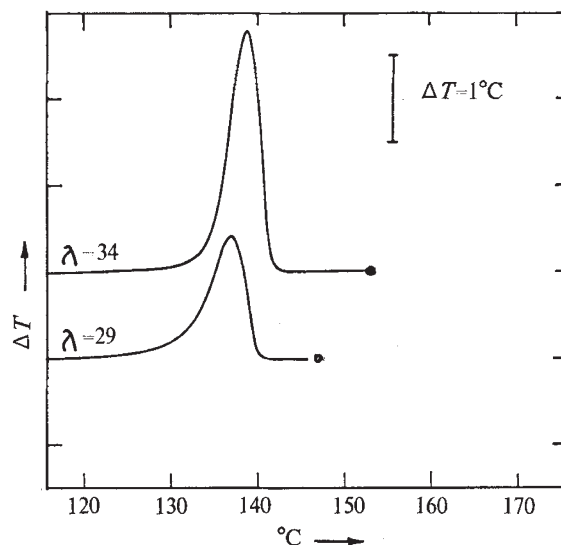


Fig. 2 Melting curves for two samples. Upper curve, sample 2; lower curve, sample 1.

A more complete account will be published elsewhere.

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## Closed Time and Absorber Theory

In the closed time model universe recently proposed by Davies<sup>1</sup> as an explanation of the 3 K black body radiation, the arrow of time points forward in the first cycle AB and backward in the second cycle BC, where point C is identified with point A,