Superheating effects on the melting of ultra-high modulus linear polyethylene

J. Clements and I. M. Ward
Department of Physics, University of Leeds, Leeds LS2 9JT, UK
(*Received* 15 *January* 1982)

New results are reported on the superheating behaviour of ultra high modulus polyethylenes which have been restrained from shrinkage during the melting programme. Very high degrees of superheating were observed, which were somewhat dependent on the polymer molecular weight. It is considered that the ultra high modulus polyethylenes do not contain extended chain crystalline material, and that the superheating effects are associated with the presence of a molecular network which can be prevented from relaxing by mechanical restraint.

Keywords Superheating; melting; ultra-high modulus polyethylene; shrinkage; molecular network; mechanical restraint

INTRODUCTION

Superheating effects in the melting of crystalline polymers are associated with an increase in the peak melting temperature with increasing heating rate[1]. Although these effects have been mainly observed in extended-chain polyethylene[2,3] produced by crystallization at elevated pressures, they have also been observed in oriented polymers. In oriented polymers the superheating effects have been attributed to the entropic restrictions on molecules which connect two or more crystalline regions of the same or different crystals. These entropic effects have been discussed quantitatively by Zachmann[4].

The experiments reported here were designed to examine more closely the superheating which is observed in the melting of highly oriented linear polyethylene (LPE) fibres, and to throw more light on the results of previous measurements performed in this laboratory[2].

EXPERIMENTAL

Two commercial grades of linear polyethylene produced by B.P. Chemicals International were used in all experiments.

The grades are Rigidex 50 (sample 1) and H020-54P (sample 2).

Drawn monofilaments were produced using a laboratory scale melt extruder to give fibre monofilaments with low degrees of molecular orientation. Products of draw ratio 25 were then obtained by stretching the monofilament between two rollers in a glycerol bath maintained at 120°C.

The samples were examined by differential scanning calorimetry (d.s.c.) at different heating rates with a Perkin-Elmer DSC-2. In the d.s.c. of the fibres, two methods of sample placement were adopted. One is the normal method in which fibre was cut and fitted without restraint in the sample pan. In the other method, the fibres were restrained by winding tightly around brass wire and tying up the ends, and then placed in the sample pan. In this way the fibre length was kept constant during much of the heating.

RESULTS

Plots of the peak melting temperatures *versus* heating rate of all fibre samples examined are shown in *Figures 1* and *2*.

The low molecular weight sample (sample 1) shows slight superheating at the higher heating rates. However, if it is restrained during the heating programme, sample 1 shows a significant degree of superheating. The high molecular weight sample (sample 2) shows a greater degree of superheating in the unrestrained state, and a very high degree if restrained.

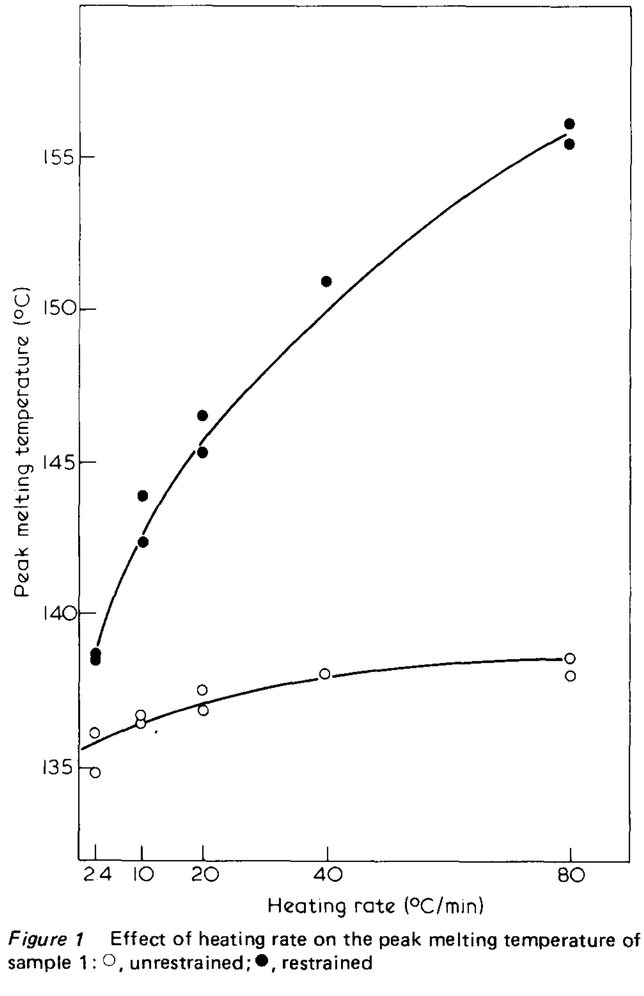

Figure 1 Effect of heating rate on the peak melting temperature of sample 1: ○, unrestrained; ●, restrained

0032-3861/82/060935-02$03.00

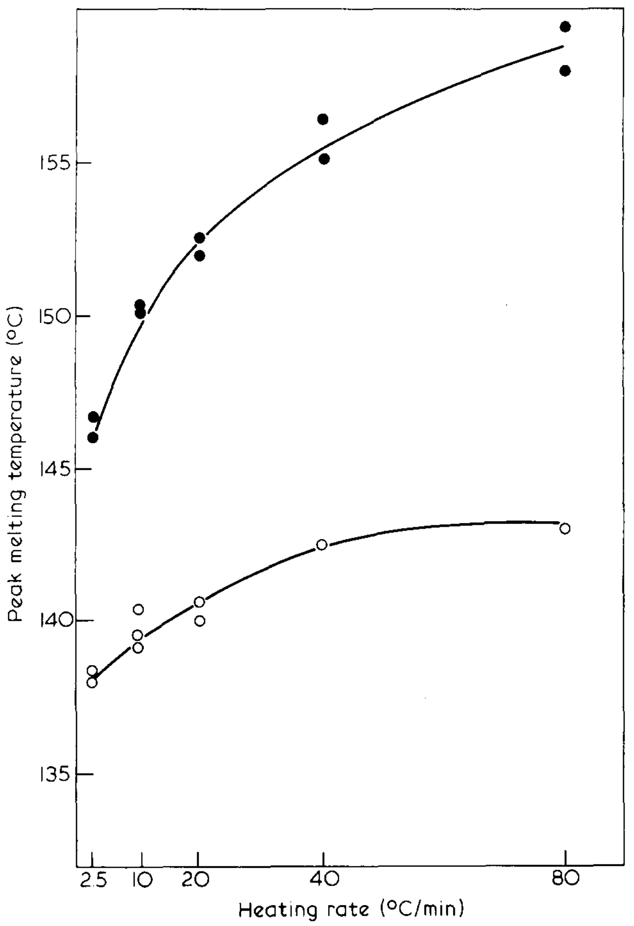

Figure 2 Effect of heating rate on the peak melting temperature of sample 2: ○, unrestrained; ●, restrained

DISCUSSION

It can be seen from *Figures 1* and *2* that the peak melting temperature is increased by restraining the sample during the heating programme. The application of restraint prevents the substantial shrinkage of the fibres which would otherwise occur. These results are consistent with the view that it is essential to retain orientation of the amorphous component of the fibres during the heating programme so that the change in entropy is reduced and hence the melting point increased. It is considered that there is a highly oriented network whose junction points are primarily crystalline, but can also include molecular entanglements.

The present results differ substantially from those obtained previously for restrained samples, the melting temperature continuing to rise with increasing heating rate instead of approaching a plateau at high heating rate. It is considered that this is due to particular care being taken in the present experiments to prevent any possible relaxation of the fibre.

Significant differences are obtained between the low molecular weight and high molecular weight samples. These differences can be attributed to the more effective molecular network in the high molecular weight polymer. The greater effectiveness of the network in such materials has also been concluded from tensile drawing studies, where a greater degree of strain hardening was observed.

Previous experiments[2] performed to determine melting points at very low heating rates, as low as 0.62 and 0.31°C/min, have indicated that extrapolation to 'zero' heating rate is a doubtful procedure. The rate at which peak melting temperature increases with increasing heating rate indicates that the peak melting temperature at extremely low heating rates will be very low indeed, and to a large extent indeterminate by differential scanning calorimetry. However best estimates place T_p possibly as low as 134°–135°C in all cases for highly oriented LPE. Conversely, best estimates of T_p at extremely low heating rates for extended-chain LPE are somewhat higher, at about 138°C. Faced with this evidence, we propose that ultra-high modulus products contain little if any extended-chain crystallization. This proposal is quite consistent with our observations on the melting behaviour of both restrained and unrestrained samples.

ACKNOWLEDGEMENT

We are indebted to Mr D. L. M. Cansfield for provision of the fibre samples.

REFERENCES

1 Wunderlich, B. *Polymer* 1964, **5**, 611
2 Clements, J., Capaccio, G. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **7**, 693
3 Jaffe, M. and Wunderlich, B. in 'Thermal Analysis', Vol. 17, (Eds. R. F. Schwenker and P. D. Garn), Academic Press, New York, 1969, p. 387
4 Zachmann, H. G. *Kolloid Z. Z. Polym.* 1965, **206**, 25; *ibid.* 1967, **216–217**, 180