

## **Influence of Thermal History on Fusion Curves of Polyethylene**

R. W. FORD and R. A. SCOTT,  
*Research and Development Laboratories,  
Dow Chemical of Canada, Limited,  
Sarnia, Ontario, Canada*

### **Synopsis**

The effect of thermal history on the melting behavior of several linear polymers and copolymers of ethylene has been studied by using a Perkin-Elmer DSC-1 differential scanning calorimeter. Samples of film were heated above their melting point and then cooled at various rates in order to establish a known thermal history. During melting, homopolymers showed one peak and the copolymers two peaks in the DSC scan. The positions and relative sizes of the peaks were dependent on the prior cooling rate. It is suggested that two crystal types occur in the case of copolymers because of entanglements in the branched segments of the molecules. The position of the lower melting endotherm in blown films suggests that cooling rates of about 500°C./min. are achieved in this process.

### **Introduction**

The advent of commercially available, high-performance differential thermal analyzers has given the polymer chemist a powerful tool for the study of polymers and the effect of thermal treatment thereon. For instance, Clampitt<sup>1</sup> reported a method based on DTA whereby the composition of linear high-pressure polyethylene blends could be determined. In a later publication,<sup>2</sup> the same author concluded that such blends could be divided into two groups, depending on crystallite size of the linear component. At about the same time Gray and Casey<sup>3</sup> showed that the melting behavior of an ethylene-butene copolymer of 0.920 g./cc. density could be markedly influenced by prior thermal history. By using an unusual annealing procedure no less than 17 distinct melting peaks were detectable on the DTA melting curve.

In the course of work in this laboratory with similar resins,<sup>4,5</sup> some interesting melting phenomena were observed, which form the subject for this communication.

### **Experimental**

The differential thermal analyses were carried out on a Perkin-Elmer DSC-1 with the use of 4-6 mg. samples in covered aluminum sample

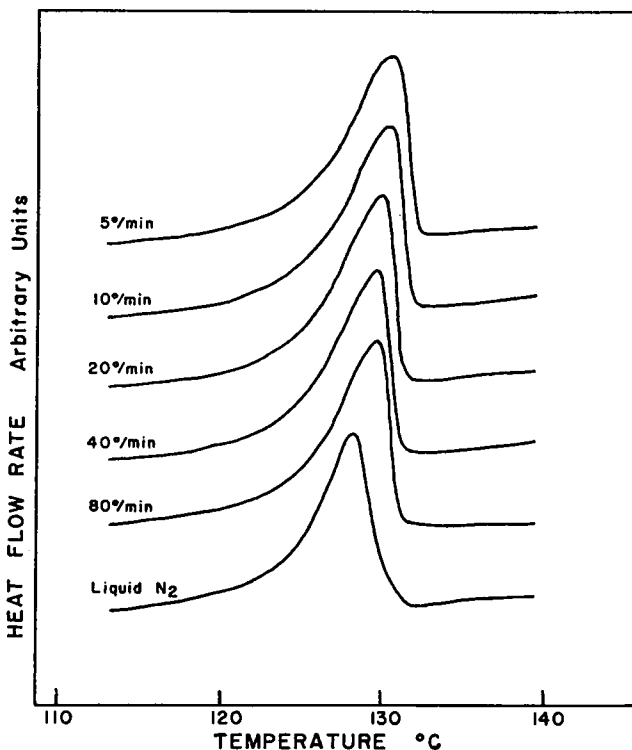


Fig. 1. Melting curves for sample G-1.

pan. The instrument was calibrated with an indium standard (melting point: 156°C.). In general, the samples were cut from several layers of blown film using a cork borer. Thermal history was imposed by heating the samples to at least 25°C. above the melting point and then cooling at various rates, including quickly removing the sample from the DSC measuring head and plunging it into liquid nitrogen. All melting

TABLE I

| Sample number | Melt index, °C./min. | Density, g./cc. | Resin type  |
|---------------|----------------------|-----------------|---|
| F-1           | 3.5                  | 0.923           | Commercial ethylene-butene-1 copolymer                                    |
| G-1           | 5.5                  | 0.957           | Commercial ethylene homopolymer   |
| H-1           | 5.8                  | 0.935           | Experimental ethylene-C <sub>6</sub> /C <sub>7</sub> 1-olefin copolymer*  |
| J-1           | 6.5                  | 0.927           | Experimental ethylene-C <sub>6</sub> /C <sub>7</sub> 1-olefin copolymers* |
| J-2           | 5.3                  | 0.935           |   |
| J-3           | 7.6                  | 0.941           |   |

\* Resin H-1 and those in series J were produced with different catalyst systems.

points were determined at a scan rate of 5°C./min. Samples used were similar to those studied previously in this laboratory.<sup>4,5</sup> Pertinent properties are included in Table I.

### Results and Discussion

DSC melting curves for sample G-1, a homopolymer, and sample J-2, a representative copolymer, are shown in Figures 1 and 2. The notations on the curves indicate the cooling rate to which the sample was subjected prior to the melting point determination. The most obvious difference between the two samples is the occurrence of two endotherms in the copolymer melting curves, and only one in the case of the homopolymer. The size, shape, and position of the two peaks in the copolymer melting curves are also obviously dependent on prior thermal history. Holden,<sup>6</sup> who has also reported such double peaks, considers them to be due to heterogeneous and homogeneous nucleation. A second view<sup>7</sup> is that they are due to blocks of high branching interspersed with blocks containing little or no branching. The latter hypothesis certainly appears the more tenable in the present case since the double peaks have, in our experience, only been observed in copolymers.

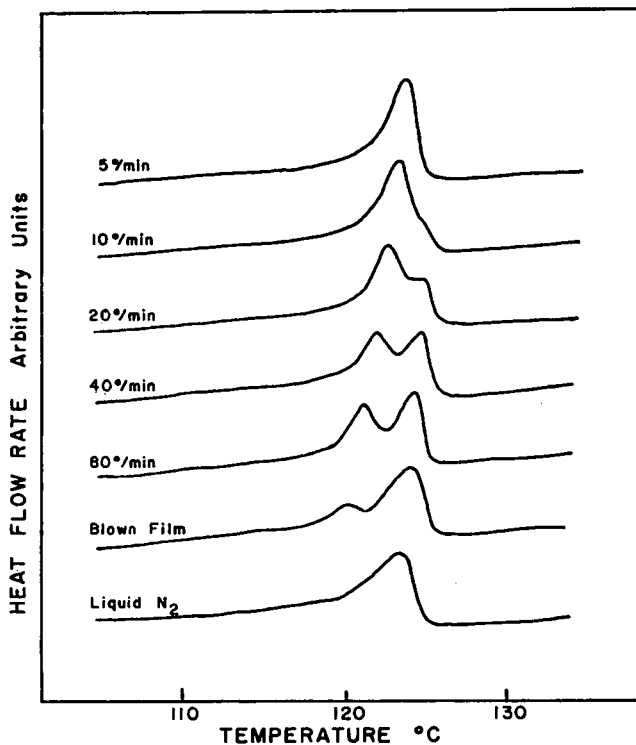


Fig. 2. Melting curves for sample J-2.

When the logarithm of the prior cooling rate is plotted against the temperature of the lower melting peak, a family of straight lines results for the five copolymers studied. These relationships are shown in Figure 3. The arrows indicate the temperature of this peak in the blown film samples as received. This suggests that in the fabrication of blown film, cooling rates greater than  $500^{\circ}\text{C./min.}$  are achieved. In the case of the samples quenched in liquid nitrogen, this first peak disappears altogether.

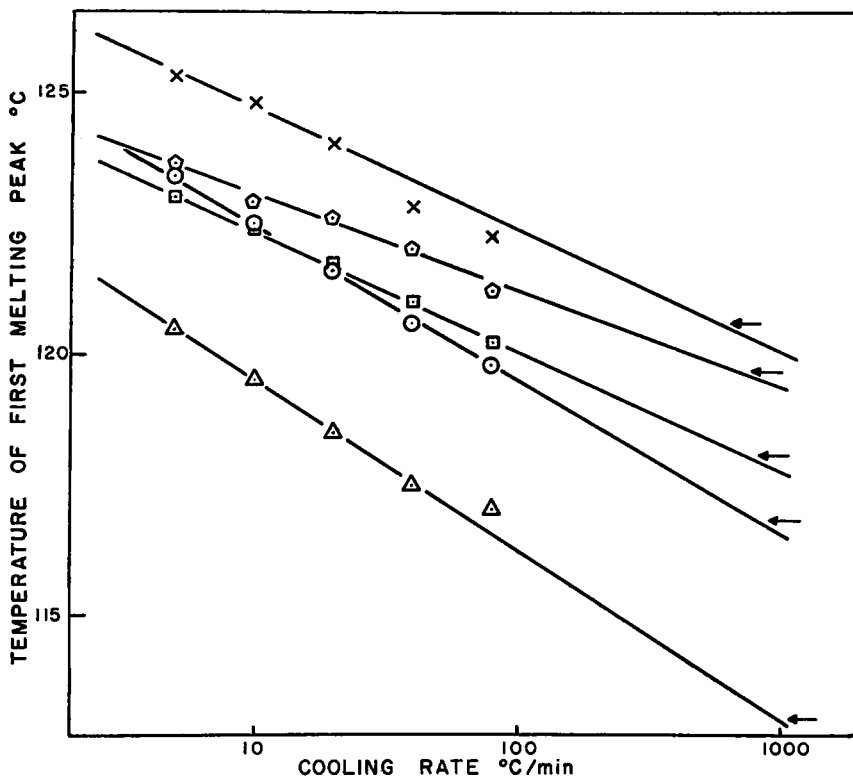


Fig. 3. Relationship between first melting peak temperature and previous cooling rate: ( $\Delta$ ) sample F-1; ( $\times$ ) sample H-1; ( $\circ$ ) sample J-1; ( $\square$ ) sample J-2; ( $\diamond$ ) sample J-3.

Unlike the lower melting peak, the position of the higher endotherm does not appear to be markedly dependent on thermal history, although its magnitude is. The effect of cooling rate on the degree of supercooling can be seen in Figure 4.

Holden<sup>6</sup> expresses the view that the two peaks can arise from different crystal forms produced by heterogeneous and homogeneous nucleation. In addition, the rapid crystallization at high supercoolings can lead to appreciable heat build-up in the sample under adiabatic conditions thus giving an annealing effect and further accentuating the two peaks. In

the DSC-1 instrument, however, the fact that extremely small, thin samples completely encapsulated in aluminum are used rules out any appreciable heat build-up during crystallization. Thus this factor can be disregarded in the present case.

Apparently, at low rates of cooling, only one crystal type is formed which includes chain segments of both high and low branching densities. As cooling rate increases, however, the more linear chain segments begin to form their own higher melting crystal form while the branched segments, possibly because of entanglements, are able to crystallize less and less

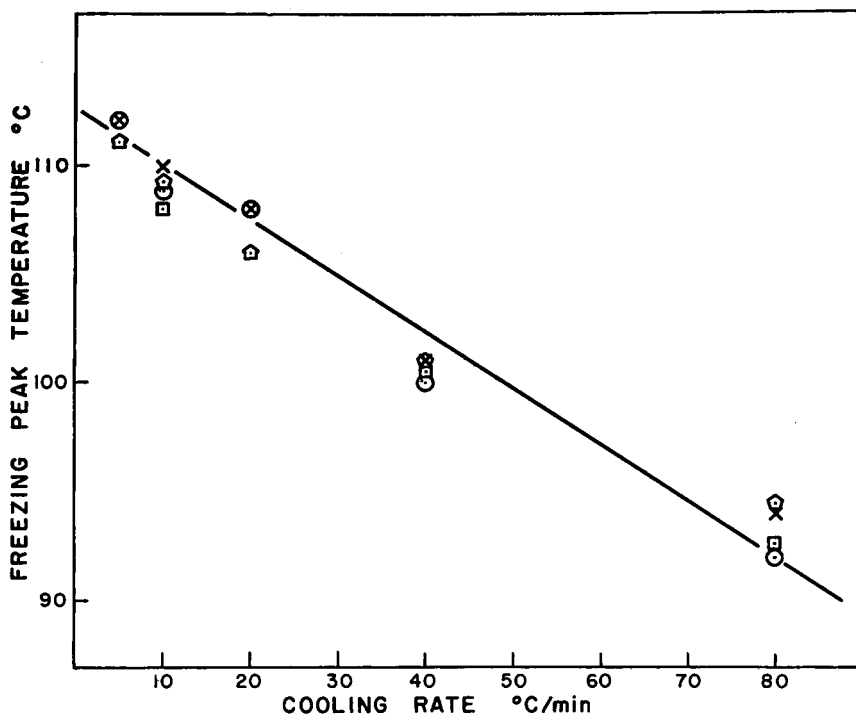


Fig. 4. Effect of cooling rate on freezing peak temperature. Symbols same as Figure 3.

perfectly and hence the lower melting peak drops in both temperature and magnitude. Finally, at the highest rates of cooling, the crystal type based on the more linear segments completely dominates the structure and the lower melting crystals disappear as a separate peak.

Further elucidation of this process appears to require x-ray diffraction or electron microscopy studies in order to determine the nature of the crystallites responsible for the two different melting peaks.

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### References

1. B. H. Clampitt, *Anal. Chem.*, **35**, 577 (1963).
2. B. H. Clampitt, *J. Polymer Sci. A*, **3**, 671 (1965).
3. A. P. Gray and K. Casey, *J. Polymer Sci. B*, **2**, 381 (1964).
4. R. W. Ford, *J. Appl. Polymer Sci.*, **9**, 2879 (1965).
5. I. J. Bastien, R. W. Ford, and H. D. Mak, *J. Polymer Sci. B*, **4**, 147 (1966).
6. H. V. Holden, in *Thermal Analysis of High Polymers (J. Polymer Sci. C, 6)*, B. Ke, Ed., Interscience, New York, 1963, p. 53.
7. A. P. Gray, private communication.

### Résumé

L'effet de l'histoire thermique sur le comportement à la fusion de nombreux polymères linéaires et copolymères d'éthylène ont été étudiés en utilisant un calorimètre enregistreur différentiel Perkin-Elmer DSC-1. Des échantillons de film ont été chauffés au-dessus de leur point de fusion et en-suite refroidis à différentes vitesses en vue d'établir l'histoire thermique. Au cours de la fusion les homopolymères montraient un pic et les copolymères deux pics, à l'enregistrement DSC. Les positions et les grandeurs relatives de ces pics dépendaient de la vitesse de refroidissement antérieur. On suggère que deux types de cristaux se présentent dans le cas des copolymères, à cause des entrelacements des segments ramifiés des molécules. La position de l'endotherme de fusion plus basse dans les films soufflés suggère que des vitesses de refroidissement d'environ 500°C par minute, ont été atteintes au cours de ce processus.

### Zusammenfassung

Der Einfluss der thermischen Vorgeschichte auf das Schmelzverhalten einiger linearer Äthylenpolymerer und -copolymerer wurde mit einem Perkin-Elmer-DSC-1-Differential-scanningkalorimeter untersucht. Zur Erreichung einer bekannten thermischen Vorgeschichte wurden Filmproben über ihren Schmelzpunkt erwärmt und dann mit verschiedener Geschwindigkeit abgekühlt. Während des Schmelzens zeigten die Homopolymeren ein Maximum und die Copolymeren zwei Maxima im DSC-Diagramm. Lage und relative Grösse der Maxima hing von der vorherigen Abkühlungsgeschwindigkeit ab. Es wird angenommen, dass im Falle der Copolymeren wegen der Verschlingungen der verzweigten Molekülsegmente zwei Kristalltypen auftreten. Die Lage der niedrigeren Schmelzendothemerme in geblasenen Filmen lässt erkennen, dass bei diesem Prozess Abkühlgeschwindigkeiten von etwa 500°C/min erreicht werden.

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