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THE EFFECT OF SAMPLE GEOMETRY ON THE MELTING POINT OF POLYETHYLENE

I. R. Harrison and W. D. Varnell

Polymer Science Section, Dept. of Materials Sci. and Eng. The Pennsylvania State University University Park, Pennsylvania 16802 U.S.A.

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We have examined the influence which sample geometry has on the melting point of isothermally melt crystallized polyethylene. The peak positions of curves obtained using a Perkin—Elmer DSC were used as the apparent melting points (*T*m). With a constant sample weight (ca. 0.05 mg), we observed an increase of 1.7 K for *T*m when the sample thickness was increased from 1 to 8 μm. Experiments which demonstrate the heat transfer problems related to the melting of polymer samples are also presented. This work indicates that, if one is attempting to reduce the heating rate dependence of polymer samples, reduction of sample weight alone is not suffiicient. Rather one should aim at increasing the sample pan contact area and reducing the sample thickness simultaneously.

Recently we reported that the melting points of isothermally bulk crystallized polyethylene samples are heating rate dependent [1]. Using slow heating rates (2.5°/min) and small sample weights (0.04 – 0.05 mg) poor thermal conductivity and/or poor contact with the sample pan still appeared to influence the position of (Tm). This observation contradicts the conclusions of another study performed at PSU, where we examined the thermal properties of polyethylene single crystals [2]. When sample weight was reduced to approximately 0.1 mg of single crystal, no heating rate dependence was observed for the position of the melting endotherm. We attribute this difference in behavior of bulk and solution crystallized samples to differences in the sample geometries used for the two studies. The purpose of this work is to further demonstrate the effect of sample geometry on the *T*m of polymer samples.

Experimental

A linear polyethylene (Marlex 6001) was crystallized isothermally at 126.5° for 10 000 minutes. The details of this crystallization have been previously reported [1]. Thin sections of the sample were prepared using a microtome at cryogenic temperatures. Sample thicknesses of 1, 2, 4, 6 and 8 μm were obtained. Small "chunks" of the sample were also produced in order to study the effects of other sample geometries typically used in thermal studies. Samples 0.04 – 0.05 mg in weight were encapsulated in standard Perkin Elmer DSC pans.

Melting point data were obtained using a Perkin Elmer DSC-2. A thermal analysis data station (TADS) was utilized to determine the position of the maximum from the melting endotherm. This maximum is being used here as the apparent melting point of the sample. DSC curves were recorded from 350 to 450 K. Corrections were made for changes in apparent melting point as a function of heating rate using indium standards [3].

Briefly this correction involves matching the peak position with the leading edge from an indium reference obtained at the same heating rate as the sample. The *T*m is determined from the point of intersection of the leading edge with the sample baseline.

Results and discussion

The heating rate dependence observed for isothermally crystallized bulk polyethylene is shown in Fig. 1. An increase of 5.1 K for *T*m occurred when the heating rate was increased from 2.5 to 80°/min. This increase is actually a measure of the extra time needed to melt through the polymer samples, which are poor conductors compared with the indium standards. As the heating rate is increased the temperature differential between the top and bottom surface of the sample also increases. This manifests itself as an apparent temperature increase in the recorded position of the melting endotherm.

When small samples of polyethylene single crystals were melted, no increase in the position of the melting endotherm was observed as the heating rate was increased. Assuming that PE single crystals and bulk crystallized samples, made from the same base polymer, have equal heat transfer coefficients, differences in heating rate behavior must arise from differences in sample geometries and/or inherent morphologies which may effect the tendency for superheating in the sample [4].

PE single crystals are lamellae 100 – 200 Å in thickness. The surface area to weight ratio for single crystals is much larger than that ratio for samples crystallized in bulk. In the heating rate study of single crystals, suspensions of crystals were

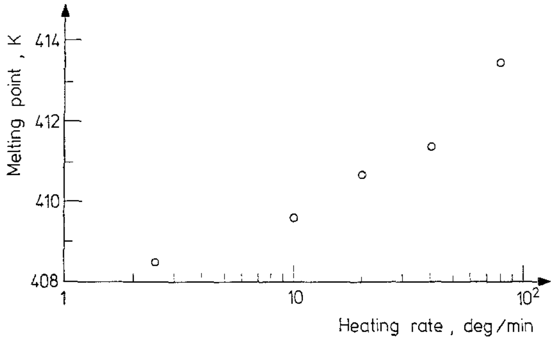

Fig. 1. Plot of *Tm vs* heating rate (log scale) for isothermally melt crystallized polyethylene chunks. Sample wt. = 0.05 mg

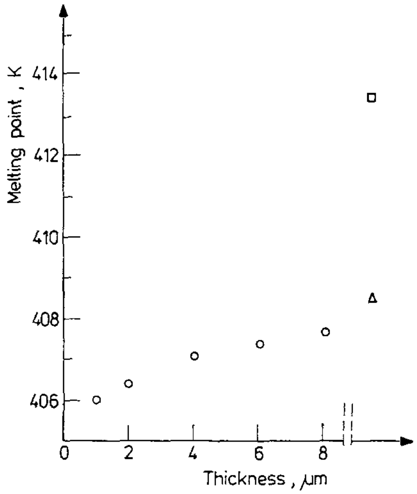

Fig. 2. Plot of *Tm vs* sample thickness. ○ — Thin sections. Also shown are the melting points of chunk samples; △ — Sample wt. = 0.05 mg; □ — Sample wt = 1.17 mg

used. These suspensions were allowed to evaporate in the sample pans to form a very thin coating of crystals. The absence of a heating rate dependence could be related to the achievement of excellent sample-pan contact and the fact that the sample was extremely thin.

To test this idea, slices of isothermally bulk crystallized PE of increasing thickness but equal weight (0.04–0.05 mg) were heated in the DSC at a rate of 20°/min. The melting points observed, plotted as a function of sample thickness are shown in Fig. 2. Typical melting curves are shown in Fig. 3. An increase of 1.7 K for *T*m occurred when sample thickness was increased from 1 to 8 μm. To be sure that the

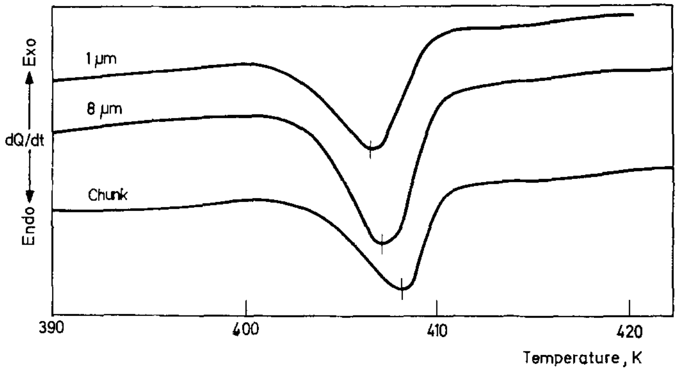

Fig. 3. Typical melting endotherms of thin section and chunk sample geometries. All weights are 0.05 mg

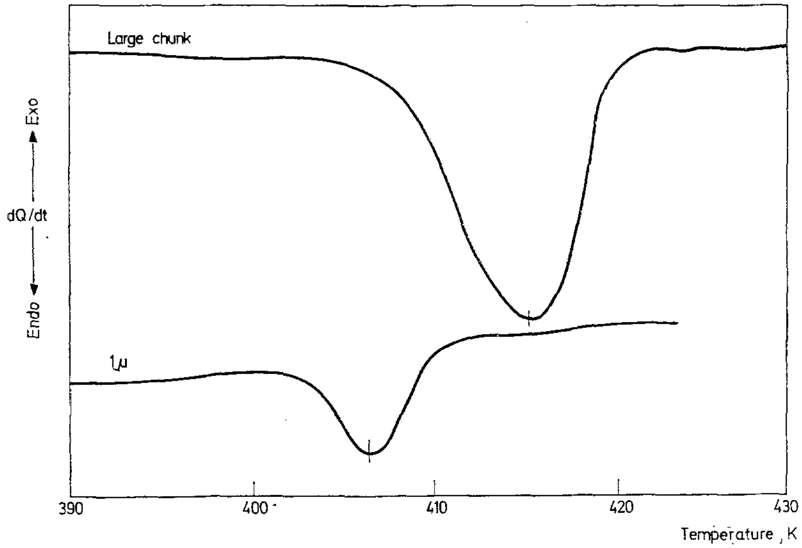

Fig. 4. Melting endotherms of a 1 μm slice (wt. = 0.05 mg) and a large chunk sample (wt. = 1.17 mg)

observed increase was not due to differing amounts of sample deformation from sectioning, the 2 μm slices were stacked to give 2, 4, 6 and 8 μm thick samples. The melting points from the stacked samples were identical to the melting points of the single slices of appropriate thickness.

Chunks of sample equal in weight to the slices but with observably less sample-pan contact area were also melted. The *Tm* of these samples were 0.7 to 1.2 K higher than the 8 μm samples. Again, this is an indication that sample geometry is an important factor in determining the thermal behavior of polymer samples in a DSC. Note that most of the "chunk" samples were of comparable weight to that of the slices i.e. 0.05 mg. In contrast, the majority of "routine" samples, in industry and academia, are one or two orders of magnitude greater than this. A chunk sample of 1.17 mg was melted. This had a *Tm* some 7.5 K above that of the 1 μm sample! (Fig. 4).

A further indication of the heat transfer problem related to polymers was demonstrated by melting two indium samples in the same open sample pan. One chip of indium was placed in the pan and then melted. Over this was placed a 2 μm slice of PE, followed by a second fragment of indium. This "sandwich" was heated in the DSC sample chamber with the platinum chamber covers in place. The curve obtained is shown in Fig. 5. Two endothermic maxima are observed from the indium samples. The first is at the expected position for the *Tm* of indium; the second is 1.8 K higher than expected. The ~2 degree shift is due to the time required to transfer heat through the PE slice. (When standard encapsulation procedures

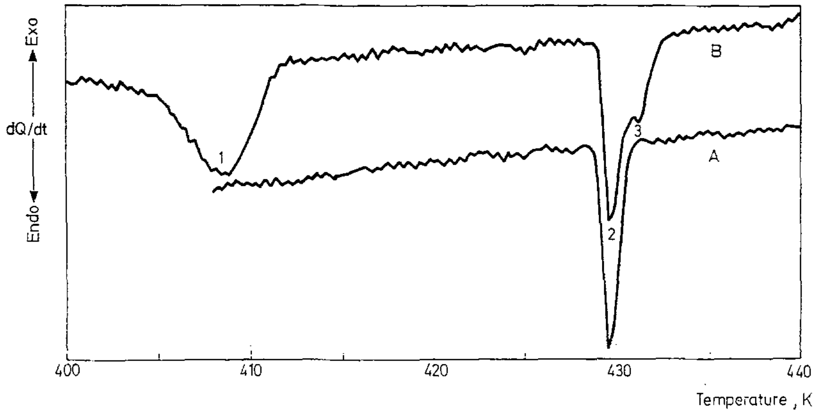

Fig. 5. Melting endotherms from indium samples in open sample pans. A — indium standard (*Tm* = 429.5 K). B — (indium-PE-indium) sandwich; *Tm* (1) = 407.0 K, *Tm*(2) = 429.5 K, *Tm*(3) = 431.3 K

are followed, a shift of *T*m still occurs but is reduced in magnitude. The pan was left open to accentuate the effect.)

It has been proposed that the previously discussed differences between the melting point/heating rate dependence of single crystal and bulk crystallized samples is due to sample geometry (thickness). It follows, that if sample thickness is kept constant, then the weight of sample used should not effect the position of the melting endotherm. The results of heating samples of uniform thickness but increasing weight is shown in Fig. 6. As the weight of sample is increased the area under the endotherms increases but the position of the *T*m remains the same.

For this study the peak position from the DSC curves was used to determine the *T*m of the sample. Other authors have suggested that the onset of melting is more

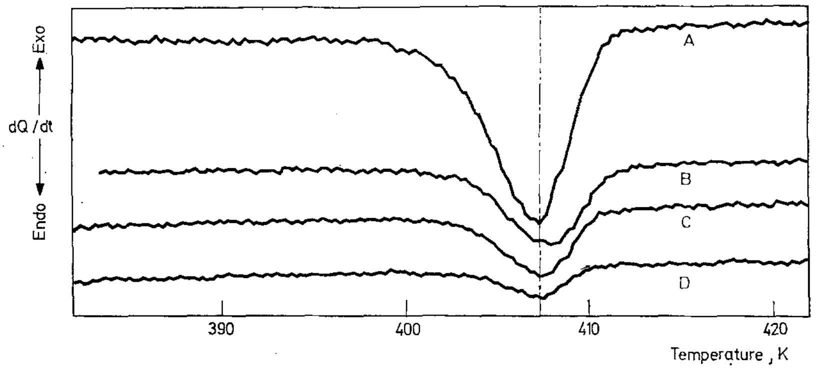

Fig. 6. Melting endotherms from PE slices of uniform thickness but decreasing weight; A — wt. = 0.15 mg, B — wt. = 0.07 mg, C — wt. = 0.04 mg, D — wt. = 0.02 mg

appropriate [5]. The onset of melting should be independent of heating rate and sample geometry effects. Unfortunately, the determination of the onset of melting for polymers is subject to large experimental errors. These errors arise from the complex distribution of crystal thicknesses, the distribution of molecular weights, and improper baseline construction.

Superheating may also occur in melt crystallized samples [4]. However, by keeping the heating rate and sample weight constant the shift of *T*m due to superheating should be constant. This implies that the existence of superheating is an additional consideration, but should not effect the conclusions reached in this work.

Conclusions

Reduction of the weight of sample used for thermal experiments on polymers has been shown not to be the correct approach to reduce the heating rate dependence of *T*m. Instead, increasing the sample-pan contact area and reducing the sample thickness are necessary. The use of slow heating rates would also yield a more accurate value for *T*m if no annealing or reorganization of the sample occurred. Unfortunately, annealing of polymer samples at slow heating rates is often observed. When sample geometry effects are not accounted for in melting point experiments, the *T*m could be as much as 7.5 K too high using the usually accepted heating rates. This may account for some of the discrepancies found in the reported literature concerning melting points of polymers.

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Zusammenfassung — Der Einfluß der Probengeometrie auf den Schmelzpunkt isotherm geschmolzenen kristallinen Polyäthylens wurde untersucht. Die Peakpositionen in den mit einem Perkin—Elmer DSC erhaltenen Diagrammen wurden als scheinbare Schmelzpunkte (*T*m) benutzt. Bei konstantem Probengewicht (etwa 0.05 mg) wurde für *T*m ein Anstieg um 1.7 K beobachtet, wenn die Schichtdicke der Probe von 1 auf 8 μm erhöht wurde. An Experimenten werden auch die mit dem Schmelzvorgang bei Polymerproben zusammenhängenden Wärmeübergangsprobleme aufgezeigt. Diese Arbeit macht deutlich, daß eine Verminderung des

Probengewichts allein zur Verminderung der Aufheizgeschwindigkeitsabhängigkeit der Polymerproben nicht ausreichend ist. Es soll vielmehr eine gleichzeitige Vergrößerung der Probenträgerkontaktfläche und Verringerung der Probenschichtdicke angestrebt werden.

Резюме — Исследовано влияние геометрии образца на точку плавления изотермически плавленного кристаллизационного полиэтилена. Положения пиков термограмм, полученных с помощью ДСК (фирмы Перкин-Эльмер), были использованы как кажущиеся точки плавления $T_{пл}$. При постоянном весе образца (около 0.05 мг), но при увеличении его толщины от 1 до 8 ммк, наблюдалось увеличение $T_{пл}$. на 1.7 К. Представлены эксперименты, показывающие проблемы переноса тепла, связанные с плавлением образцов полимера. Исследования показывают, что одна попытка понизить зависимость скорости нагрева образцов полимера одновременно уменьшая вес образца, является недостаточной. Скорее должна преследоваться цель одновременного увеличения поверхностного контакта печи с образцом и уменьшение толщины образца.