Macromolecules **1994,** *27,* 6145–6146

Equilibrium Melting Point of Deuterated Polypropylene

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Received February 15, 1994; Revised Manuscript Received July 26, 1994®

ABSTRACT: The crystallization behavior of high molecular weight deuterated polypropylene has been studied using hot stage optical microscopy and differential scanning calorimetry. It is found that the equilibrium melting point is 8.3–8.9 °C below that of polypropylene, correlating well with a theoretical estimate of 8.7 °C.

Introduction

The deuterated polypropylene used is an isotactic polypropylene where all hydrogen atoms have been replaced by deuterium atoms. The aim of this study is to determine the influence of deuteration on melting temperatures of polypropylene. For this purpose two methods, depolarized light microscopy (DLM) and differential scanning calorimetry (DSC), are to be used.

The effect of deuteration on the melting behavior of synthetic polymers has received some attention in the past.[1–3] Theoretical predictions tend to indicate that there should be a general depression of the melting point caused by the deuteration. Such predictions have been borne out in practice for polyethylene.[4] However, in the case polypropylene the situation is not clear. What data are available suggest that no depression exists.[1,2] These reports were based simply on one experiment involving finite cooling rates and did not involve an estimation of the equilibrium melting point.

Both polymers have very high and similar molecular weights, about 257K. If there is any difference in equilibrium melting temperature, $T_m°$, between the two polymers, it could be compensated only by the C–D bond being slightly shorter than the C–H bond. As reported by Bates et al.,[4] C–H and C–D bond lengths differ by 0.005 Å. The equilibrium melting point has been determined using the Hoffman–Weeks approach,[5] and it will be shown that there is a depression of the equilibrium melting point which correlates well with predicted values, within experimental error.

Experimental Section

The deuterated polypropylene was supplied by Dr. John Rabolt of IBM Corp. The values of M_n, M_w, and M_z were 98.6K, 258K, and 522K, respectively. Isotactic polypropylene was supplied by Exxon Corp. and had an isotacticity of >99% as determined by Exxon using NMR methods. The values of M_n, M_w, and M_z were respectively 72K, 257K, and 528K.

Depolarized light microscopy (DLM) was carried out using a Mettler hot stage mounted on an Olympus microscope under cross-polar conditions. A trinocular was used, one beam passing to a camera, and second to a photomultiplier tube attached to a chart recorder, and the third for direct observation. The hot stage was calibrated using an Omega, type J, calibrated thermocouple. The polymer sample was placed between two glass cover slips. Using another hot stage the sample was heated to 200 °C and then rapidly transferred to the hot stage, which had been set to the desired crystallization temperature. This procedure assured the isothermal crystallization of the polymer. Following crystallization, the melting behavior was observed using a heating rate of 10 °C/min. Determination of $T_m°$ using DLM was conducted for short times of crystallization in order to minimize the effects of polypropylene's unusual thickening behavior on the results.[6]

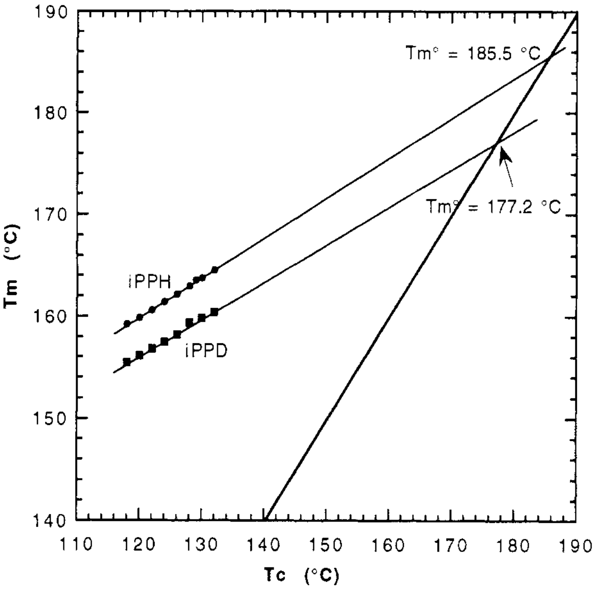

Figure 1. Equilibrium melting temperature, $T_m°$, of iPPH and iPPD using DSC peak temperature.

Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC7 instrument. The DSC was calibrated using pure indium as a standard (T_m = 156.60 °C). The polymer sample was heated to 200 °C and held for 10 min, in order to lose its thermal history; then it was rapidly cooled at a rate of 80 °C/min to the desired crystallization temperature. The sample was held at the crystallization temperature, T_c, for 10–70 min depending on T_c and then melted at a rate of 10 °C/min.

Results and Discussion

The equilibrium melting temperature, $T_m°$, of polypropylene was discussed in a previous paper involving lamellar thickness studies, in which it was demonstrated that the correct value is 186.1 °C.[6] It was also demonstrated that polypropylene has a peculiar lamellar thickening process which results in abnormally high estimates of $T_m°$ if long crystallization times are used. In the case of deuterated polypropylene, it is anticipated that a similar problem exists and so short crystallization times are used in the procedure to be discussed. The results that were determined by DSC and DLM experiments are summarized in Figures 1 and 2, respectively. According to Figure 1, the equilibrium melting temperatures of iPPH and iPPD are determined to be 185.5 and 177.2 °C, which results in a difference of 8.3 °C. Figure 2 represents the DLM results which yield two distinct equilibrium melting temperatures,

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® Abstract published in *Advance ACS Abstracts,* September 1, 1994.

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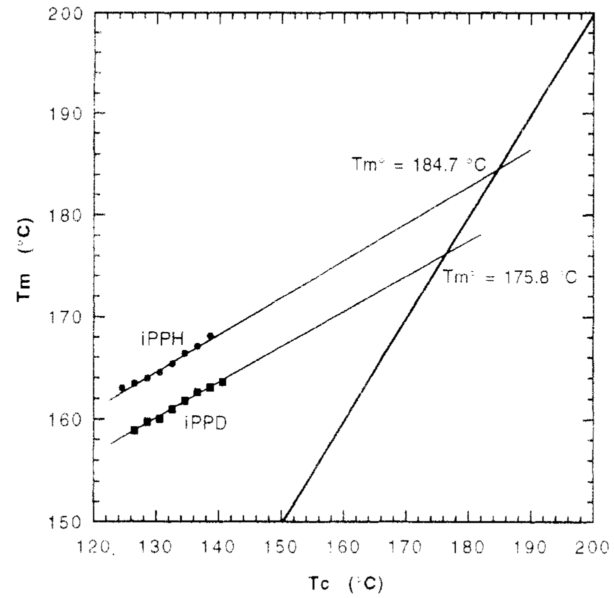

Figure 2. Equilibrium melting temperature, $T_m°$, of iPPH and iPPD using DLM experimental results.

184.7 °C for iPPH and 175.8 °C for iPPD, and a difference of 8.9 °C.

As argued in the previous paper,[6] the accurate value of $T_m°$ can only be determined by measuring the lamellar thickness as a function of melting temperature. This measurement can be done by using both SAXS and WAXS. But, this procedure is very long and requires large amounts of material, which is not possible in the case of iPPD because of the high cost of the raw material.

Using X-ray experimentation, Bates et al.[4] have shown that substitution of deuterium for hydrogen results in a slight reduction in the parameters *a* and *b* of the unit cell of $C_{36}H_{74}$. This change is believed to be the result of a reduction in the C–H bond length with deuterium substitution. In fact the C–D bond is 0.005 Å lower than the C–H bond. This reduction is manifest as a decrease in the molar volume and polarizability.

As described by Bates et al.,[4] the equilibrium melting temperatures of iPPH and iPPD can be correlated to the molar volume and polarizability as follows:

$$\frac{T_{mH}°}{T_{mD}°} \cong \left[\frac{\alpha_H}{\alpha_D}\frac{V_D}{V_H}\right]^2 \qquad (1)$$

where α and V represent the bond polarizability and molar volume of a polymer, respectively. H and D indices are symbols for iPPH and iPPD polymers. The values of $T_m°$ are in Kelvin. Perdeuteration leads to a slight reduction in the molar volume.[7] Based on the assumption that the *c* unit cell parameter is unaffected by isotope substitution, the estimation of $V_H/V_D = 1.0014$ results only from the change in the bond length with deuterium substitution in iPP.[4] The ratio $\alpha_H/\alpha_D = 1.0110$ is calculated from the polarizability change.[4,8] Using these values, eq 1 yields:

$$\frac{T_{mH}°}{T_{mD}°} = \left[\frac{1.0110}{1.0014}\right]^2 = 1.0193 \qquad (2)$$

This implies that

$$T_{mH}° - T_{mD}° = 0.0189 T_{mH}° \qquad (3)$$

Therefore, theoretically if $T_{mH}° = 186.1$ °C, the difference in equilibrium melting temperatures is 8.7 °C and $T_{mD}° = 177.4$ °C. The experimental differences are 8.3 and 8.9 °C for DSC and DLM determinations, respectively. The correlation between theory and experiment is therefore very strong for polypropylene.

The principle of this theory is based on the assumption that the entropy of fusion is dominated by an isotope independent conformational entropy and that the crystal structure remains unaffected by isotopic substitution. Using neutron scattering results, Stamm[2] has confirmed that both iPPH and iPPD have the same crystal structure.

Conclusions

The results show that, for the same crystallization conditions, iPPD has a lower melting temperature than iPPH and that the extrapolation of melting temperatures yields a lower equilibrium melting temperature than that of iPPH. The difference obtained experimentally is close to that predicted theoretically of 8.7 °C. Even though both polymers have different $T_m°$ values, they both share the same slope of the extrapolated lines. As a consequence, for any crystallization temperature, T_c, the melting temperature of iPPD is lower than that of iPPH, in agreement with theoretical predictions.

Acknowledgment. This research has been supported by the Polymer Program of the National Science Foundation under Grant DMR 9107675. The grant of a scholarship to K.M. by AID is gratefully acknowledged.

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