DSC Evidence for Microstructure and Phase Transitions in Polyethylene Melts at High Temperatures

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ABSTRACT: Thermal/microstructural transitions were found at 208 and 227 °C in commercial polyethylenes of types HDPE, LDPE, and LLDPE. DSC data were obtained for a range of heating and cooling rates, over a broad high-temperature regime (30− 280 °C) that spans the melt processing regime. Six samples, from four resin suppliers, were tested; all were of moderate molecular weight ($\bar{M}_w = (36-85) \times 10^3$). Results are discussed in terms of molecular order and transitions between different degrees of ordering. No transitions were detectable in highly branched metallocene samples. The DSC results are in agreement with our previous rheology findings of order and high-temperature transitions in polyethylene melts.

Introduction

Recent rheological studies of polyethylene (PE) blends in our laboratory[1−3] incorporated measurements of torque ($\mathcal{T}$) in a rotary blender as a function of temperature (T) for the separate PE components that were later to be melt-blended. These and subsequent measurements of steady shear viscosity and normal stress difference for high-density polyethylene (HDPE) melts[4] suggested the existence and persistence of molecular order at high temperatures. Indications of surprisingly high order in these melts have been reported previously at temperatures significantly above the melting range. For example, NMR measurements[5] on HDPE melts ($\bar{M}_w = 2 \times 10^5$) identified an "ordered phase" in the temperature range 140−204 °C. Recently, Kolnaar and Keller[6] reported a liquid-state transition (from hexagonal to "super hexagonal") in HDPE at about 150 °C.

In the torque measurements, anomalies appeared in two ways: (a) the overall $\mathcal{T}(T)$ behavior was distinctly non-Arrhenius in nature, suggesting that ordered molecular conformational states prevailed, as opposed to the disordered random coils expected[7] for high-T melts, and (b) transitions in the $\mathcal{T}(T)$ descent appeared abruptly at about 208 °C (T_1) and 227 °C (T_2). Typical $\mathcal{T}(T)$ data are shown for resin A in Figure 1. The polystyrene data in Figure 1 show $\mathcal{T}(T)$ expected for fully amorphous melts. We now report thermal evidence of such PE transitions, observed by differential scanning calorimetry (DSC), apparently for the first time.

Experimental Section

Three commercial HDPE samples were used in this DSC study. Also, commercial samples of low-density polyethylene (LDPE) and two linear-low-density polyethylenes (LLDPE) were examined. Four different resin manufacturers were represented. Characterization data are given in Table 1. $\bar{M}_w$ and $\bar{M}_n$ were obtained by GPC.

Specimens of the as-received resin samples (about 5−10 mg) were compressed into aluminum sample pans for testing in a TA Instruments DSC 2910 equipped with a nitrogen gas flow. Various T-scan rates were used; however, only low cooling rates (1−2 °C/min) were capable of revealing the high-temperature transitions of polyethylenes. Each sample was tested in two heating and cooling cycles (30−280 °C) in nonhermetic pans.

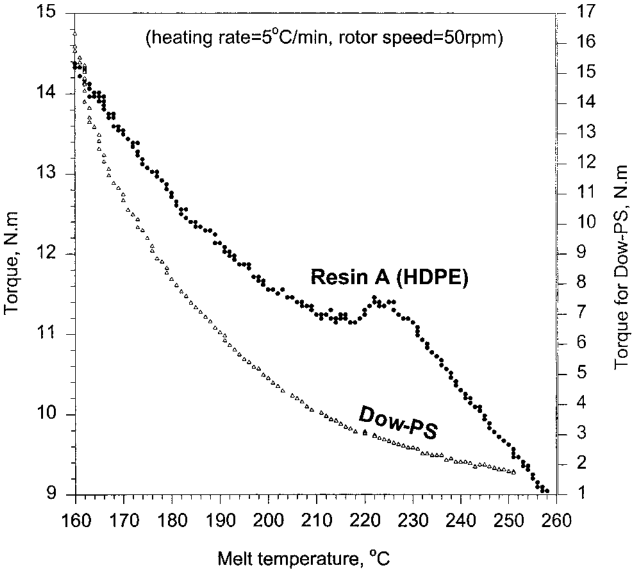

Figure 1. Torque evidence of high-temperature transitions in HDPE melt.

Results and Discussion

The reason that DSC evidence of these two transitions has not been previously reported is probably related to the fact that the heat released in these transitions is small[2] compared to that of the conventional melting peak (T_m). Contributing factors could be that a systematic search has not been motivated by any industrial need, together with the fact that the molecular structure of PE is so simple that transitions would not be expected. Moreover, the generally favored high scan rates (e.g., 10 °C/min) were not effective in revealing the transitions in either heating or cooling scans. Finally, the heating scan (which usually receives most of the attention) is less effective in detecting the "melting" phenomenon than is the cooling scan in detecting the "freezing" phenomenon. Some results were checked for reproducibility in hermetic pans.

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Table 1. Characterization and Source of Polymers

type	supplier	code	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	branch content (CH_3/1000 C)	transitions
HDPE	Quantum	A	785 149	17 347	4.93	0	T_1, T_2
HDPE	Exxon	B	35 946	10 823	3.32	0	T_2
HDPE	Nova	C	251 500	19 400	12.96	<0.5	T_1; T_2
LLDPE[a]	Dow	D	99 717	29 462	3.38	13.7	T_2
LDPE	Dow	E	95 114	17 849	5.33	N/A	T_2
LDPE	Nova	F	99 464	15 458	6.45	22[b]	T_1

[a] Hexene comonomer. [b] Total number of short and long branches.

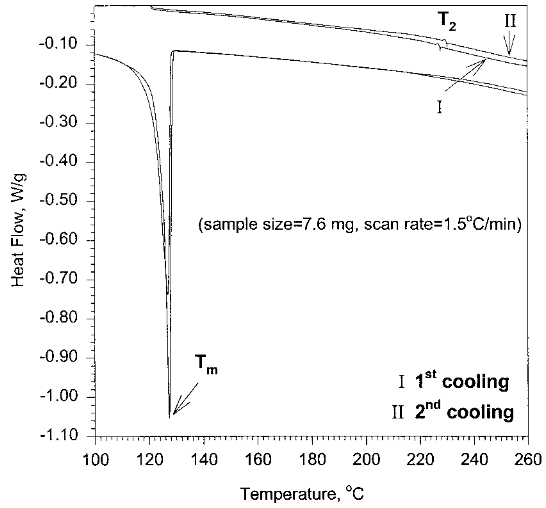

Figure 2. DSC plot for as-received HDPE (resin B) in the temperature range 100−260 °C.

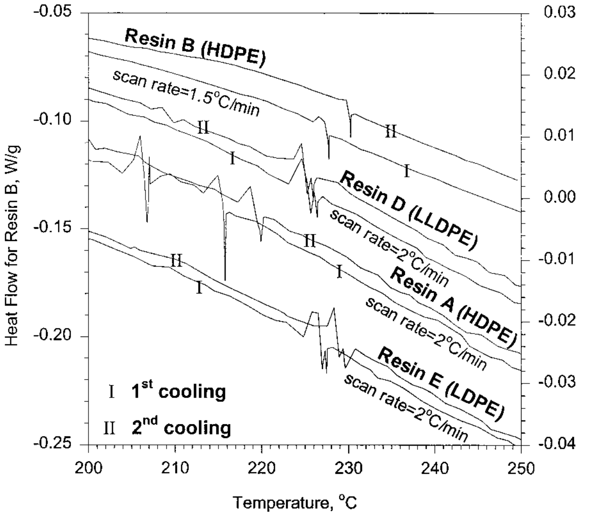

Figure 3. DSC data for resins A, D, and E (read right vertical scale) and for resin B (read left vertical scale).

1. HDPE. Results for resins A, B, D, and E are displayed in Figures 2 and 3. Two full cycles of heat/cool scans are involved, all at rates of 1.5 or 2 °C/min. The two cooling scans for B in Figures 2 and 3 both exhibit freezing peaks in the range 227−230 °C and are only slightly displaced vertically from each other. Figure 2 shows the relative sizes of the T_m peak and the peak at the T_2 transition temperature. At T_2, the heat evolved[2] was very small when compared to that of T_m. The small ΔH_2 also means that the corresponding entropy $\Delta S_2 = \Delta H_2/T_2$ is small, too. The reproducibility of the T_2 transition in the second cool after a complete cycle of cooling and heating is quite remarkable and indicates the validity and reliability of these observations. The reversibility of the transition (accompanied by small ΔH) and its appearance only in the cooling cycle is similar to the reported behavior of LCPs.[8−10]

A specimen of resin C (HDPE of higher M_w) was tested at scan rates of 3 and 1 °C/min. Results[2] displayed evidence of a lower T peak at 210 °C and a higher T peak at 227 °C, which matched well the mechanical evidence $\mathscr{T}(T)$ from the blender.

It is important to note that the T_2 transition shown above for HDPE is not a consequence of oxidation or other degradation reactions; HDPE is extremely stable under these DSC testing conditions.[11−13] Furthermore, the DSC analysis (under the same test conditions) of an atactic polystyrene (PS) revealed *no* transitions above its T_g (in agreement with its $\mathscr{T}(T)$ behavior in Figure 1). The results on PS suggest that the observed transitions in polyethylene are a consequence of neither oxidation nor instrument artifacts, but rather a product of a physical phenomenon. High-temperature transitions in DSC tests were also displayed by HDPE samples obtained from several other resin producers (see Table 1).

2. Branched Species. The LLDPE (resin D; Figure 3), made by Ziegler−Natta catalysis, and the LDPE (resin E; Figure 3), were both tested at cooling rates of 2 °C/min. For both specimens, a first and second scan are shown, displaying good reproducibility, and the data for the two resin types resemble each other closely, with a major peak near 227−230 °C. One difference between resins D and E is that the former displays a small but clear peak near 208−210 °C, resembling in this detail the behavior of the unbranched linear chains of resins A and B. On the other hand, resin E does not show strong evidence of T_1. Nonetheless, the T_1 transition was detected in another LDPE (resin F) with different molecular weight characteristics. Results for T_1 and T_2 are collectively displayed in Table 1.

The DSC test was repeated on a highly branched (36.2 CH_3/1000 C) metallocene LLDPE (butene) at a scan rate of 1.5 °C/min. No evidence of high-temperature transitions was detectable. The DSC results for the metallocene resin were supported by $\mathscr{T}(T)$ measurements[2], in which T_1 and T_2 were also undetectable.

3. Interpretation of Transitions. The 227 °C transition was seen by DSC in all PE resins (except the highly branched metallocene LLDPE resin), regardless of supplier and scan rate and regardless of whether light branching was present in the molecules. Furthermore, these reproducible transitions show a unique "signature" that is totally different from the strong exothermic peaks[2,11,12] associated with oxidative degradation of polyethylene.

Instead, we believe the collective evidence supports the view that the 227 °C transition represents a LCP-like transition of some sort,[4] meaning that ordinary polymethylene sequences (independent of length and unimpeded by light branching) are capable of either localized chain order or collective assembly behavior that provides other forms of ordering. Somewhat similar concepts have appeared before, though never based on DSC evidence.[14] Kruger et al.[15] used acoustic measurements with low-$\bar{M}$ PE and identified a transition near 230 °C (attributed to a transformation from an ordered phase to an isotropic phase). The contention of LCP behavior in melts of polyethylene is supported by previous TEM and electron diffraction studies.[16]

However, we doubt that the 227 °C transition represents conversion to isotropy, since the earlier torque/rheology studies[3] showed non-Arrhenius $\mathscr{T}(T)$ character above 227 °C. Moreover, our previous measurements[4] of viscosity and normal stress suggested the persistence of LCP-like order in HDPE at temperatures above 227 °C. However, LC-like transition from one type of order to some other type at T_2 seems possible, as does a reduction of aggregate sizes at 227 °C.

The 208 °C transition always presented a smaller DSC peak than the one at 227 °C, which is consistent with the $\mathscr{T}(T)$ evidence that much sharper rheological transitions occurred at 220−230 °C than at 208 °C. Indeed, the latter transition was not at all abrupt in $\mathscr{T}(T)$ but seemed to signal the nearly smooth merger of regimes above and below 208 °C. This could indicate that polymethylene chains in the melt state possess substantial backbone order beginning at T_m but lose it progressively (or change it) as T increases toward 208 °C. Our results are consistent with previous Raman spectroscopic studies[17] on linear polyethylene (UHMWPE) melts reported only up to 208 °C (which is unlikely to be merely coincidence but remained without commentary by the authors). The weakening of evidence for the 208 °C transition in DSC cooling curves with the presence of branching to interrupt the polymethylene sequences is compatible with increased difficulty in achieving molecular order along the backbone for any long polymethylene chain within the molecule.

Conclusions

1. New DSC evidence confirms the existence of molecular and microstructural transitions near 208 and 227 °C in HDPE, LDPE, and LLDPE. However, highly branched LLDPE produced with metallocene catalysts did not show these transitions.

2. These transitions are independent of molecular weight and nearly independent of details of molecular structure. This behavior is not explicitly related to various anomalies reported for UHMWPE.[13]

3. The evidence for ordered structures and thermal/structural transitions strongly implies that PE melts are structured liquids that mimic LCPs in many ways.[17]

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