Characterization of Polyolefins by Solution DTA

INTRODUCTION

Differential thermal analysis (DTA) has been used frequently to study the crystallization of polymers from solutions,[1-4] and recently[5] the applicability of DTA has been extended to studies of the polymer solution process itself. Using whole and fractionated linear polyethylenes, it was shown that when suspensions of polymer crystallites in various solvents were heated slowly (1.2°C/min), complex endotherms indicative of recrystallization during solution were generated. A fractionation effect, operative during recrystallization/solution was also reported.[5] Subsequent experiments based on a broader range of polyolefins have shown the DTA endotherm to be a characteristic property of the particular polymer involved. The latter studies have therefore suggested the use of the method as a rapid, qualitative means of analysis applicable to single polymers as well as to polymer blends. Some more quantitative relationships between molecular structure parameters and parameters drawn from the solution endotherm are also worth noting for their potential applied usefulness in simple polymer characterizations. The present note is directed toward these considerations.

EXPERIMENTAL

The DTA cells used in the solution studies have been described in detail in an earlier publication.[5] The "analytic cell" was employed in all work reported here. However, experiments of the type discussed could also be performed with commercially available apparatus; in a number of trials, the Perkin-Elmer differential scanning calorimeter (Model 1B) has been used successfully. In view of the well-known dependence of polymer solution processes on thermal history and on solvent environment,[1,2,5,6] a closely reproduced reference scan procedure was adopted for this work. Tetralin solutions of polyolefins (2.0 g/100 ml) were prepared in the cell at a temperature near 150°C. Solutions were cooled at 1.2°C/min to about 50°C, then more rapidly to room temperature. Suspensions of crystallites in the fluid were reheated at 1.2°C/min, and the endotherm so generated was taken as the "solution signal." Descriptive parameters drawn from a typical endotherm (for a linear polyethylene) are illustrated in Figure 1. The endotherm shows the double peak resulting from recrystallization during solution.[1,2,5] A_s' and A_s'' are areas under the lower and higher temperature peaks, characterized by the peak

TABLE I
Polymer Characterization Data

Sample	$M_w \times 10^{-4}$	[CH$_3$]/ 1000 C	[CH$_3$]/ molec.	d_{ref}[a]
HDPE	10.5	0.8	6.0	0.9608
EPCP	11.5	2.7	22.1	0.9455
EBCP-1	0.61	8.0	19.1	0.9491
EBCP-2	0.58	15.5	64.2	0.9432
IDPE	9.7	7.7	55.0	0.9422
LDPE-1	13.0	16.0	148	0.9236
LDPE-2	84.5	5.7	343	0.9278
LDPE-3	44.0	19.0	597	0.9197
PPR	—	—	—	0.9080
HDPE/PPR (85/15)	—	—	—	
LDPE/PPR (85/15)	—	—	—	

[a] ASTM D1505-67.
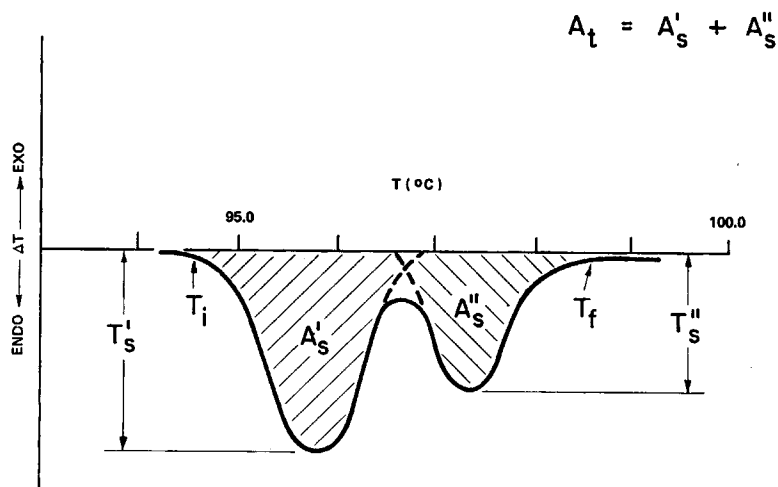
$$A_t = A_s' + A_s''$$

Fig. 1. Solution endotherm for high-density polyethylene, showing characterization parameters.
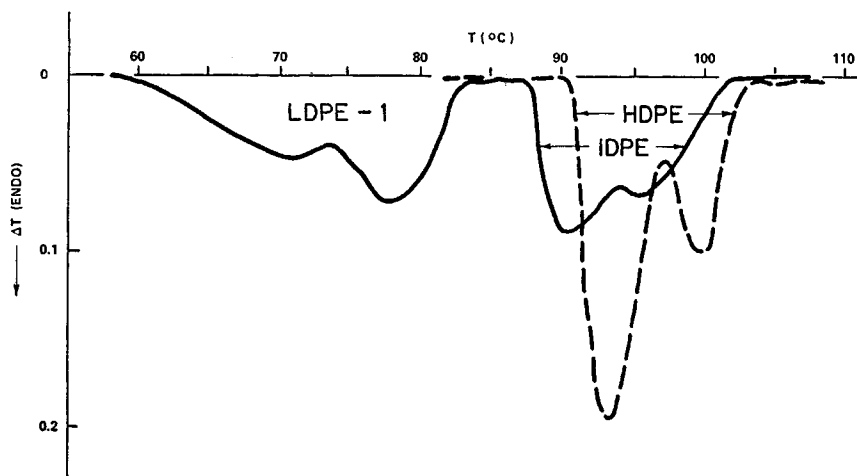

Fig. 2. Comparison of solution endotherms for high-intermediate-, and low-density polyethylene.

maxima T_s' and T_s''. T_i and T_f represent initial and final deviation from the baseline of the DTA trace.   The symbol A_t represents the sum of area parameters A_s' and A_s''.

The polymers and polymer blends investigated are noted in Table I, along with their weight-average molecular weights ($\bar{M}_w$, from light scattering determinations) and the pendent methyl group concentration (from infrared spectra).   Reference densities are also given in Table I.   The codes refer to high-density polyethylene (HDPE), ethylene-propylene and ethylene–butene copolymers (EPCP, EBCP), intermediate and low-density polyethylenes (IDPE, LDPE), and polypropylene (PPR).   The latter was a commercial material, but no structural detail was available for the polymer.   Blends of polypropylene with the HDPE and LDPE were prepared by roll milling the polymers at 190°C in the presence of 0.1% antioxidant.
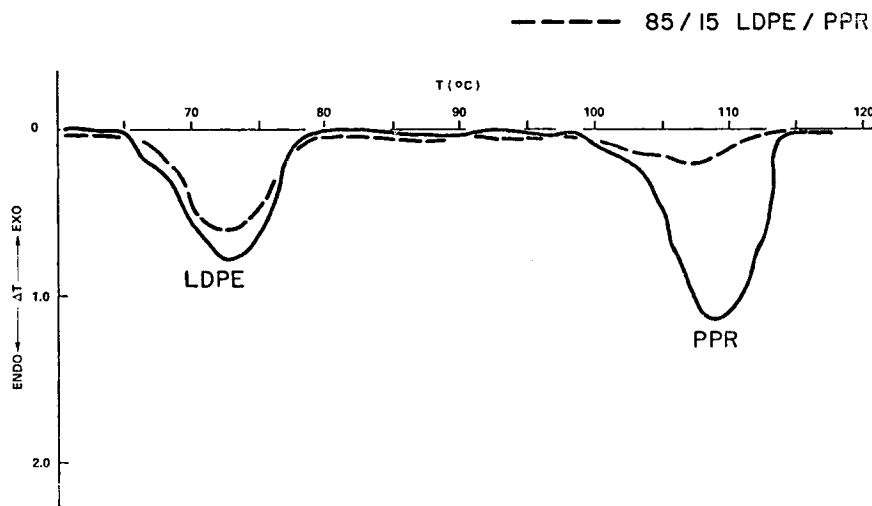
Fig. 3. Composite endotherm for the LDPE/PPR system.

RESULTS AND DISCUSSION

The qualitative differences in the solution endotherms for diverse polyolefins, as generated by the standard scan, are illustrated in Figure 2. Expectedly, the entire endotherm shifts toward lower temperatures as the branch frequency of the represented polyethylenes increases. In the same sequence, the marked reduction in the areas under the endotherms, indicative of reduced crystallite number and perfection, is also noteworthy. The secondary, higher temperature signal, attributed to recrystallization (annealing) during solution of the HDPE sample,[5] is much less pronounced for the IDPE and LDPE polymers. This finding agrees with those reported by earlier workers.[1,2]

Table II presents a summary of the endotherm parameters for solution of the set of polymers described in Table I. The parameters amount to a distinct characterization of the polymer in question, reflecting particularly on morphologic properties. The span of the endotherm signal, $T_f - T_i$, may be of interest in this connection, representing an index of the morphologic distribution generated during a defined temperature cycle in the reference solvent environment. The entries for the two polyblends demonstrate that the DTA method is capable of resolving qualitatively and quantitatively between blend components. Qualitatively, the endotherm is the resultant of the individual signals, thus allowing for identification of the blend components. This is shown in more detail by Figure 3 for the LDPE/PPR system. Similar resolution has been observed by the present method for minor component concentrations of 1–1.5%. Quantitatively, the observed A_t values in Table II are well within 10% of expectations based on sums of individual A_t values and polymer weight fractions. Following qualitative identification of polyblend constituents, therefore, simple calibrations with the pure materials would be sufficient to permit computation of the constituent concentrations from the composite endotherm.

The implication of correlations between endotherm parameters and structural variables of the polymers, contained in the foregoing remarks, is tested in Figure 4. Because of the generally recognized difficulty in evaluating the branch incidence in polyolefins, the (weight-average) molecular branch frequency has been plotted against two of the endotherm parameters. The correlation suggested by Figure 4a shows a strong decrease in the initial solution temperature T_i with increasing branch frequency. The polyolefin families are well separated in the diagram, so that a T_i determination may suffice for
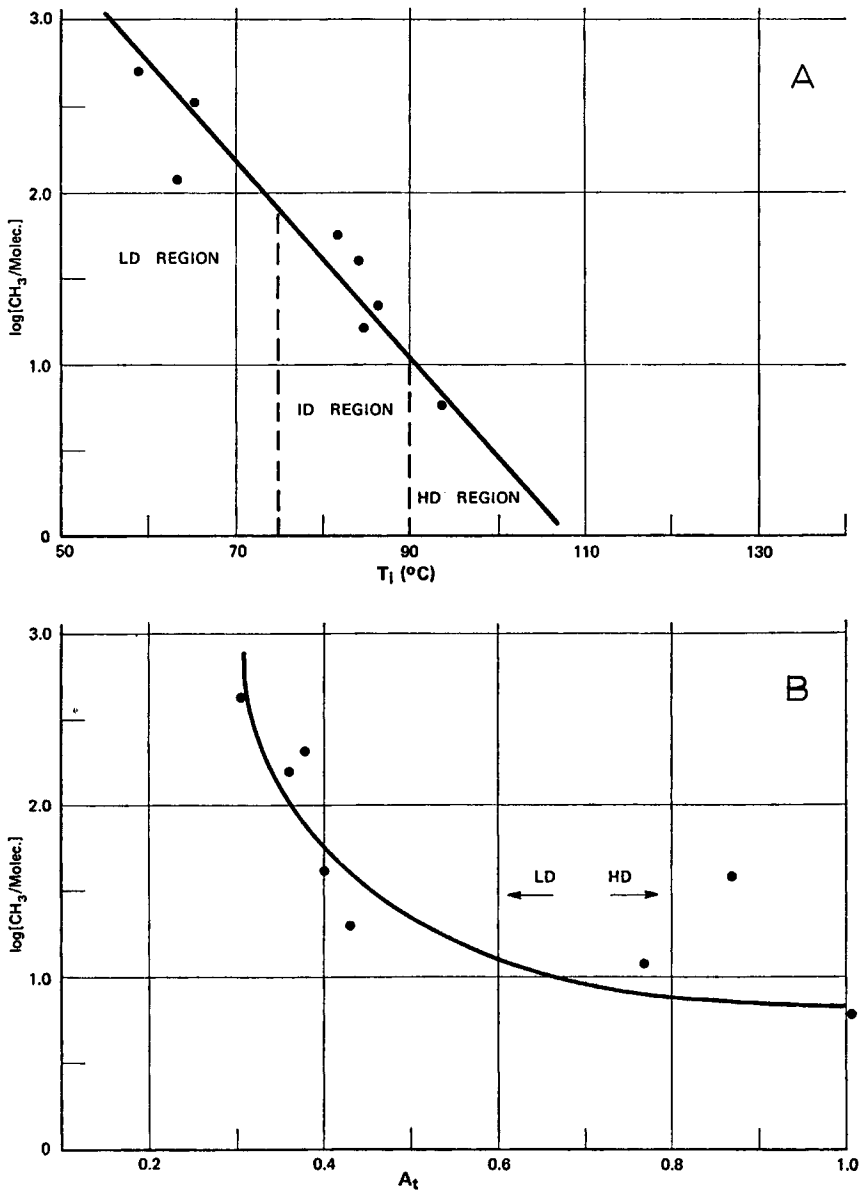
Fig. 4. (A) Apparent linear correlation between T_i and molecular branch frequency in polyolefins.   (B) Apparent complex correlation between A_t and the molecular branch frequency.

family classification as well as for an index of the important branching parameter.   The plot in Figure 4b assumes a relationship between total crystallinity in the suspensions and molecular branch frequency.   The correlation is not as well defined as in the earlier case, though some family classification may be seen again in this complex function. Empirical relationships have been found to exist also between reference density and

TABLE II
Endotherm Parameters[a]

Sample	T_s',°C	T_s'',°C	A_t	T_i,°C	T_f,°C	$T_f - T_i$, °C
HDPE	95.0	99.2	1.01	93.0	101.5	8.5
EPCP	92.6	96.4	0.77	86.5	100.0	13.5
EBCP-1	90.1	94.5	0.43	84.0	96.6	12.6
EBCP-2	89.7	94.0	0.40	81.7	95.5	13.8
IDPE	90.5	94.3	0.87	87.0	102.0	15.0
LDPE-1	72.0	77.5	0.36	63.2	79.7	16.5
LDPE-2	— 72.5 —		0.38	65.0	78.5	13.5
LDPE-3	— 74.5 —		0.31	58.5	79.0	20.5
PPR	— 109.6 —		0.59	99.5	114.5	15.0
HDPE/PPR(85/15)	93.4	98.7	0.88	88.0	114.7	26.7
LDPE/PPR(85/15)	— 71.7 —		0.39	65.0	113.5	48.0

[a] Standard scan at 1.2°C/min; 2% solutions in tetralin.

T_f or A_t. None of these correlations can be considered firmly established by the few experiments in hand. Subject to their further confirmation, however, they could serve a useful purpose in analytic and quality control functions of polymer synthesis or processing operations.

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