A comparative study of ULDPE utilizing DSC and TREF [1]

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INTRODUCTION

The study of short chain branching (SCB) distribution of crystallizable polymers utilizing temperature rising elution fractionation (TREF) is a well known and established methodology. TREF utilizes the "crystallizability" of polymers in order to fractionate them. Crystallizability is dependent on factors such as short chain branching type, tacticity, and copolymer composition. However, as normally practised, TREF can be both labor and time intensive.

Another probe of crystallizability which is generally available is differential scanning calorimetry (DSC). In this work, both solution- and melt-crystallized samples were analyzed by DSC to ascertain the feasibility of utilizing DSC as an alternative or supplementary technique. The DSC results are compared with TREF runs using ultra-low-density polyethylene (ULDPE) as the test polymer.

Initial work addressing the suitability of using DSC as a complimentary technique to TREF has been reported in the literature [1] for low density polyethylenes. More recently, work has also been reported on linear low density polyethylenes [2,3]. After performing crystallization of DSC samples in a TREF-type microprocessor-controlled oven, a remarkable degree of similarity was observed between TREF- and DSC-generated curves.

EXPERIMENTAL

The ultra low density polyethylene (ULDPE) employed for this study is a commercially available (Dow Attane) copolymer of ethylene and 1-octene.

The sample has a density ρ of 0.912 g cm^{-3}, a melt index of 1, with $M_w = 120\,000$ and $M_w/M_n = 6.32$.

TREF (temperature rising elution fractionation)

Temperature rising elution fractionation was performed on the ULDPE sample in both the analytical and preparative modes. The ULDPE was dissolved at 160°C in 1,2,4-trichlorobenzene and then loaded onto a heated inert support (Chromasorb P). This support–polymer–solvent mixture was loaded into a microprocessor-controlled oven where a programmed temperature gradient of 1.5°C h^{-1} was applied from 130°C to room temperature. During this crystallization process, separation and fractionation of chains takes place based on the distribution of short chain branches. A complete description of TREF can be found in the literature [4–6].

Once crystallization was complete, the sludge-like mixture was loaded into a column, which was placed into an oven. A controlled heating rate of 25°C h^{-1} was applied together with an eluant flow rate of 4 ml min^{-1}. Polymer chains were eluted off the beads in the reverse order to that in which they were deposited. The eluting solution was collected as fractions; the corresponding temperature ranges of each designated fraction are U2 = 30–60°C, U3 = 60–70°C, U4 = 70–75°C, U5 = 75–85°C, U6 = 85–95°C, and U7 = 95–105°C. These fractions were subsequently dried to recover the polymer for further analysis with TREF and DSC.

DSC (differential scanning calorimetry)

In order to reasonably compare samples from TREF with those characterized by DSC, it is necessary to ensure that both sorts of samples are subjected to the same thermal history. Samples for DSC were crystallized following the same programmed temperature gradient as that experienced by the TREF materials; namely, they were cooled from 130°C at 1.5°C h^{-1} to room temperature. Two different types of DSC samples were prepared: melt-crystallized and solution-crystallized whole polymer. In addition, the fractions obtained from TREF were crystallized in a similar manner: from the melt and from solution. The original prepared TREF fractions and "as received" whole polymer were also examined by DSC. In all cases, thermograms were obtained using a Perkin-Elmer DSC-7 with a sample size of ≈ 5 mg and a heating rate of 10°C h^{-1}.

RESULTS AND DISCUSSION

It is well known that linear low-density polethylene prepared from the copolymerization of ethylene and alpha-olefins can produce TREF curves showing a distinct bimodal distribution of branches in the polymer. It is not
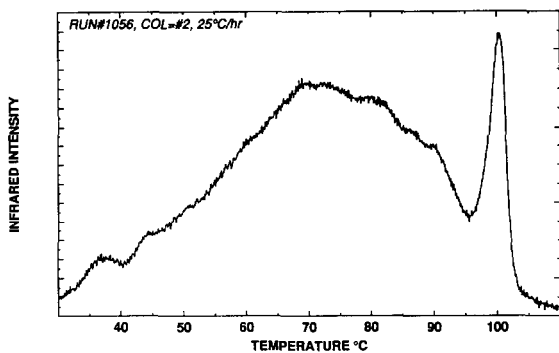
Fig. 1. TREF chromatogram of ultra low density polyethylene.

surprising that ULDPE shows a similar type of response (Fig. 1). A major broad peak, centered at approximately 70°C, stretches from around 30°C to around 95°C and is considered indicative of a broad distribution of branch concentrations in the polymer. There is also a small, but characteristic, sub-peak at around 35°C which is an artifact of the crystallization process. When the initial TREF crystallization is extended to lower temperatures and elution started at these same low temperatures, the broad peak approaches the baseline asymptotically [7]. Those chains that elute in the sharp peak from 95 to 105°C are through to be largely linear, closely resembling those of HDPE.

If those fractions which were derived from a preparative TREF experiment are re-treffed using an analytical-scale TREF unit, then relatively sharp peaks are obtained, compared to the original TREF curve (Fig. 2). Peak positions of re-treffed polymer correspond approximately to the appropriate temperature range over which the fractions were originally collected. However, there is some overlap of peaks which presumably arises from the linearly increasing temperature ramp which was used in this study. Better resolution is obtained when a step-wise ramp is employed.
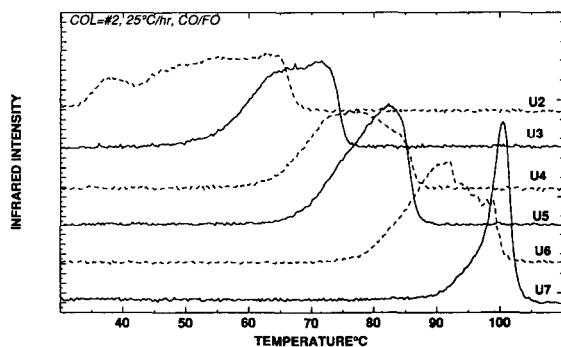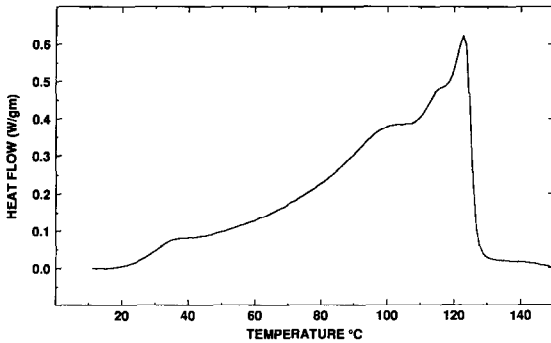

Fig. 2. TREF chromatograms of ULDPE fractions.

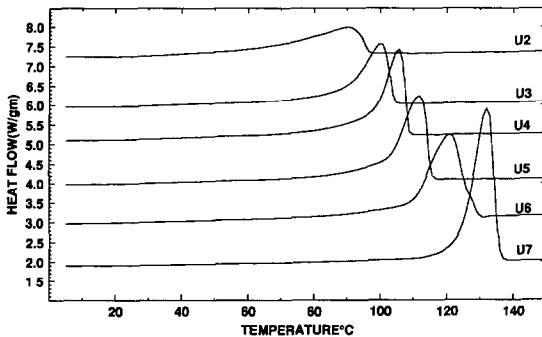Fig. 3A. Thermal behaviour of "as received" ULDPE.

Fig. 3B. Thermal behavior of "as prepared" fractions.

The DSC trace of "as received" whole polymer is shown in Fig. 3A and the DSC traces of the "as prepared" fractions are observed in Fig. 3B. The whole polymer shows three discernable peaks over the approximate range 100–125°C although melting may start at much lower temperatures. There is no apparent similarity with the TREF peak of whole polymer. The "as prepared" TREF fractions all show relatively sharp melting responses; however, there is evidence of a low temperature tail to a greater or lesser extent in all the "as prepared" fractions.

An initial examination of the DSC response of TREF-type crystallized melt shows a curve which is remarkably similar in shape to the original TREF curve (Fig. 4). However, in this case, the DSC trace is spread over a broader temperature range. Similarly, TREF fractions which were melt-crystallized show a sharp melting response although there is still evidence of low-temperature tails in these samples (Fig. 5).

In general, solution-crystallized samples show much sharper DSC traces: the whole polymer has a DSC curve (Fig. 6) which appears to be similar in overall shape to the TREF response. Fractions that have been solution-crystallized (Fig. 7) give even sharper peaks than melt-crystallized fractions
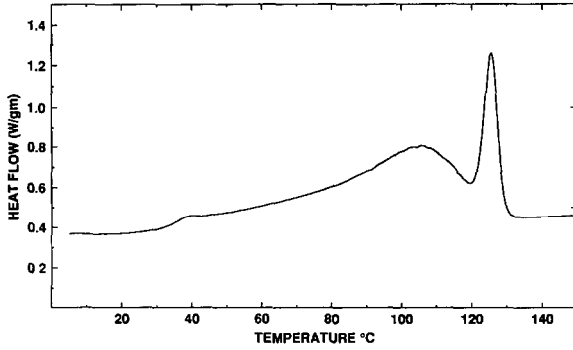
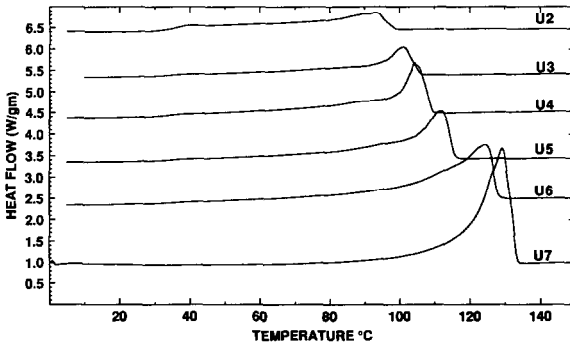Fig. 4. Thermal behaviour of melt-crystallized ULDPE.

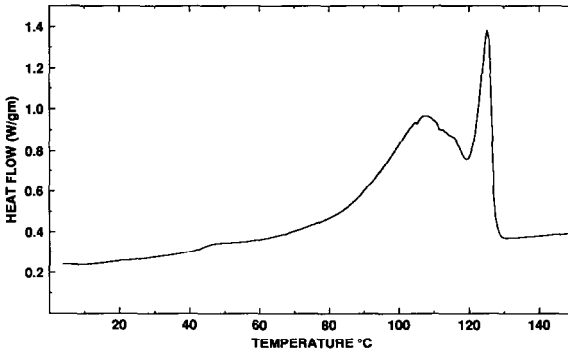Fig. 5. Thermal analysis of ULDPE melt-crystallized fractions.

Fig. 6. Thermal behavior of solution-crystallized ULDPE.

(compare Fig. 5) and there is little evidence for low-temperature tails. It is assumed that variations in chain mobility between the solution and melt states are responsible for differences in ease of segregation and account for disparity in peak sharpness between these TREF fractions.
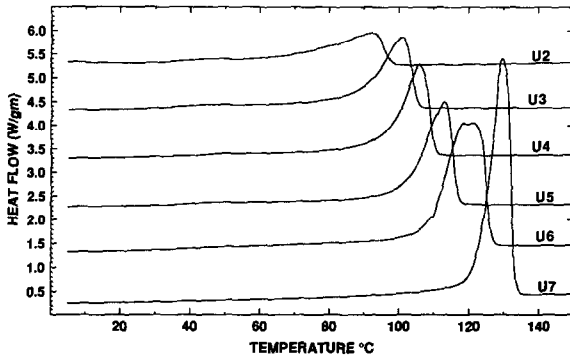
Fig. 7. Thermal analysis of ULDPE solution-crystallized fractions.

While there appears to be a reasonable shape correlation between the TREF and DSC responses of similarly crystallized materials, there are significant differences between the two techniques. In TREF, samples are heated from the crystal state to the "melt" at 25°C h^{-1}; in contrast, in DSC, the heating rate is 10°C min^{-1}. Furthermore, in TREF, the polymer is "melting" in the presence of a solvent; samples in this DSC study were run as dry powders. In general, it would appear as though TREF specimens are quite susceptible to reorganization at these slow heating rates. Whether such reorganization occurs is questionable in light of the fact that TREF samples experience an extremely slow initial crystallization process which tends to favor the establishment of near-equilibrium segregation and structures. Overall, the greatest difference appears to be that TREF specimens are, in fact, dissolving. Such an experimental set-up can be arranged in the DSC; however, one might anticipate problems with solvent evaporation at the high temperatures necessary for these experiments, and a corresponding change in polymer concentration.

It should also be realized that TREF and DSC detectors are measuring different properties. With the normal IR detector, TREF is reporting the total number of molecules (actually the C–H stretch) that go into solution in any temperature interval. In contrast, DSC is only concerned with the number of crystallizable units that are converted to melt in a particular temperature interval. With a knowledge of the level of crystallinity of several TREF fractions, it would be possible to construct a table of conversion factors to transpose DSC response to a TREF-type curve.

CONCLUSIONS

Overall, it is felt that the results reported from the DSC and TREF studies of a continuous slow TREF-type crystallization indicate a significant improvement over the stepwise isothermal procedure previously reported [2]. Because this crystallization was so slow, it also yields sharper

and more distinct peaks than in the earlier work [3]. Both TREF and DSC can provide similar compositional distribution information, even though the shapes of the curves are not identical. Needless to say, it would be impossible to justify these statements without the availability of TREF-type fractions, which simply cannot be produced through a DSC approach. Solution-crystallized specimens appear to have a better correlation with TREF than do melt-crystallized samples.

ACKNOWLEDGEMENT

REFERENCES

1 C. Bergstrom and E. Avela, Kem.-Kemi, 3 (1976) 47.
2 T. Kamiya, N. Ishikawa, S. Kambe, N. Ikegami, H. Nishibu and T. Hattori, ANTEC '90, (1990) 871.
3 L. Wild, S. Chang and M.J. Shankernarayanan, ACS Polymer Preprints, 31(1) (1990) 271.
4 L. Wild, T. Ryle, D. Knobeloch and I.R. Peat, J. Polym. Sci., Polym. Phys. Ed., 20 (1982) 441.
5 L. Wild, T.R. Ryle and D.C. Knobeloch, ACS Polymer Preprints, 23 (1982) 133.
6 D.C. Knobeloch and L. Wild, Polyolefins IV — Innovations in Process, Products, Processing and Additives, Dallas, Texas, 27–28 February 1984, Soc. Plastics Engineers, Brookfield Center, CT, pp. 427–442.
7 L. Wild, personal communication, First Penn State TREF Workshop, November 30–December 1, 1988.