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The similarity of compositional distribution information generated by DSC and TREF

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Abstract

This paper demonstrates the generation of DSC thermograms from TREF chromatograms. The reverse is clearly possible, and shows that compositional distribution information is obtainable from DSC using solution crystallized material. However, TREF is essential, at least initially, in providing fractions for calibration curves.

Keywords: TREF; ULDPE; Short chain branching distribution

1. Introduction

This paper examines the possibility of obtaining the same kind of compositional distribution information from curves produced by differential scanning calorimetry (DSC) as is obtained from chromatograms generated from temperature rising elution fractionation (TREF). This similarity, exemplified by peak shapes, has been reported by a number of authors[1–4]. The intent of this work is to demonstrate how one may produce a DSC curve of ultra low density polyethylene (ULDPE) starting from its TREF chromatogram; clearly the reverse is also possible. The resulting thermogram will be compared with that of a solution-crystallized DSC specimen.

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2. Experimental

The polymer employed in this study is a commercially available ultra low density polyethylene (Dow Attane[®]) and is a copolymer of ethylene with 1-octene. The sample has a density, $\rho \approx 0.912 \text{ g cm}^{-3}$, melt index ≈ 1 , $M_w \approx 120.000$ and a $M_w/M_n \approx 6.3$.

2.1. Differential scanning calorimetry

The polymer specimen was dissolved in hot 1,2,4-trichlorobenzene and then subjected to a programmed crystallization cycle from 130°C to room temperature at 1.5°C 1 h⁻¹. Polymer was recovered by filtering it through a Teflon[®] filter, then drying at room temperature for 3 d under vacuum. A DSC curve was obtained using a sample size of $\approx 5 \text{ mg}$ and a heating rate of 10°C min⁻¹ in a Perkin–Elmer DSC-7.

2.2. Temperature rising elution fractionation

The ULDPE sample was dissolved in hot 1,2,4-trichlorobenzene, to which was added heated inert support material (Chromasorb[®] P). The polymer, support, and solution formed a sludge-like mixture which underwent controlled crystallization from 130°C to 30°C at a rate of 1.5°C/h⁻¹ at the same time and in the same oven as the previously mentioned DSC samples. During this cycle, separation on the basis of “crystallizability” occurs, in which the most crystallizable and least branched components crystallize first, followed by chains with increasing levels of branching and decreasing crystallizabilities. Detailed descriptions of the TREF experimental process are found in the literature [5–7]. Six fractions were collected over the elution range, NMR was employed to determine branching content, and DSC to determine melting point.

3. Results and discussion

Experimental characterization of the ULDPE specimen using analytical TREF yielded the bimodal copolymer distribution chromatogram of Fig. 1. Similar distributions are also found in the LLDPE family of polymers. In order to quantify this normalized plot into a short chain branching (SCB/1000 C) distribution curve it is necessary to determine an appropriate calibration curve for this particular polymer. Such a curve (Fig. 2) was obtained by collecting a series of fractions (six in this case) and measuring their branching content by use of ¹³C NMR (Table 1). Appropriate substitution using the initial chromatogram yields the quantified branching distribution curve of Fig. 3.

Additionally, as the objective is to obtain a DSC curve from the original TREF it is necessary to relate comonomer content to melting point. This is made possible by determining the melting points of the individual fractions by DSC. The resulting melting point data are plotted as a function of branching content in Fig. 4. Applying

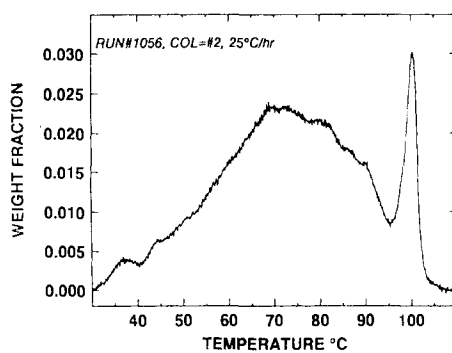


Fig. 1. TREF chromatogram of ultra low density polyethylene.

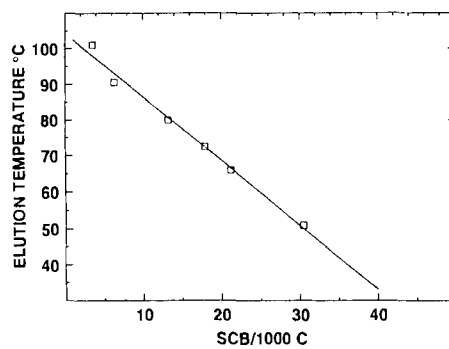


Fig. 2. Calibration curve relating branching content and elution temperature.

Table 1
Fractions with corresponding branching contents, melting temperatures, and heats of fusion

Fraction #	SCB/1000 C	Melting Point/°C	Heat of fusion, ΔH_f /(J/g ⁻¹)
U2	30.5	92.7	67.6
U3	21.2	101.0	97.9
U4	17.9	105.9	100.6
U5	13.2	113.0	128.0
U6	6.3	118.5	201.0
U7	3.5	129.6	215.5

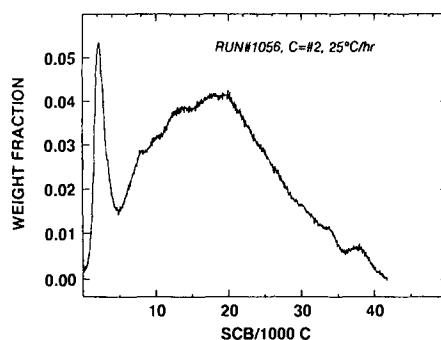


Fig. 3. Short chain branching distribution of ultra low density polyethylene.

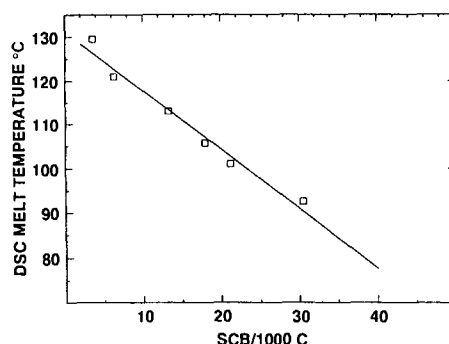


Fig. 4. Calibration curve relating branching content as a function of DSC melting temperature.

this second calibration curve to the branching distribution plot (Fig. 3) generates an “interim” DSC curve (Fig. 5).

This DSC curve is termed an “interim” or uncorrected DSC curve because it has not taken into account heat of fusion differences between fractions created by differences in branching content: these heat of fusion differences are function of temperature [2]. A third calibration curve is necessary to accommodate these differences and is generated by expressing the heat of fusion of the most linear fraction versus the other fractions as a ratio. The resulting ratio $\Delta HT_{130}/\Delta HT$ is plotted as a function of melt temperature and shown in Fig. 6. A second-order polynomial with a correlation coefficient of 0.965 gave the best fit for this data and is shown as the dashed line. The interim DSC curve is “corrected” by multiplying the vertical component of Fig. 5 with the inverse of the ratio $\Delta HT_{130}/\Delta HT$ from Fig. 6. The final calculated DSC curve is shown in Fig. 7. This curve can be compared with the DSC of solution-crystallized polymer whose curve is shown in Fig. 8. Fig. 7 and 8 are very similar in shape and in temperature range; peak temperatures of the two curves are within 2–3°C.

However, there are differences between the two curves. In particular there exists a more pronounced separation between the high temperature linear component and

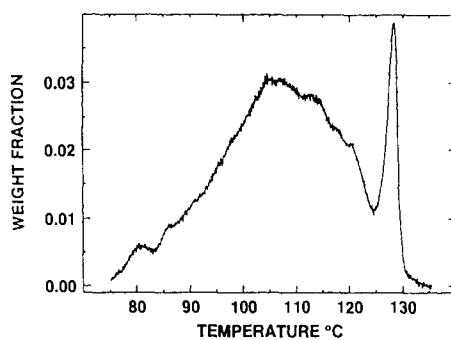


Fig. 5. Generated "interim" DSC curve.

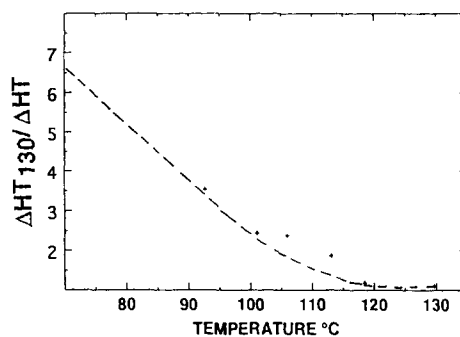


Fig. 6. Conversion factor necessary to take into account differences in heats of fusion between fractions.

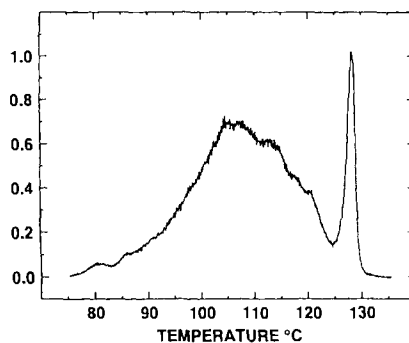


Fig. 7. Final corrected DSC curve of ULDPE generated from Fig. 1.

the low temperature branched peak in the TREF – generated system, versus a much more gradual transition in the DSC curve. Furthermore, the high temperature peak in the DSC sample is broader. These two differences could well be simply a reflection of differences in heating rate. In TREF heating rate is $25^{\circ}\text{C}/\text{h}^{-1}$, while for DSC it is

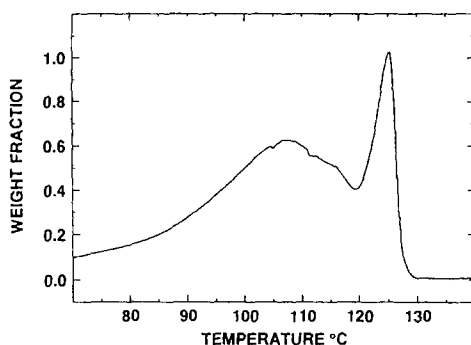


Fig. 8. Direct DSC curve of very slowly cooled (TREF rates) solution-crystallized ULDPE.

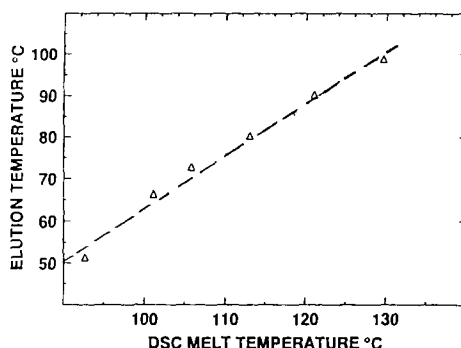


Fig. 9. Elution temperature as a function of melt (DSC) temperature.

$10^{\circ}\text{C}/\text{min}^{-1}$; a faster rate is consistent with broadening of the peak. However, despite these differences the results show that suitably formed solution-crystallized DSC specimens can provide compositional distribution information with appropriate calibration curves.

An additional simplifying step can be used to combine the elution temperature vs. branching content calibration curve (Fig. 2) with the melting point vs. branching content calibration curve (Fig. 4) to give an elution temperature vs. melting point relationship. Such a graph illustrating elution temperature as a function of melt temperature is shown in Fig. 9. This makes it possible to proceed from Fig. 1 to Fig. 5 with fewer intermediate steps.

4. Conclusions

The preceding discussion shows the possibility of “generating” DSC curves from TREF chromatograms. Similarly it is possible to take the reverse step from DSC curves to TREF chromatograms. However, the significance of this exercise lies in demonstrat-

ing that compositional distribution information is obtainable with DSC utilizing solution-crystallized specimens. These curves are very similar to those generated from TREF chromatograms. Needless to say TREF is initially essential to provide those fractions necessary for the calibration curves, and DSC can only be used to measure the crystallized component in the previously described protocol.

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