A novel calibration for the characterization of polyethylene copolymers by temperature rising elution fractionation

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A fresh appraisal of the analytical temperature rising elution fractionation (TREF) technique is presented. It is shown that by using linear paraffins and low molecular weight polyethylenes as standards, a new, generalized calibration procedure for TREF can be defined. This allows polyethylene copolymers to be characterized in terms of the length of the methylene sequences between branches. Such a calibration relates directly to the crystallization behaviour of the copolymer, and is very useful for a proper understanding of chain structure in linear low density polyethylene materials.

(Keywords: polyethylene; copolymer; fractionation)

Introduction

Interest in the structural characterization of ethylene/α-olefins copolymers has been growing rapidly in recent years. This is due to the advent of new technologies for the production of materials, especially linear low density polyethylenes (LLDPE), and the need to understand in detail their structure and performance.

The measurement of comonomer distribution is of particular interest as the placement of comonomer units in LLDPE materials is known to be heterogeneous. A predominant technique for the measurement of comonomer distribution is temperature rising elution fractionation (TREF)[1-5]. This technique has recently been well reviewed[6,7].

In TREF, molecules are separated by selective dissolution, with the fraction of highest comomomer content being eluted first. If sufficient polymer is fractionated, comonomer contents of the fractions can be determined from measurement of short chain branching (SCB) by either infra-red or nuclear magnetic resonance spectroscopy. However, when TREF is performed on an analytical scale, a calibration for comonomer content *versus* elution temperature has conventionally been employed. Such an approach ignores differences in branch placement that may occur for any given branch concentration, and it seems to be generally agreed that a universal relationship between elution temperature and SCB content is unlikely to exist.

The present communication describes a fresh appraisal of the calibration of analytical TREF. It is shown that for a given set-up, a general calibration can indeed be defined, based not upon the levels of SCB as such, but on the lengths of crystallizable sequences between SCB points, commonly referred to as the methylene sequence length. This parameter makes interpretation of TREF data more directly relevant to both polymerization processes and material properties.

Experimental

The samples used for the calibration were a linear paraffin, $C_{104}H_{210}$, and three narrow molecular weight distribution unbranched polyethylenes, with peak molecular weights of 700, 1000 and 2000 (supplied by Polymer Laboratories). For comparative purposes a further narrow molecular weight polyethylene ($\bar{M}_w/\bar{M}_n = 1.19$) with a peak molecular weight of 12 500 (SRM 1482, National Bureau of Standards) was also used.

Analytical TREF experiments were carried out as follows. A chromatographic pump was used to provide a constant flow of solvent through a stainless steel column (length 30 cm, diameter 0.7 cm) which was packed with 100 μm glass beads and held in an oven fitted with a temperature programmer. The polymer eluted was detected using an infra-red detector set at a wavelength of 3.48 μm. The voltage output from the detector was recorded on both a chart recorder and a data logger linked to a computer.

The solvent used was 1,2,4-trichlorobenzene (TCB) stabilized with 200 ppm Santanox R antioxidant (Monsanto). Polymer was loaded into the column by injecting $\sim$10 ml of a 0.2% w/v solution. The column was then cooled from 140°C to room temperature at 1°C h^{-1}. The loaded column was placed in an oven at 22°C and flushed with stabilized TCB at a flow-rate of 1 ml min^{-1}. The column was heated at a rate of 20°C h^{-1} until all the polymer had been eluted from the column.

Results and discussion

In the pursuit of a reliable TREF calibration, it is instructive to consider the principle upon which the technique is based. The elution of specific fractions is controlled by their dissolution temperature; this in turn is controlled primarily by the crystal thicknesses achieved during the cooling stage of the experiment. An equilibrium maximum crystal thickness is associated with any particular combination of thermal conditions, solvent and polymer concentration; in dilute solutions at a low degree of supercooling, the formation of thick crystals is favoured.

For homopolymers, if the available molecules are, in their fully extended configuration, shorter than the maximum crystal thickness, then the attainable thickness is controlled simply by molecular weight. For higher molecular weights, chain folding intervenes and

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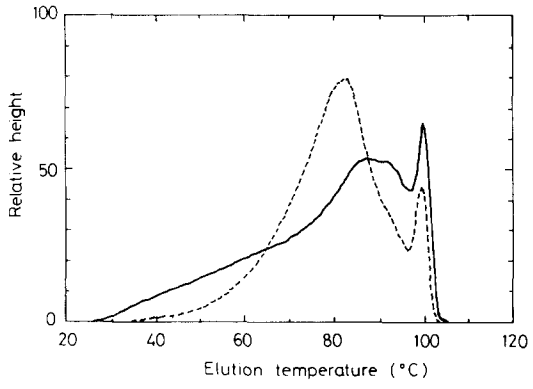

Figure 1 Detector response *versus* elution temperature for two commercial LLDPEs

the equilibrium crystal thickness achieved is virtually independent of molecular weight. For copolymers, the side-groups are usually excluded from the crystalline regions for energetic reasons. It follows that when the methylene sequence length (MSL) is less than the critical value for the onset of chain folding, the MSL controls the attainable crystal thickness. A notable exception to this rule is the case of methyl branches (propene comonomer), which in certain conditions may be incorporated into the crystal lattice[8,9]. This lack of discrimination in SCB placement between crystalline and non-crystalline regions makes this class of copolymers unsuitable for the present analysis.

Thus, in principle, the effect of MSL on crystal thickness, and hence dissolution temperature, provides a sound basis for the interpretation of the TREF data. Also, low molecular weight homopolymers or linear hydrocarbons should provide an ideal model system for calibration.

Implicit in the argument presented above is the necessary condition for a reliable determination of branch distribution; the maximum MSL between branches must be less than the equilibrium crystal traverse length unperturbed by the presence of side-groups. For MSLs greater than this, it is not possible to ascribe crystal size effects solely to branching. This means that in general there is a clear cut-off point in terms of MSL above which the analysis becomes invalid. As this cut-off in MSL corresponds to the onset of chain folding, published work on the crystallization of long linear hydrocarbons[10,11] suggests that interpretation of TREF data in terms of MSL should be valid up to an MSL of about 250. It will become immediately apparent from the results below that such a cut-off in MSL does not greatly affect the TREF analysis of typical LLDPE materials.

Raw TREF data for the two LLDPE samples are shown in *Figure 1*.

The calibration curve for elution temperature *versus* MSL was constructed using the selected reference samples. Both crystallization and subsequent dissolution were carried out under the same experimental conditions as used for fractionation of LLDPEs. The results obtained for the five calibrants are shown in *Figure 2*. For the materials of molecular weight up to 2000 (MSL $\approx$ 143) the peak elution temperature is shown in *Figure 2*; the elution range is given for SRM 1482 (MSL $\approx$ 890) as it is likely that some chain folding will have taken place for this material.

The form of relationship between chain length and dissolution temperature is known to follow closely that for melting temperature *versus* chain length[12]. Therefore, the data points of *Figure 2* were fitted by the following form of the Flory melting equation[13]:

$$T_d^{tcb} + 273.2 = \frac{1}{\frac{1}{T_0^{tcb} + 273.2} + C\frac{\ln \text{MSL}}{\text{MSL}}} \quad (1)$$

where T_d^{tcb} is the dissolution temperature in TCB (in °C), T_0^{tcb} is essentially the equilibrium dissolution temperature in TCB and C is a constant. The line in *Figure 2* shows this equation with $T_0^{tcb} = 109.3$°C and $C = 6.36 \times 10^{-3}$. The former value represents the temperature at which the last trace of linear polymer has been seen to elute from our TREF system, and the value for C was obtained by constraining equation (1) to provide a good fit for the observed elution temperatures of the linear hydrocarbons. It is interesting to note that in reference 12 a 36°C shift was required to superimpose melting and dissolution data (in xylene); the value of 109.3°C found here for 'equilibrium dissolution' in TCB is also close to 36°C below the accepted value for equilibrium melting.

Figure 3 shows the MSL distributions derived by applying the MSL calibration to the raw data of

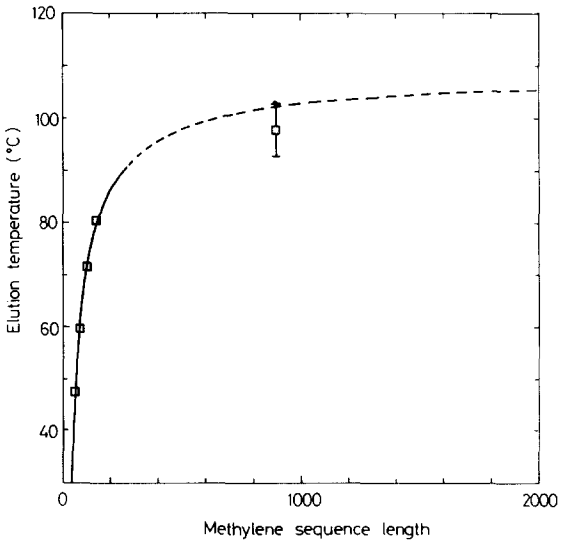

Figure 2 Elution temperature *versus* methylene sequence length for a series of calibrants (□) and equation (1) (——)

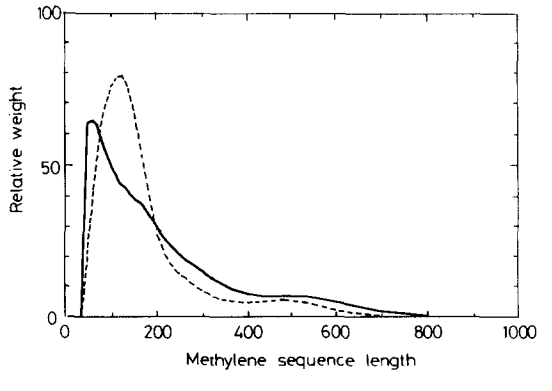

Figure 3 Methylene sequence length distributions for the two commercial LLDPEs of *Figure 1*

Figure 1. It should be noted that in converting the distributions from the temperature scale to the MSL scale, it is imperative that the slope of the calibration curve be taken into account, as is standard practice for gel permeation chromatography with non-linear calibrations. An appropriate equation is given in the Appendix.

The following points are worthy of note.

(a) It can be seen that the greater part of the distributions lies in the MSL range below 250, so it is concluded that for the major part of the data the crystal thicknesses have been controlled by MSL rather than chain folding.

(b) There is a striking difference between the appearance of the data in *Figures 1* and *3*. This is due to the very shallow slope of the calibration curve in the region of high MSL; the peaks at high elution temperature in *Figure 1* become fairly shallow features in *Figure 3*, indicating a wide spread of species between 400 and ~800 MSL for both samples. With hindsight, it is now easy to see that a wide range of MSL species are artificially compressed into a narrow range of elution temperatures by the onset of chain folding. It is likely that the peaks at high temperature seen in TREF therefore reflect extended 'tails' of the MSL distribution in the high MSL region, rather than a distinctly separate molecular population.

(c) It is interesting to speculate as to whether the range of *reliable* application of the analytical TREF technique could actually be extended to MSL values greater than 250. It is certainly true that homopolymers of higher molecular weight than SRM 1482 elute at higher temperatures, so some separation mechanism based upon molecular weight must be taking place. However, the key barrier to extension of the technique must be the onset of chain folding for the unbranched polymer, as once this occurs it is impossible to say whether or not elution is controlled by SCB points. As far as we are aware, a precise figure has not been established for the MSL at which the onset of folding occurs during crystallization under conditions typical of TREF analysis, i.e. from solution in TCB at a constant cooling rate of $1°C\,h^{-1}$.

(d) The choice of linear paraffins as calibration samples for analysis of polymeric materials deserves comment, as the gain in entropy for a linear paraffin when dissolving will be different from the gain in entropy for a polymer chain segment with the same MSL between comonomer units, which is influenced by the rest of the chain. It is believed that this effect is small, and the data of Mandelkern for hydrocarbons and polymers[14] indicate that the melting temperatures of the two are very close to one another. That said, it may be that refinement of equation (1) is possible to take account of this effect, especially if better calibrants and more data than presented so far can be obtained.

Conclusions

For a given TREF set-up and experimental procedure, a general calibration curve can be derived which is based on the unique relationship between methylene sequence length and dissolution temperature. With the exception of ethylene–propylene copolymer, such a calibration is applicable to any LLDPE and does not depend upon assumptions about the statistics of the comonomer distribution along the molecule backbone. It has been identified that, due to the onset of chain folding during the crystallization process, there is an upper limit for resolution of the technique.

The methylene sequence length distributions derived by this procedure describe quantitatively the branch placement and provide direct information on those elements of the polymer structure responsible for the crystallization behaviour and hence material properties.

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Appendix

Transformation of TREF raw data to an MSL distribution. Treating the raw data as a histogram of weight fraction $W(T)$ *versus* temperature T, and the MSL distribution as a histogram of w(MSL) *versus* MSL, the following relationship must be obeyed to retain the same relative areas for each slice of the distributions:

$$W_i(T)[T_i - T_{(i-1)}] = w_i(\mathrm{MSL})[\mathrm{MSL}_i - \mathrm{MSL}_{(i-1)}] \quad (2)$$

and hence, in order to transform $W(T)$ to w(MSL), $W_i(T)$ must be multiplied by $\Delta T_i/\Delta \mathrm{MSL}_i$ which is the slope of the calibration curve.