

Fractionation Process in TREF Systems: Validation of Thermodynamic Model and Calculation Procedure by Raman LAM Studies

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ABSTRACT: In this paper, possible sources for the unexpected distributions of crystalline sequence lengths calculated from temperature rising elution fractionation (TREF) calibration experiments, as reported in a previous work, are investigated. With this aim, chain folding and cocrystallization phenomena were explored in the conditions of crystallization as used for TREF or crystallization analysis fractionation (CRYSTAF). Slow crystallizations were performed from xylene solutions of model low molecular weight ethylene homopolymers with narrow molecular weight distributions. The same experiments were performed with homopolymers having narrow molecular weight distributions and with blends having wide molecular weight distributions. The resulting distributions of the lengths of crystalline methylene sequences were directly studied by Raman in the so-called longitudinal acoustic mode (LAM) and by DSC. For ethylene homopolymers with molecular weights below 2000 g/mol, the results from Raman LAM indicate that slow crystallization in TREF or CRYSTAF systems occurs in the extended-chain mode. For higher molecular weights, evidence of chain folding was found. In the case of blends, independent crystallization was observed for each molecular weight when the molecular weight ranges used for the blends are relatively narrow. Cocrystallization was observed when this range was increased. Overall, these results strongly support the inverse technique calculation procedure developed by our group for the calculation of distributions of lengths of crystallizable sequences from TREF spectra. In this context, the results confirm that the unexpected crystallizable sequence lengths found in our previous work really exist and can be associated to chain folding or cocrystallization phenomena.
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INTRODUCTION

Two methods of analysis are routinely used to fractionate semicrystalline ethylene (or propylene) copolymers by homopolymer crystallizable sequence lengths. Temperature rising elution fractionation (TREF) consists of a slow crystallization of a dilute copolymer solution inside packed columns. This allows the selective formation of polyethylene or polypropylene crystals in a range of thicknesses that are expected to reflect the distribution of homopolymer crystallizable sequence lengths. The basic idea of the method is making use of the well-established relationship between crystallites' thickness and their melting temperatures, which in turn are related to the equilibrium solution temperature. For this purpose, the temperature of the columns is slowly lowered. Copolymer fractions containing longer crystallizable sequences are capable of producing thicker crystals, and therefore crystallize at higher temperatures. Fractions with higher branching contents crystallize at lower temperatures.¹⁻⁶ The cooling rate is tested to make sure that the operation conditions essentially correspond to crystal-solution equilibrium. Raising the column temperature and pumping the solvent yield solutions of copolymer fractions with increasingly larger average crystallizable lengths. The fractions can then be collected, precipitated, and analyzed with a combination of experimental techniques (DSC, FTIR, ¹³C NMR, X-Ray Diffraction) to characterize details of the molecular structure such as comonomer content and statistical distributions.⁷

Crystallization analysis fractionation (CRYSTAF) also consists of slow crystallization of dilute solutions of copolymers, similar to the TREF cooling stage, but now aliquots of the solution remaining at the column are taken at fixed temperature intervals and analyzed using the same techniques as for TREF. CRYSTAF needs shorter experimental time than TREF because only the cooling stage needs to be performed. On the other hand, only TREF can be used for preparative purposes when there is a need to study the fractions by other techniques.⁸⁻¹¹

The raw information obtained is very similar for both methods. Weight fractions of a polymer expressed as a function of column temperature is known as TREF or CRYSTAF spectrum. This information could be used in at least two ways: (a) for routine comparison for process repeatability control, using TREF or CRYSTAF spectra as obtained; (b) to obtain quantitative information

about the distributions of lengths of crystallizable homopolymer sequences. In the second case, much more information about fundamental details of the polymerization process, such as catalyst behavior or monomer-comonomer reactivity ratios, could be obtained. As this information cannot be directly obtained from the spectrum, mathematical models relating the crystallization conditions inside the TREF or CRYSTAF columns with the microstructure details of the polymer are needed.

Some steps have already been done in this direction.¹²⁻¹⁴ Our group has proposed a simple model, based on the Flory-Huggins approach, to relate distributions of crystallized sequence lengths with the amount of amorphous polymer linked to the crystallizable sequences, the solvent molecular size, the melting temperature for each crystallized length, the molar melting enthalpy for pure crystals, the Flory-Huggins interaction parameter, and the solid polymer-liquid solution equilibrium temperature. In this simple approach, it is assumed that there is no topological connection between crystallites obtained from the low concentration solutions that are routinely used for TREF or CRYSTAF. Under this assumption, the thermodynamic model regards copolymer molecules as composed of alternating blocks of length x , crystallizable homopolymer sequences of lengths $x C(x)$, and other highly branched noncrystallizable blocks of lengths $x(1 - C(x))$. Crystallization is assumed to take place always in the extended-chain mode. The crystallizable blocks are assumed to be incorporated into crystallites whose thicknesses are controlled by the lengths of the blocks. Melting and solution-solid equilibrium temperatures are assumed to be directly related to crystallizable homopolymer sequence lengths. Topological effects, arising from the coexistence of very long and very short crystallizable blocks in the same molecule, are disregarded for the simple model used, as other approaches are far more complicated. The solution-solid equilibrium temperatures are calculated as

$$\frac{1}{T} = \frac{1}{T_{F_i}} - \frac{R}{\Delta H_{F_i}} \left\{ 1 + \ln \phi_i - x_i \left[\sum_{j=1}^n \frac{\phi_j}{x_j} + \frac{\phi_0}{Y_0} \right] + x_i \chi \phi_0^2 \right\} \quad (1)$$

where T_{F_i} is the melting temperature of the crystals of thickness $x_i C(x_i)$, ΔH_{F_i} is the melting enthalpy per mole of crystals of thickness $x_i C(x_i)$, ϕ_i is the volume fraction of blocks of length x_i in the solution, ϕ_0 is the volume fraction of solvent

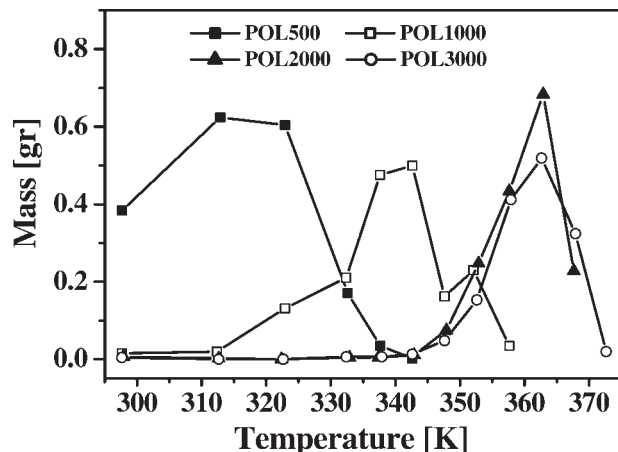


Figure 1. Raw TREF data from Reference 14. POL stands for ethylene linear homopolymer and the numbers correspond to the nominal molecular weights of the linear ethylene homopolymers.

in the solution, Y_0 is the ratio between the solvent molar volume and the molar volume of the repeating polymer unit that forms crystals (methylene for polyethylene), χ is the Flory–Huggins interaction parameter, R is the gas constant, and n is the number of different blocks lengths that can be present in the polymer. For any column temperature, eq 1 predicts the coexistence of solid crystallites with a distribution of thickness, in equilibrium with a solution of copolymer molecules with another distribution of crystallizable blocks with smaller average size.

A simple test for the model consists of the comparison of its predictions with TREF or CRYSTAF fractionations of homopolymers having molecular weights in the range of those of the crystallizable blocks of commonly used copolymers. In this way, topological effects can be avoided, the amount of amorphous polymer is minimized, and C_x can be considered a constant. The thickness of the crystallites should be controlled by the molecular weight of the homopolymers,¹⁵ provided all molecules crystallize in the extended-chain mode. Low molecular weight homopolymers could then be used to adjust the thermodynamic model parameters for quantitative calculations of distributions of crystallizable block lengths, provided their molecular weights are properly chosen.

This type of experiments were carried out in our group with a set of well-defined low molecular weight ethylene homopolymers without any branching and with narrow molecular weight distributions.^{13,14} Based on the fact that the number

average crystallizable homopolymer length for a commercial LLDPE is in the range of 200 methylene units, the molecular weights of the ethylene homopolymers were selected at or below 3000 g/mol. The results of the aforementioned studies allowed the quantitative verification of the model and the validation of the inversion technique required to calculate true homopolymer crystallizable lengths distributions from TREF spectra.¹⁴ Even though the calculation scheme yielded quantitatively correct results, some unexpected details were also found: First, preparative TREF spectra for pure ethylene homopolymers with molecular weights 2000 and 3000 g/mol, crystallized from xylene solutions, were found to be almost the same, as is shown in Figure 1.

This result suggests that linear homopolymers with molecular weights higher than 2000 g/mol might have crystallized in some folded chain mode during the slow cooling step of the TREF fractionation process. Folding of homopolymer crystallizable blocks may form thinner crystallites that will melt at temperatures corresponding to shorter blocks crystallized in the extended-chain mode. In a second set of experiments, we fractionated blends made with equal masses of ethylene homopolymers with molecular weights 500, 1000, and 3000 g/mol. Typical raw TREF data are shown in Figure 2. The distributions of the crystallizable lengths of homopolymers, calculated from the blends TREF spectra with the inversion technique mentioned above, are shown in Figure 3.

In Figure 3, peaks at 50, 64, 83, 102, and 130 methylene units correspond to molecular weights of 700, 896, 1162, 1428, and 1820 g/mol. Although

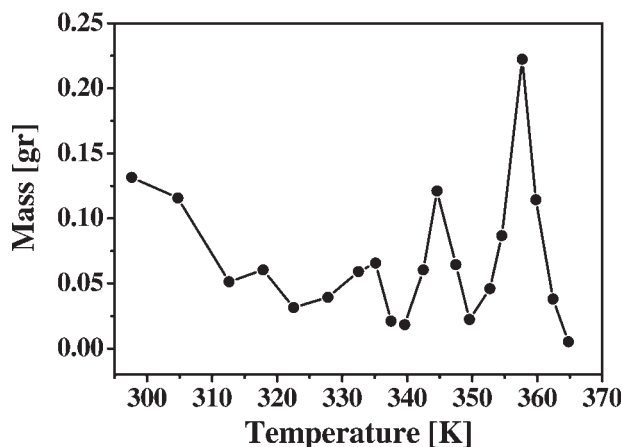


Figure 2. Raw TREF data from Reference 14 for a blend of three homopolymers with molecular weights 500, 1000, and 3000 g/mol.

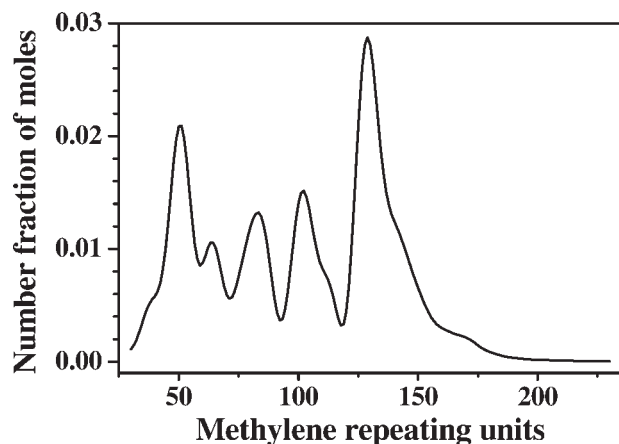


Figure 3. Uncorrected homopolymers crystallizable length distributions calculated from the raw data shown in Figure 2. Peaks at 50, 64, 83, 102, and 130 methylene units correspond to molecular weights of 700, 896, 1162, 1428, and 1820 g/mol.

the peaks of 700, 896, and 1162 g/mol roughly correspond to the values of the pure components (500 and 1000 g/mol), there is no equivalence for the peaks corresponding to 1428 and 1820 g/mol, which correspond to none of the constituents of blends. This fact might indicate cocrystallization of homopolymer crystallizable sequences with different lengths.

In this work, we explore the possibilities for chain folding and cocrystallization to occur for low molecular weight homopolymers in the same conditions as used for TREF experiments in our previous work, with the specific purpose of assessing the validity of the TREF calibration scheme based on using these low molecular weight homopolymers. As the crystallization modes are expected to depend on solution concentrations, molecular weights of polymers, and cooling rate, the TREF crystallization conditions were carefully replicated. Slow crystallizations of the same low molecular weight ethylene homopolymers used in previous TREF experiments were performed from xylene solutions.^{13,14} Open glass tubes (instead of TREF columns) were used to recover the solid crystallites as they were formed, without the dissolution step needed to recover the TREF fractions from inside the columns. Crystallites were filtered out from the remaining solution, and then distributions of thicknesses of crystallites were directly studied by Raman spectroscopy in the so-called longitudinal acoustic mode (LAM), and by DSC. The same experiments were performed for homopolymers with narrow molecular weight distributions and for blends.

EXPERIMENTAL

A series of four low molecular weight linear ethylene homopolymers, made by Baker–Petrolite, were used in our experiments. They are marketed by the manufacturer as Polywax 500, 1000, 2000, and 3000. These samples have very narrow molecular weight distributions ($M_w/M_n < 1.1$), with nominal average molecular weights of 500, 1000, 2000, and 3000 g/mol. Characterization data for these materials, including those provided by the maker, can be found in Table 1.

In addition to the pure homopolymer samples, four homopolymer blends were studied: three binary blends made from a 1:1 w/w mixture of (a) Polywax 500 and Polywax 1000, (b) Polywax 500 and Polywax 3000, (c) Polywax 1000 and Polywax 3000; and one ternary blend prepared from a 1:1:1 w/w/w mixture of Polywax 500, Polywax 1000 and Polywax 3000.

The pure homopolymers and the homopolymer blends were crystallized from 1.2% w/v solutions in xylene, containing about 200 ppm of antioxidant (Santnox, Ciba–Geigy). Approximately 20 mL of the corresponding solution were placed into specially designed glass tubes. The upper part of the tubes was continuously refrigerated with cold water to prevent loss of xylene. Nitrogen was continuously flushed in the system to prevent sample degradation. The solutions were heated at 125 °C, and then cooled from 125 °C to room temperature at a cooling rate of 2 °C/h. The precipitated polymer crystals were filtered at room temperature, washed many times with cold methanol, and

Table 1. Characterization Data for the Polywax Samples used in this Work

Sample	Polywax 500	Polywax 1000	Polywax 2000	Polywax 3000
M_n^a (g/mol)	500	1000	2000	3000
PI ^a	1.08	1.08	1.10	1.10
Density ^a (g/cm ³)	0.93	0.96	0.97	0.98
M_n^b (g/mol)	490	990	2000	2830
M_w^b (g/mol)	550	1150	2370	3280
Melting point ^c (K)	351	387	400	403
Crystallinity ^c (%)	61	87	86	89

^a Manufacturer data.

^b GPC data from our laboratory.

^c DSC data from our laboratory, corresponding to samples crystallized from the melt.

finally dried under vacuum for 2 days at room temperature.

Melting endotherms for homopolymers and their blends were measured by differential scanning calorimetry (DSC) with a PerkinElmer Pyris II DSC instrument. About 5 mg of the solution-crystallized homopolymer or homopolymer blends were placed in the DSC pan at room temperature. Then, the sample was heated at 10 °C/min up to 170 °C. Melting endotherms reported and shown in the figures correspond to this heating step.

Low frequency Raman-active LAM spectra were acquired in a Jobin-Yvon Ramanor HG-2S (1 cm⁻¹ spectral resolution). The 514 nm line of an Argon ion laser was used as the excitation source.

Raw Raman LAM spectra are usually obtained in the form of intensity of Raman scattering as a function of frequency shifts. The low frequency Raman scattering in the LAM mode gives direct information about the length of the ordered sequences, which are in turn related to crystallite thicknesses. For polyethylene the ordered sequences correspond to all-trans planar zigzag. The shift in frequency of the *m* acoustic mode is related with the length *L* of the ordered sequence by:

$$\Delta\nu = \frac{m}{2cL} \left(\frac{E_c}{\rho} \right)^{1/2} \quad (2)$$

where *c* is the speed of light, *E_c* is the crystal Young's modulus in the chain direction, and *ρ* is the density of the vibrating sequence. A value of *E_c* = 2.9 × 10¹² dyn/cm² was used, as proposed by Strobl and Eckel from their studies on LAM frequencies of series of *n*-alkanes.¹⁶ For the density *ρ*, a value of 1 g/mL was used. The intensity of the first-order LAM spectrum reflects the distribution of crystallizable lengths, as derived by Snyder and coworkers.¹⁷ The distribution function *f(L)* derived by the authors is directly related to the intensity of Raman scattering *I* at the frequency shifts $\Delta\nu$ as follows:

$$f(L) \propto \left[1 - \exp\left(-\frac{hc \Delta\nu}{kT}\right) \right] (\Delta\nu)^2 I(\Delta\nu) \quad (3)$$

where *f(L)* is proportional to the number of crystallizable segments of length *L*. The exponential factor between squared parenthesis accounts for an intensity correction for the Boltzmann population of vibrational energy levels.

As LAM spectra for low molecular weight species are found at very low frequency shifts, they appear superposed to the Rayleigh line. A cor-

rected LAM spectrum is usually obtained by baseline subtraction. Generally, it is not possible to describe the Rayleigh band with analytical functions, such as Gaussian or Lorentzian, and the baseline correction is performed manually. It has been recognized that this procedure is one of the main sources of errors, particularly when the area under the Raman band is the parameter of interest.¹⁸ However, it does not affect the band maximum position in the frequency shifts' scale. In the present case, baselines with 15 points homogeneously distributed along the abscissa axis were used. The points were manually fixed by extrapolating the baseline observed on either side of the LAM peaks.

RESULTS AND DISCUSSION

Figure 4 shows raw Raman LAM data in the form of Raman scattered intensity as a function of frequency shifts for the solution-crystallized pure homopolymers. The peaks at 66 and 77 cm⁻¹, observed in all the samples, correspond to the plasma lines of the Argon ion laser.

In addition, local maxima at about 52 cm⁻¹ for Polywax 500 (curve 1), 26 cm⁻¹ for Polywax 1000 (curve 2), 14 cm⁻¹ for Polywax 2000 (curve 3) and 21 cm⁻¹ for Polywax 3000 (curve 4), are observed. The peak profile is related to the distribution of sequence lengths of crystalline polymethylene units.^{1,3,15,18,19} The value of frequency shift corresponding to the peak maximum decreases with the increasing homopolymer chain length, showing

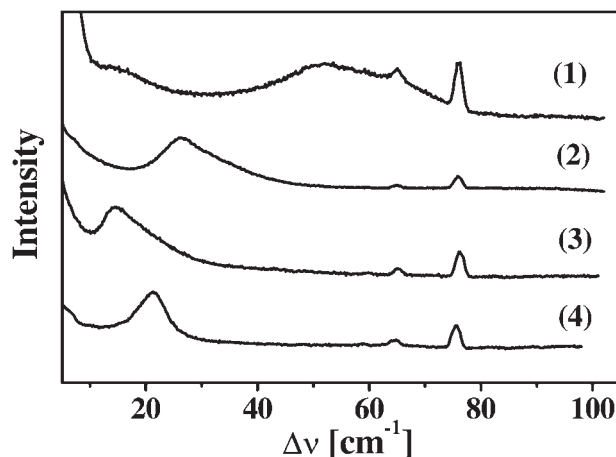


Figure 4. Raw Raman LAM spectra for pure PE homopolymers: Polywax 500 (curve 1), Polywax 1000 (curve 2), Polywax 2000 (curve 3), and Polywax 3000 (curve 4). Peaks at 66 and 77 cm⁻¹ correspond to the Argon ion laser plasma lines.

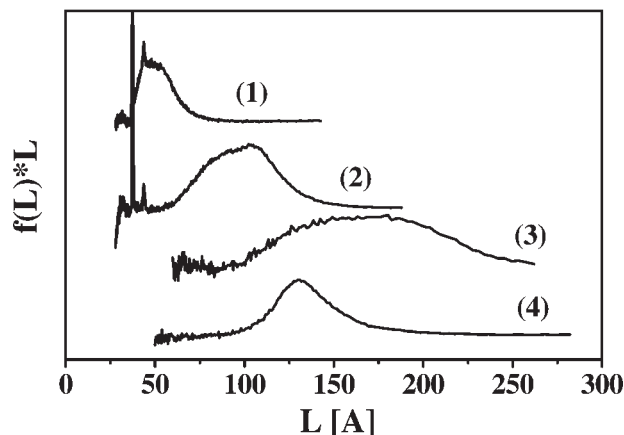


Figure 5. Distribution of mass of crystallizable lengths for pure Polywax samples. Distributions were obtained from the raw spectra shown in Figure 1, previously corrected by baseline subtraction. Polywax 500 (curve 1), Polywax 1000 (curve 2), Polywax 2000 (curve 3), and Polywax 3000 (curve 4).

that higher molecular weights produce thicker crystallites. The only exception is Polywax 3000, which shows a peak maximum intermediate between Polywax 1000 and Polywax 2000.

To translate these curves into distributions of crystallized sequence lengths, we first corrected the intensities of the raw Raman spectra by subtracting the Rayleigh line, which appears as a tail in the LAM spectra at the lowest Raman shift values. This tail was removed by adjusting manually the spectrum baseline following the trend of the Raman peaks, as detailed in the experimental section. Then, the corrected Raman spectra were transformed into plots of distributions of crystallized sequence lengths with eqs 2–3. These equations were used to calculate $f(L)$, the number distribution of species with crystallized chain length L , where L is directly related with the crystallite thickness. Figure 5 shows a plot of the product $f(L) \cdot L$ versus L , for the Polywax samples shown in Figure 4. Notice that the product $f(L) \cdot L$ is proportional to the mass distribution of species with crystallized chain length L .

For Polywax 500 (curve 1), the relative maximum in the plot $f(L) \cdot L$ versus L appears at 47 Å. The calculation of the molecular weight corresponding to all-trans extended polymethylene sequences of 47 Å yielded a value of 522 g/mol. Similarly, calculations for Polywax 1000 (curve 2, peak maximum at 100 Å) and for Polywax 2000 (curve 3, peak maximum at about 170 Å) yielded molecular weight values of 1100 g/mol and 1900 g/mol, respectively. As the calculated molecular weights

for extended polymethylene sequences are almost coincident with the nominal molecular weights of the samples, we conclude that these pure polymers crystallize in the extended-chain mode. The only exception is Polywax 3000. The data for this polymer (curve 4) shows a maximum around a crystallite thickness of 135 Å. The molecular weight of the extended polymethylene sequence corresponding to this thickness value is 1500 g/mol, which indicates that the Polywax 3000 sample crystallized in the simple folded-chain mode.

The crystallization of normal paraffins (low molecular weight polyethylenes), from the melt and from solution, has been described in detail in a series of articles.^{20–24} In the pioneering work by Ungar,²⁰ it was shown that chains as short as C_{150} (molecular weight of 2100 g/mol) crystallize in a chain-folded manner. The fold length was found to be dependent on the crystallization conditions, with values always corresponding to an integral reciprocal of the full chain length. This indicates that the chain end groups are located at the lamellae surface and that the fold has a sharp reentry. In our experiments, the onset of chain folding (Polywax 3000) and the folding mode (chain folded in a half, with chain ends at the lamellae surface) are in agreement with the results reported by Ungar.

To investigate interactions during the process of crystallization, we examined the distribution of crystallizable lengths in the homopolymer blends detailed in the experimental section. Figure 6

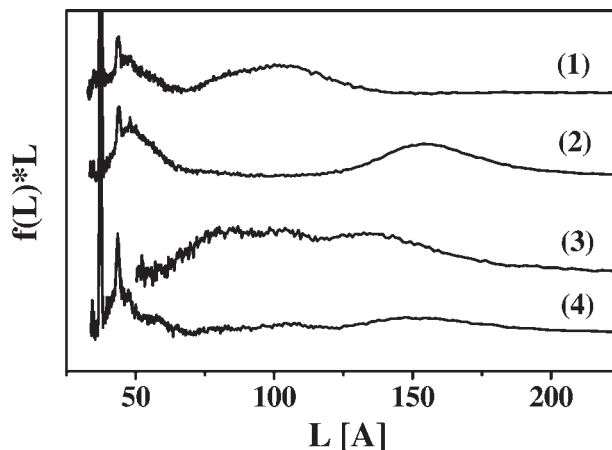


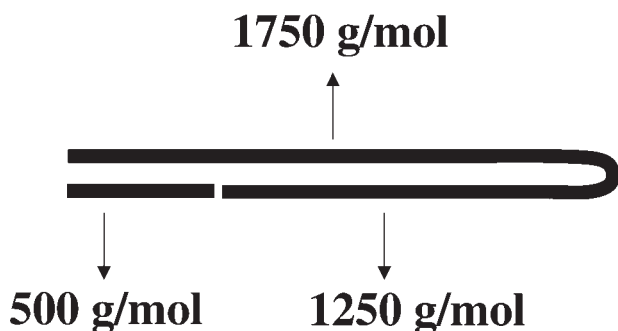
Figure 6. Distribution of mass of crystallizable lengths for binary (curves 1–3) and ternary (curve 4) blends of Polywax samples. Distributions were obtained from the raw spectra, previously corrected by baseline subtraction. Polywax 500–1000 (curve 1), Polywax 500–3000 (curve 2), Polywax 1000–3000 (curve 3) and Polywax 500–1000–3000 (curve 4).

shows the experimental data for all the binary and ternary blends used in this work, presented in the same fashion as for Figure 5.

We analyzed the data in Figure 6 using the same concept of associating crystallized chain lengths with homopolymer molecular weights. For the binary blends corresponding to Polywax 500 and 1000 (curve 1) and Polywax 1000 and 3000 (curve 3), the observed relative maxima correspond to the molecular weights of the pure constituents of blend. In curve 1, the maxima are located at the same abscissa values as for pure components (curves 1 and 2 in Fig. 5). The same characteristic is observed in curve 3 (the maxima are located at the same abscissa values as for curves 2 and 4 in Fig. 5). These data strongly support a process of independent crystallization for each of the blends components. For some molecular weights combinations, the TREF model assumption of independent crystallization can be safely used.

For the binary blend made out of Polywax 500 and 3000 (curve 2, Fig. 6) the relative maxima are observed at 47 and 155 Å. They correspond to molecular weights of 522 and 1720 g/mol respectively. While the blend contains 50 wt % of species with nominal molecular weight of 500 g/mol, there is no parallel for the value of 1720 g/mol. The presence of this maximum could be explained if we assumed that both species cocrystallize. One possible way of cocrystallization is the folding of the 3000 g/mol chain in two (see Scheme 1): (A) one piece of about 1750 g/mol and (B) one piece of about 1250 g/mol. This scheme allows cocrystallization of (A) in parallel with (B) plus one chain of molecular weight 500 g/mol, locating at the same time the chain ends at the surface of the lamellae.²⁰

This idea gains some support by calculating the areas under both maxima, which are proportional to the mass fraction of each crystallized sequence.



Scheme 1. Possible crystallization scheme for the 1:1 w/w Polywax 500-3000 binary blend.

We fitted the LAM peaks to *log-normal* functions using a standard nonlinear curve-fitting procedure. The fit yielded excellent results from the point of view of the goodness of fit. The ratio of areas corresponding to the peak located at 155 and 47 Å yielded a value of 1.5. This result is in good agreement with what one would expect if we assumed that each 3000 g/mol chain cocrystallize in parallel with one 500 g/mol chain. For a 50/50 (w/w) mass ratio in this blend, there are 6 molecules of Polywax 500 per each one of Polywax 3000. If each chain of molecular weight 3000 g/mol cocrystallized with one chain of molecular weight 500 g/mol, then the area under the peak centered at 47 Å should decrease by a factor of 1/6, and the areas under the relative maxima should be in a ratio of 7/5 = 1.4. This result is in excellent agreement with the 1.5 value obtained from the curve-fit procedure.

For the ternary blend made of Polywax 500, 1000, and 3000 (curve 4, Fig. 6) the more easily observed relative maxima correspond to molecular weights of 500, 1100, and 1750 g/mol. Also a broad halo is observed at the zone between 45 and 170 Å, corresponding to molecular weights between 500 and 1800 g/mol, suggesting that a broad distribution of crystallite thickness is obtained. A considerable fraction of the 1000 g/mol chains seems to crystallize independently, while apparent cocrystallization of 500 and 3000 g/mol chains is again observed at the maximum located at about 155 Å. The maximum observed at 155 Å corresponds to the peak shown in Figure 3, located at 130 methylene units. The peak located at 102 methylene units in Figure 3 may be hidden in the broad halo of Figure 6 already mentioned. As the preparative TREF is operated in temperature intervals, fractions of the halo may be contained in different fractions, and some experimental error may be magnified by the highly sensitive inverse calculation procedure.

Other authors have also found effects that may be due to cocrystallization of homopolymer blocks of very different lengths. In the work by Nieto et al.,²⁵ a detailed CRYSTAF study on ethylene homopolymers is discussed, and some effects of the low molecular weight tails are quantitatively described. In the CRYSTAFF plots shown in Figure 1 of this work, the peak temperatures for homopolymer samples named A, B, and C, with average molecular weights 18,500, 12,600, and 10,910, respectively, are shifted at lower temperatures as the average molecular weight decreases. For these homopolymers, lower molecular

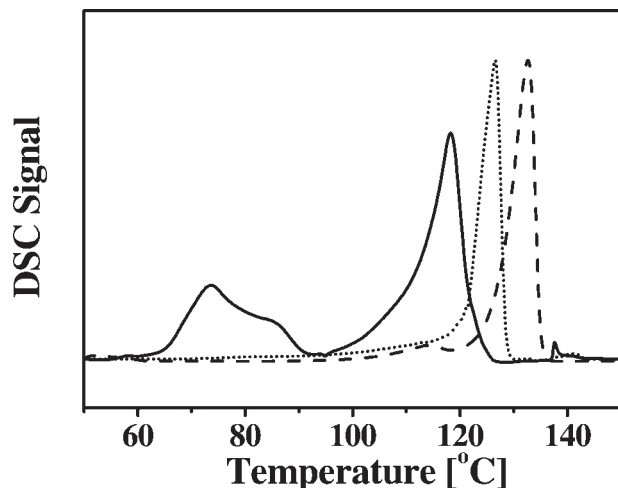


Figure 7. DSC runs for solution-crystallized Polywax 3000 (dotted line), melt-crystallized Polywax 3000 (dashed line), and the binary blend made of Polywax 500 and 3000 (solid line).

weights are associated with much larger low molecular weight tails, as is shown in their Figure 7. Some cocrystallization of high molecular weight molecules with others with molecular weights below 2000 g/mol might lower the CRYSTAF peaks temperatures. This effect ought to be much more pronounced for samples B or C than for sample A, because of its larger low molecular weight tail. Data shown in Table 2 and Figure 8 of ref. 25 also support this assumption: after TREF fractionation of sample B, CRYSTAF peak temperatures for its higher molecular weight fractions are increased after reduction of its low molecular weight species content. This behavior can be also inferred from our equilibrium model (eq 1), which suggests that crystallization of a number of different lengths will occur simultaneously for each CRYSTAF or TREF fraction. Overall, the data from Nieto et al.²⁵ and our data suggest that the controlling ethylene sequence for CRYSTAF and TREF is not the longest in a molecule, but some average obtained by combinations of cocrystallization and chain folding.

We end this work presenting a few DSC experiments performed on the same samples used for Raman LAM studies to analyze the problem from the perspective of the thermal analysis. Figure 7 shows the DSC runs (heating step, 10 °C/min heating rate) corresponding to Polywax 3000 pure homopolymer (dotted line) and to the 1:1 w/w blend made of Polywax 500 and 3000 (solid line). For the purpose of comparison, the DSC run of Polywax

3000 crystallized from the melt was also included (dashed line).

The DSC traces for the pure Polywax 3000, either crystallized from solution or from the melt, show a single endothermic transition associated to the melting of PE crystallites. The peak melting temperature is several degrees higher for the melt-crystallized Polywax 3000 than for the solution-crystallized Polywax 3000. Using data from the literature, it is possible to relate peak melting temperatures with crystalline sequence lengths.^{26–28} For the sample crystallized from xylene solution, the peak melting temperature at 125 °C corresponds to a crystalline sequence length of about 160 Å. This sequence length corresponds closely to a chain of 3000 g/mol folded in a half, in agreement with the Raman measurements. Differently, the sample crystallized from the melt, either by natural cooling or by controlled cooling at 1 °C/min, shows a melting peak at higher temperature (131 °C), which corresponds to a crystalline sequence length of about 318 Å, very close to a chain of 3000 g/mol crystallized in the extended-chain mode. As was observed by Ungar, normal paraffins in this range of molecular weights crystallize preferentially in the extended-chain mode when they are cooled from the melt at moderate rates, that is 1 °C/min.²⁰ At this point, DSC data have to be interpreted with caution, because refolding of chain may occur at low heating rates. Besides, for this range of crystalline sequence length, the melting temperature asymptotically approaches the melting point for a perfect crystal. Therefore, changes in crystalline sequence length correspond to increasingly smaller changes in melting temperature, and DSC measurements become much less sensitive than the Raman LAM.

The DSC trace for the Polywax 500–3000 binary blend shows two maxima, at 74 and 118 °C. The wide peak centered at about 74 °C corresponds to pure Polywax 500. The peak centered at 118 °C was originated by the melting of cocrystallized Polywax 500 and 3000, but this peak melting temperature apparently corresponds to a crystalline sequence length of 110 Å, which cannot be associated with any of the observed Raman LAM maxima. We understand that for this blend, the liquid Polywax 500 may also be acting as a solvent for the Polywax 3000 chains, decreasing the observed melting temperature as predicted by the Flory–Huggins theory. Calculations performed using the already mentioned thermodynamic model confirm this assumption.^{12–14} Remarkably, the ratio of

areas under the melting peaks observed for the Polywax 500–3000 blend is close to that expected based on the crystallization scheme proposed for the blend in Scheme 1.

CONCLUSIONS

The Raman LAM measurements presented here indicate that the slow crystallization in TREF or CRYSTAF systems, for the polymer concentrations and cooling rates used here, may occur in the extended-chain mode only for ethylene homopolymers with molecular weights below 2000 g/mol. In the same conditions and for higher molecular weights, chain folding occurs. For blends, and depending on the combination of molecular weights, cocrystallization was observed. In binary blends such as Polywax 500–3000, well-defined Raman LAM bands allow easy estimation of the average crystallite thicknesses. Some calculations were performed and schemes on probable cocrystallization modes were proposed. For blends with more components, the Raman LAM bands become quite wider, suggesting that other possible cocrystallization modes may be present. More experiments, beyond the scope of this work, are needed to quantify these effects that appear when low molecular weight homopolymers are used.

In view of the above, the use of low molecular weight homopolymers for TREF or CRYSTAF calibration, and for models validation, should be used with caution. The results verify that the unexpected crystallizable sequence lengths that we found in previous work calculations^{13,14} really exist and can be attributed to chain folding and cocrystallization phenomena. Even though the combination of thermodynamic model and inverse technique proposed give quantitatively correct results for low molecular weight homopolymers, the basic hypothesis of independent extended-chain crystallization, embedded in the thermodynamic model used ought to be reviewed, to take into account the multiple modes of crystallization possible. This task could be approached after extensive TREF and Raman experimental work using homopolymer blends and statistical and block copolymers with commercial, higher molecular weights. It can also be suggested that more reliable results will be obtained from the inverse calculation procedure if the TREF or CRYSTAF systems are operated in the continuous mode, instead of the preparative, to allow the almost continuous

crystallite thickness distributions to be correctly fractionated.

The rich information obtained by Raman in the LAM mode indicates that this is the right tool for direct examination of distributions of crystallizable lengths. DSC can be used as an accessory technique only when narrow distributions of crystallizable lengths are expected. More information on the validity of the assumptions used previously to model the TREF fractionation may be obtained by using statistical ethylene copolymers with narrow molecular weights and chemical composition distributions while performing the same type of experiments presented in this work.

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