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A new turbidimetric approach to measuring polyethylene short chain branching distributions

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Abstract

A new instrument to analyze the short chain branching distribution of polyethylenes has been described. Turbidity analysis of ethylene/α-olefin copolymers by turbidity fractionation analysis can provide short chain branching distribution information that is similar to CRYSTAF and TREF. In these experiments, the turbidity of a polymer solution is monitored while changing its temperature at a controlled rate. The turbidimetric response is to the precipitation or dissolution of the crystallized polymer at a given temperature. With an approach similar to CRYSTAF, the differential of the turbidity profile provides valuable SCBD information for polymers with broad and narrow compositions such as Ziegler-Natta LLDPE and homogeneous polymers catalyzed by single-site catalysts.

Keywords: Polyolefin characterization; Turbidity; Short chain branching distribution

1. Introduction

The short chain branching and the short chain branching distribution (SCBD) of an ethylene/α-olefin copolymer are key structural parameters that determine a resin's properties and applications. Products and applications are typically classified by their overall density which can range from plastic to elastomeric (0.96 g/cm^3, HDPE to 0.86 g/cm^3, VLDPE). The short chain branching distribution of polyolefins provides information regarding the distribution of the crystallizable components which influence the crystalline morphology and level of crystallinity.

Traditionally, the SCBD of polyethylenes have been measured and represented by analytical temperature rising elution fractionation [1,2] (aTREF or TREF) or crystallization analysis fractionation [3,4] (CRYSTAF). Both of these techniques are based on the crystallization of a polymer from dilute solution and it is generally accepted that under these conditions, polymer chains of a fixed level of short chain branching can crystallize at a given temperature. With an appropriate calibration of temperature and comonomer content, the measured crystallinity distribution can be correlated to the short chain branching distribution of the polymer. In practice the exact SCBD is not always measured since the effects of co-crystallization can never be totally avoided and is highly dependent on the experimental conditions [5].

A typical TREF cycle starts with a crystallization step in which a polymer in solution is slowly cooled and crystallized (precipitated) onto a column of glass beads. After cooling, fractions of polymer with different crystallinity are eluted with fresh solvent as the temperature of the column is increased at a constant rate. The resulting weight fractions of the eluted polymer (measured continuously) give a representation of the polymer's SCBD.

The more recently developed CRYSTAF (available from PolymerChar, Spain) provides similar information from only measurements taken during the crystallization (precipitation) step. This alternative approach measures the concentration (via IR detector) of the soluble polymer, during cooling, that remains at a given temperature after a fraction of polymer crystallizes. The first derivative of the resulting profile, of the decrease in polymer concentration with temperature, also provides a representation of the SCBD.

Both of these techniques provide similar but not identical representations of the SCBD of a polymer. TREF provides information during the melting (in the presence of solvent (dissolution) on heating) of the previously crystallized polymer and CRYSTAF during the crystallization of the polymer. In most cases, the peak temperatures measured from TREF are

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shifted higher than those from CRYSTAF due to polymer undercooling. The advantage of CRYSTAF is that it can be performed in a single crystallization step while TREF demands two full temperature cycles (crystallization and elution). For this reason, CRYSTAF is faster. By instrument design, a commercial CRYSTAF can analyze up to five samples per run. However, both analytical instruments require complex instrumentation and are expensive.

In this study, we outline our discovery that turbidity measurements can also provide SCBD information. Utilizing a turbidity fractionation analyzer (TFA) it is possible to monitor the crystallization or dissolution of a polymer in solution while changing its temperature at a controlled rate. From crystallization or dissolution profiles during cooling or heating of a polymer solution, we have been able to extract SCBD information. Given the simple setup of the TFA, we believe there is great potential of TFA to be an alternative to TREF and CRYSTAF. The distinct advantages of TFA are its inexpensive setup, it can be operated with a variety of solvents and it can monitor polymer crystallization or melting process in ‘real time’.

In the past, turbidity measurements were focused on fractionating polyolefins based on molecular weight using either a solvent–nonsolvent approach or thermal gradient technique [6]. However, Imhof from the Union Carbide Corporation did study a series of low-pressure ethylene–propylene copolymers and mixtures of ethylene homopolymers [7]. It was observed that the cloud point decreases with decreasing density and that turbidity could resolve blends of ethylene homopolymers.

To our knowledge, this work is the first implementation of a turbidimetric approach in measuring the SCBDs of polyethylenes.

2. Experimental

2.1. Turbidity fractionation analyzer

Figs. 1 and 2 show the turbidity fractionation analyzer used in these experiments to measure the turbidity of polymer solutions. Our ‘in-house’ turbidity fractionation analyzer consists of a laser diode (630 nm, 4.5 mW), an intensity detector (Si photo diode), and an aluminum cell holder that is capable of controlled heating and cooling. A 45° reference detector was also included to monitor any changes in source intensity. This instrument monitors the turbidity of a solution with changes in temperature. Under constant stirring, the excitation voltage of the detector measures the laser light that passes through the, above-mentioned, solution and cell block. Fig. 1 also shows the possibility of multi-angle detection but this was not implemented in this work.

For these experiments, polyethylene samples were dissolved at 160 °C for 2 h at a total concentration of 1 mg/mL in 1,2,4 trichlorobenzene (TCB) or 0.167 mg/mL in dodecane.

The samples were then placed into the TFA cell block and stabilized for 30 min at 105 °C and then cooled to 30 °C at a rate between 0.2 and 2 °C/min. Throughout the experiment, the samples were stirred by a Teflon (trademark of the E.I. Dupont de Nemours and Co.) stirbar at the lowest setting available on the stirplate; stirring was required to maintain a uniform temperature in the solution and to prevent the polymer crystals from floating. During cooling, the detectors’ response to the laser light passing through the center of the polymer solution was recorded via PC data acquisition.

Once completed, reduction of the data was as follows:

(1) The detector response profile was normalized by the initial voltage measured (i.e. 100% transmittance of the laser light when the sample was completely dissolved in solution). To account for any fluctuations in the laser source intensity, the detector response is the ratio of the transmittance voltage and the reference detector voltage.
(2) This normalized curve is considered the turbidity curve. A decrease in detector response indicates an increase in turbidity of the polymer solution. Refer to Eq. (1).

$$\text{Turbidity(Temp)} = \frac{\text{Initial voltage} - \text{measured voltage}}{\text{Initial voltage}} \qquad (1)$$

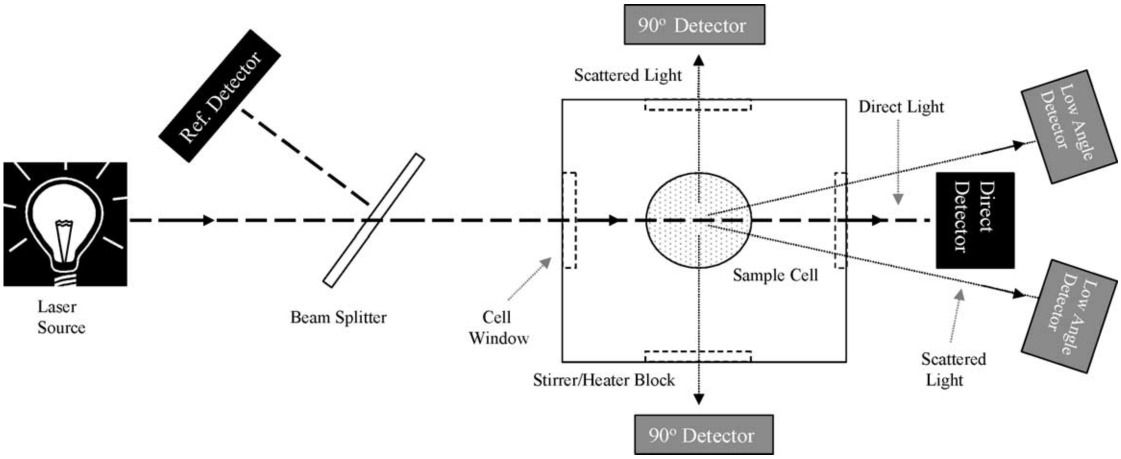

Fig. 1. Schematic of a turbidity fractionation analyzer.

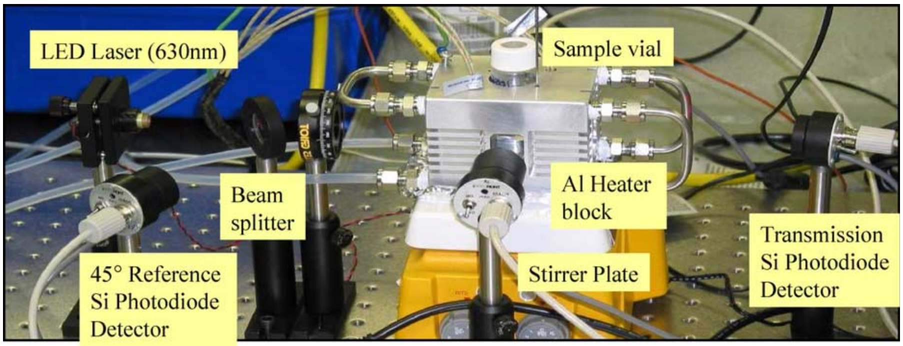

Fig. 2. Setup of the turbidity fractionation analyzer.

(3) Afterwards, a Savitzky-Golay smoothing algorithm [8] was applied to the turbidity data to smooth the turbidity data and calculate the first derivative. This algorithm was found to work quite well to obtain smooth-looking derivative profiles.

(4) The data is then plotted as turbidity versus temperature or as the derivative (dTurbidity/dTemp) versus temperature.

2.2. CRYSTAF and TREF analysis

Comparable analyses to some of the TFA experiments were carried out with CRYSTAF and TREF at similar conditions. CRYSTAF was carried out as follows. The samples were heated and dissolved at 160 °C for 1 h and then stabilized at 95 °C for 45 min followed by cooling at 0.2 °C/min until the sample reached 30 °C. TREF was carried out as follows. The samples were heated and dissolved at 160 °C for 2 h. The samples were then cooled to 30 °C at 0.2 °C/min and then eluted at 0.7 °C/min to 130 °C.

3. Results and discussion

3.1. Measurement of the short chain branching distribution of polyethylene from turbidity fractionation analysis

During a turbidity fractionation experiment, a hot polymer solution is cooled, any polymer that crystallizes and precipitates from the solution results in a corresponding increase in the solution's turbidity. The polymer during this cooling process is essentially being fractionated by crystallinity. Beigzadeh et al. have proposed that the polymer during this process is fractionated according to its longest ethylene sequence length [9]. The longest polymer chains with no short branches will crystallize first, at higher temperatures, followed by the chains with increasing number of short chain branches, at lower temperatures. More recently, Anantawaraskul et al. has suggested that the process is governed by the average ethylene sequence [5]. Although the mechanism is in debate, the fractionation process measures the crystallizability of the polymer for the level of short chain branching present. Instead of measuring the concentration of the polymer remaining in solution, after some of the polymer has crystallized, turbidity responds to the precipitated polymer that has crystallized from solution. In a standard CRYSTAF [3,4] experiment, solution samples are measured discontinuously throughout the temperature ramp and are limited in number (35–40 points). During a TFA experiment, the crystallization process can be continuously monitored to provide numerous data points and, in theory, higher resolution.

Fig. 3 compares the resulting turbidity profile and CRYSTAF cumulative and derivative curves for a typical Ziegler-Natta LLDPE. The TFA profiles show a similar response to the high density region and lower crystalline region as in CRYSTAF. Actually, TFA shows a narrower response to the high density fraction. This is represented by the plateau that was observed between 80 and 75 °C. After applying a fairly extensive smoothing algorithm (Savitzky-Golay [8]) to the turbidity data, a smooth-looking first derivative of the turbidity profile can be computed. Fig. 4 shows the first derivative of the turbidity profile for this Z-N LLDPE. This first derivative curve represents the short chain branching distribution of this Z-N LLDPE as computed from turbidity data. The TFA SCBD is remarkably similar to that obtained by CRYSTAF and actually shows higher resolution of the high density fraction. In this particular case, the high

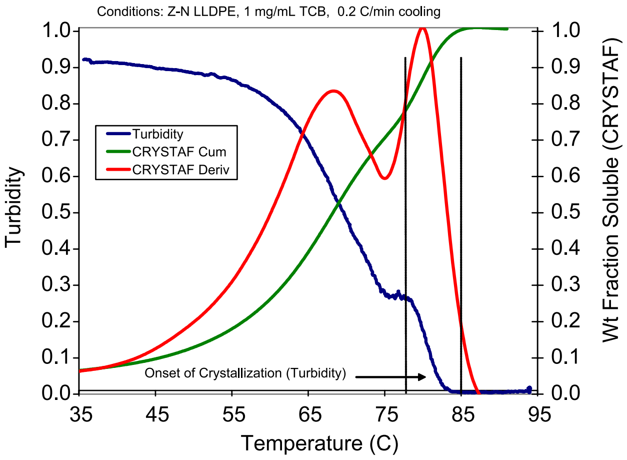

Fig. 3. Comparison of turbidity and CRYSTAF results of a typical Ziegler-Natta LLDPE.

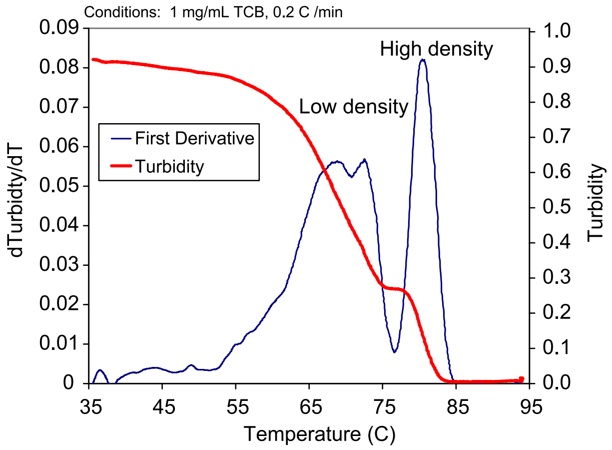

Fig. 4. Short chain branching distribution of a Z-N LLDPE from the first derivative of the turbidity profile.

density fraction of this Z-N LLDPE can be clearly identified. With other techniques, peak fitting methods are usually required to approximate the area of the high density fractions measured by TREF or CRYSTAF.

3.2. Estimating weight fractions from TFA SCBD with homogeneous ethylene–octene low/high density blends

To explore the quantitative measurement of TFA SCBDs, a blend of two homogeneous poly(ethylene-*co*-1-octene) polymers with different densities were studied.

Lower density polymer – 0.903, 3.0 MI, 8.0 I_{10}/I_2

Higher density polymer – 0.935, 2.5 MI, 9.1 I_{10}/I_2

Fig. 5(a) shows the turbidity profiles of a 50/50 wt% blend of the low and high density polymers during cooling. Two distinct regions were observed. The high temperature transition between 70 and 80 °C is associated with the higher density polymer and the lower temperature transition between 40 and 60 °C with the lower density polymer. From the first derivative plot, it shows that the SCBD are narrow for both fractions as would be expected from copolymers produced with INSITE[1] catalyst technology. Integration of the derivative profile allows for the area fractions of each polymer to be calculated. Surprisingly, both the percentages of high crystalline and low crystalline fractions measured are extremely close to the actual weight percent of the polymer present. The replicate measurement shown also suggests that the turbidity measurements are reproducible.

After cooling the polymer solution, the turbidity at 30 °C results from the polymer that has crystallized from solution and remains suspended as solids. If the reverse of the experiment is carried out, by heating the solvent and solids, the dissolution of the polymer, back into solution, can be monitored. In essence, this is similar to a TREF experiment. During a TREF experiment, fresh solvent is passed through a glass column that contains previously crystallized polymer deposited during cooling at a slow and controlled rate. As the temperature is raised at a constant rate, the polymer (depending on the short chain branching content) at a given temperature elutes and the concentration is measured using an IR detector. In TFA, heating will result in a decrease in the turbidity of the polymer solution as the polymer redissolves. Fig. 5(b) shows the turbidity profile of the same low/high density blend during heating. The heating experiment results in the two transitions expected from the two different components. Again, the first derivative results in the short chain branching distribution of the polymers. The peak temperatures that are measured are higher than the ones measured during cooling and the peak shapes remain narrow. The calculated areas for each fraction are still fairly close to the actual weight fractions present. However, the estimated fraction of lower crystalline material is approximately 5% higher than the high density polymer. A possible explanation for the observed differences is described below. Regardless, both these experiments demonstrate that TFA can be used as a quantitative tool for the measurement of short chain branching distributions during crystallization and dissolution.

Fig. 6(a) and (b), compares the results from TFA cooling and TFA heating, to CRYSTAF and TREF for the same 50/50 wt% low/high density blends. The analyses were carried out at similar concentrations and test conditions for direct comparison with each other. Remarkably, the results from TFA cooling and CRYSTAF are similar in peak temperatures, peak shapes and peak areas for this blend.

The SCBD results of TFA and TREF are also comparable. However, they do differ in peak temperatures and slightly in shape. The temperature offset might be attributed to the temperature calibration of each instrument but, at this present time, it is unknown why the peak shapes are different.

Fig. 7 compares the weight fractions of the low crystalline and high crystalline material in the blend as measured by TFA cooling, CRYSTAF, TFA heating and TREF. It is shown that the measurements during crystallization (TFA cooling and CRYSTAF) are closer to the true values than the dissolution/elution techniques (TFA heating and TREF). During crystallization, the polymer chains precipitate out of solution once their crystallization temperature is reached. The amount that precipitates is independent of the crystal structure formed. During dissolution or elution, the amount of crystallized polymer that melts or dissolves at a given temperature depends on the crystallite size. If a wide range of crystallite sizes is formed during the crystallization step, a broader temperature range will be observed during dissolution. The differences in the weight fraction estimations during cooling and heating may be related to this.

3.3. Polymer concentration dependence of turbidity

One short coming of turbidity analysis is that there is no direct measure of concentration. Without a concentration detector, the purge or soluble fraction of polymer cannot be

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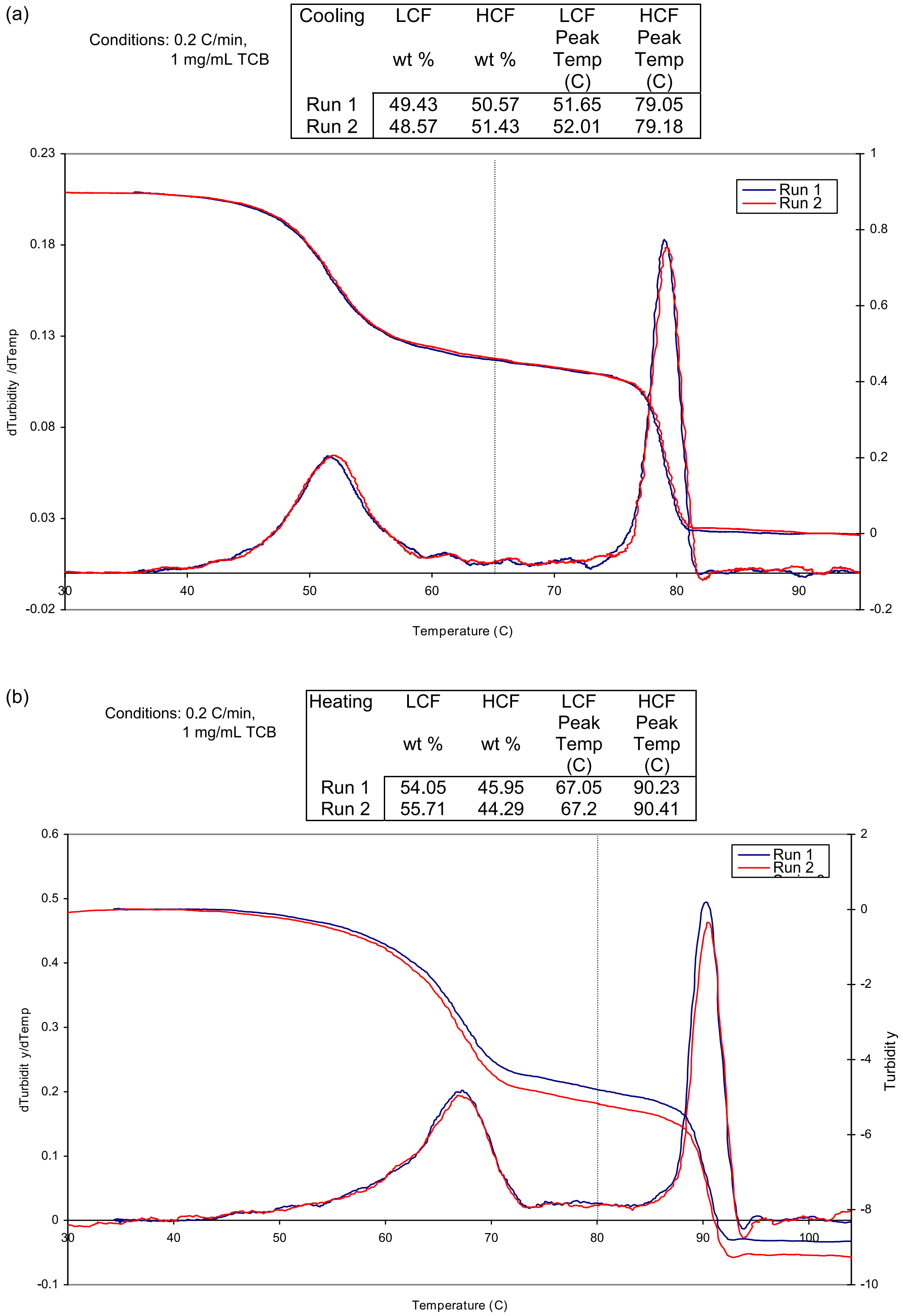
[1] Trademark of The Dow Chemical Company.



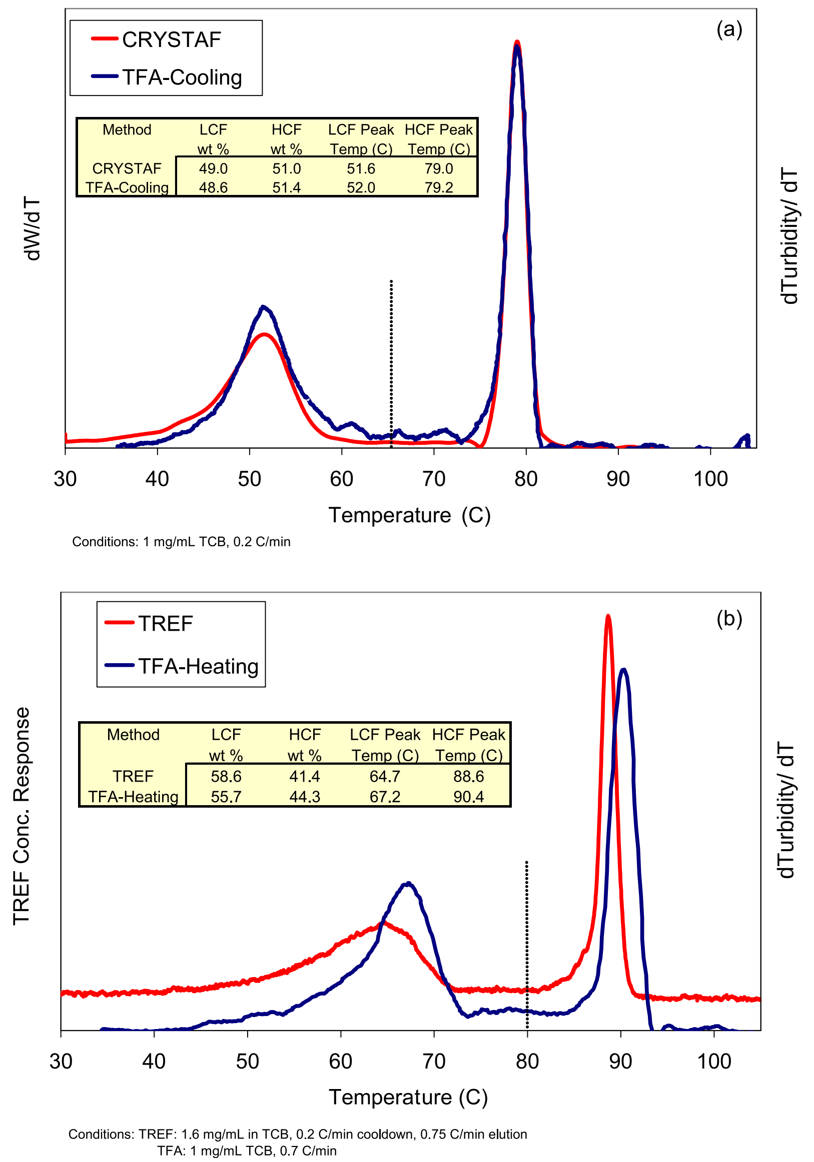
Cooling	LCF wt %	HCF wt %	LCF Peak Temp (C)	HCF Peak Temp (C)
Run 1	49.43	50.57	51.65	79.05
Run 2	48.57	51.43	52.01	79.18

Heating	LCF wt %	HCF wt %	LCF Peak Temp (C)	HCF Peak Temp (C)
Run 1	54.05	45.95	67.05	90.23
Run 2	55.71	44.29	67.2	90.41

Fig. 5. (a) SCBDs of low and high density blends measured from TFA during cooling. (b) SCBDs of low and high density blends measured from TFA during heating.

readily estimated. However, if the turbidity versus concentration relationship can be calibrated, it might be possible to make an estimate of the soluble fraction of polymer that remains.

Throughout all of the observed results, it is still surprising that the weight fractions of the individual polymers measured from TFA are quantitative. The turbidimetric response to the crystallized polymer depends on the number and size of crystals present. To further explore the nature of the turbidimetric response with changes in polymer concentration and polymer type, both the high and low density polymers were analyzed individually at different concentrations. Fig. 8(a) shows the detector's actual response and calculated SCBD during TFA cooling for the high density polymer at different concentrations. As expected, increasing the polymer concentration increases the detector response as shown by the larger



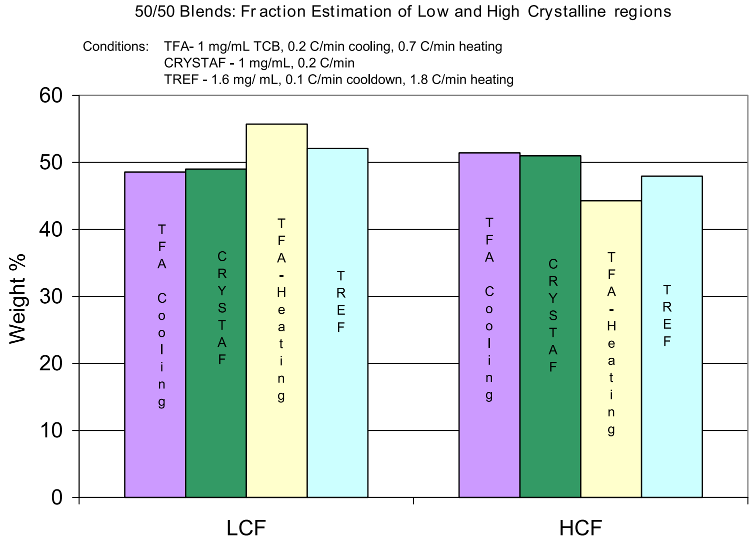
Method	LCF wt %	HCF wt %	LCF Peak Temp (C)	HCF Peak Temp (C)
CRYSTAF	49.0	51.0	51.6	79.0
TFA-Cooling	48.6	51.4	52.0	79.2

Conditions: 1 mg/mL TCB, 0.2 C/min

Method	LCF wt %	HCF wt %	LCF Peak Temp (C)	HCF Peak Temp (C)
TREF	58.6	41.4	64.7	88.6
TFA-Heating	55.7	44.3	67.2	90.4

Conditions: TREF: 1.6 mg/mL in TCB, 0.2 C/min cooldown, 0.75 C/min elution
TFA: 1 mg/mL TCB, 0.7 C/min

Fig. 6. (a) Comparison of SCBDs measured from TFA cooling and CRYSTAF. (b) Comparison of SCBDs measured from TFA heating and TREF.


50/50 Blends: Fraction Estimation of Low and High Crystalline regions

Conditions: TFA- 1 mg/mL TCB, 0.2 C/min cooling, 0.7 C/min heating
CRYSTAF - 1 mg/mL, 0.2 C/min
TREF - 1.6 mg/ mL, 0.1 C/min cooldown, 1.8 C/min heating

Fig. 7. Comparison of estimated weight fractions from TFA, CRYSTAF and TREF.

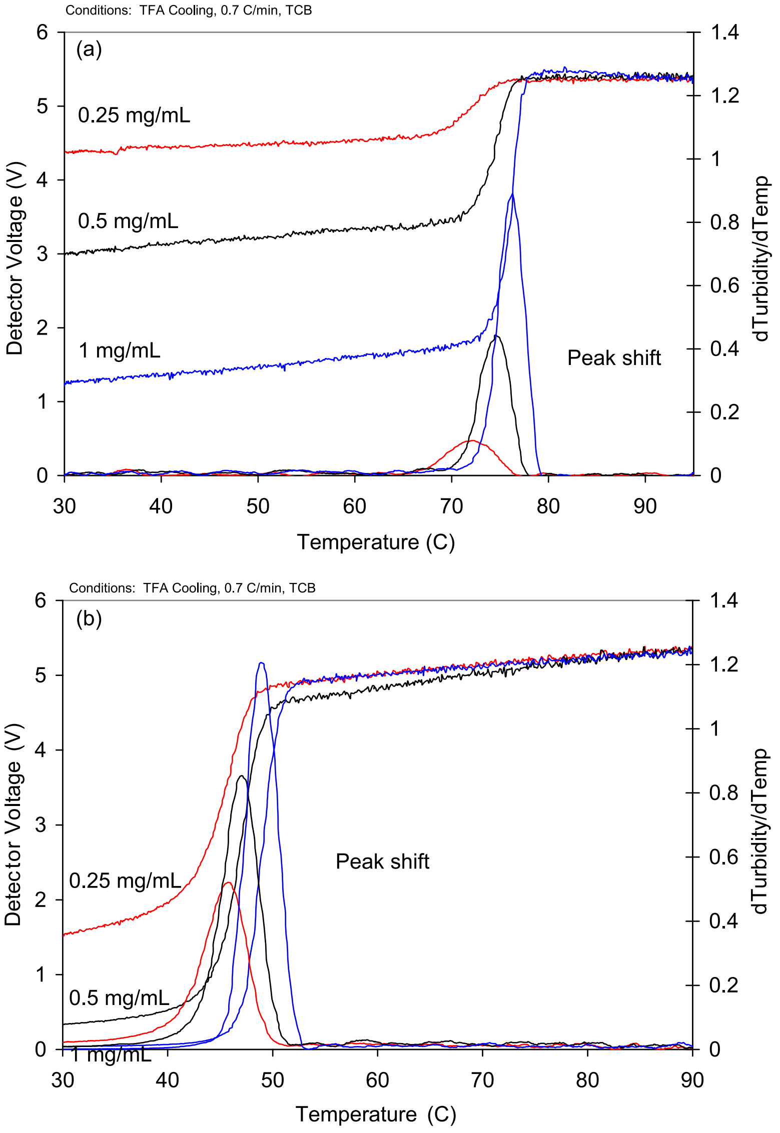


Fig. 8. (a) Concentration dependence of detector response of higher density polymer. (b) Concentration dependence of detector response of lower density polymer.

change in voltage. Similarly, Fig. 8(b) shows the response of the lower density polymer. For the same concentrations as the high density polymer, the lower density polymer shows a larger response in turbidity than the higher density polymer as shown by the even larger change in voltage. For both the polymers a shift in the peak temperatures to lower temperatures was observed with decreasing concentration. This concentration effect is also observed with CRYSTAF and exemplifies the importance of maintaining a constant concentration for sample analysis.

Fig. 9 shows the dramatic difference in the concentration dependence of the measured response of the two polymers. At a given concentration, the lower density polymer (0.909 g/cm^3) shows a larger turbidity response than the higher density polymer (0.935 g/cm^3). Another way of saying this is that for the same concentration, the lower density polymer blocks more light than the higher density polymer. Mandelkern has reported that for polyethylene homopolymers, there is a direct

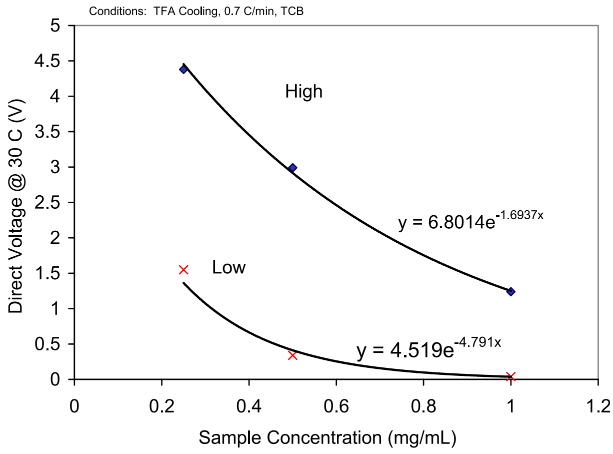


Fig. 9. Concentration dependence of turbidity with lower and higher density polymers.

relationship between the crystallization temperature and crystallite size [10]. As the crystallization temperature lowers, smaller crystallite sizes are observed and range in size from 200 to 80 Å. However, it was also emphasized that crystal structure formed from dilute solution is not as well defined as a crystal formed from the molten state. It is sometimes assumed that a single chain is involved in only one crystallite whose thickness is less than the chain length. As mentioned earlier, the turbidity depends on the size and number of particles in solution, the reduced transmission of light from the lower density polymer may be simply due to the greater number of smaller crystals present. Fig. 10(a) and (b) shows the optical micrographs of the solutions of high and low density polymers after being crystallized in a similar manner as the results discussed above. The results confirm that the lower density polymer produces numerous, small crystals that are less than 3 μm while the higher density polymer produces fewer, larger crystals that are between 15 and 20 μm. Therefore, we conclude that the observed difference in turbidity between the high and low density polymers is a result of the greater

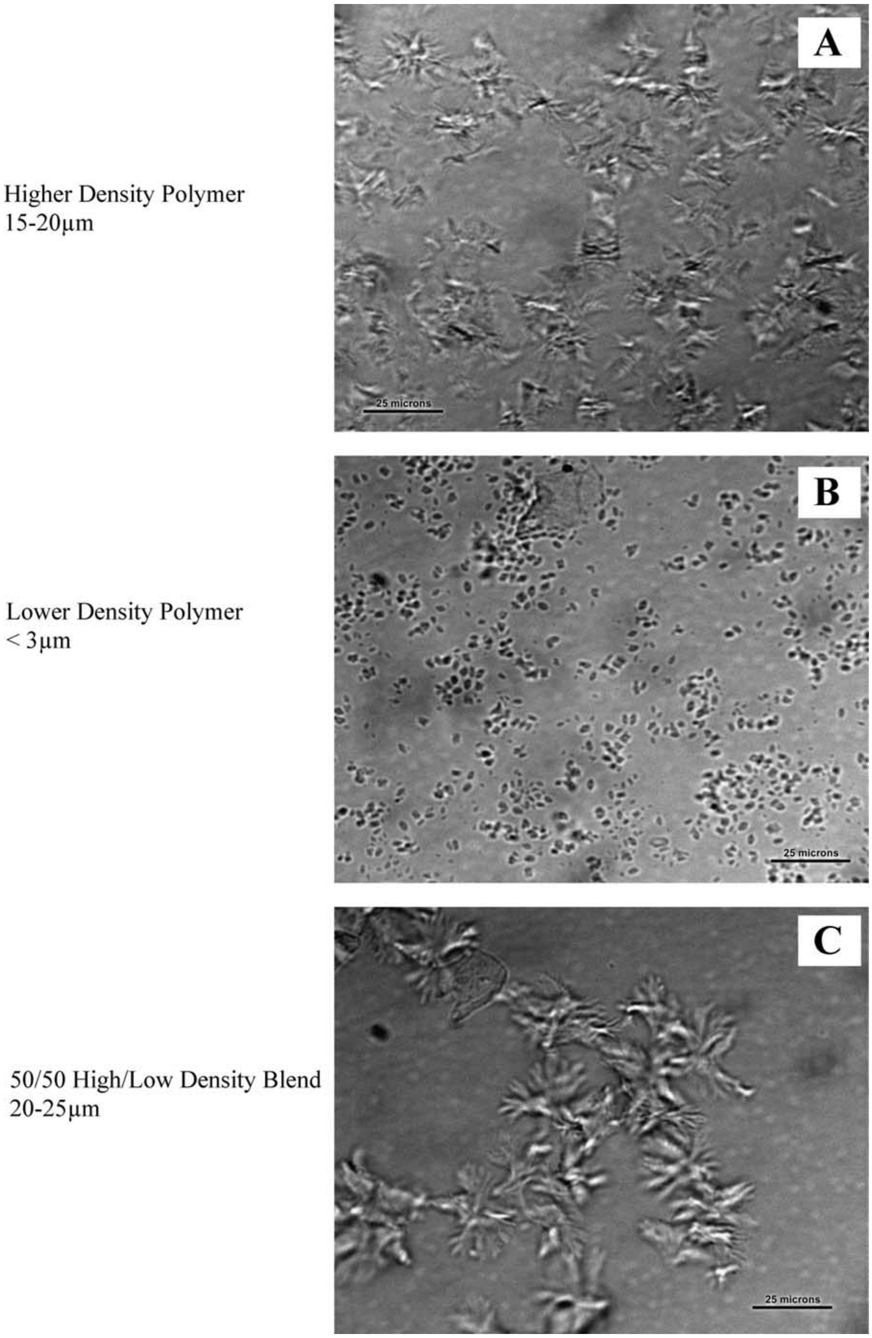


Fig. 10. Optical micrographs of high density and low density polymers crystallized from dilute solution. (a) High density polymer 15–20 μm. (b) Lower density polymer <3 μm. (c) 50/50 High/low density blend 20–25 μm.

number of crystals present for the low density polymer. However, this raises an interesting question on why the quantification of the 50/50 blends was successful.

Given the different turbidity response to the different polymers, it seems that the fraction of lower density polymer should have been much higher and certainly not equally weighted with the higher density polymer. It is obvious that there must be some interaction during the crystallization of a blend of polymers. It is hypothesized that, in the case of the blended system, during cooling, the higher density polymer that crystallized acts as a nucleating agent for the subsequent lower density polymer. Hence, the crystallized particles increase in size and not in number. The result would be that the turbidity would respond to the increase in size of the growing crystallite in a linear fashion. Fig. 10(c) shows the optical micrograph of a 50/50 solution blend of the high and low density polymers after crystallization. As shown, few and large particles are observed that are between 20 and 25 μm and they are slightly larger than the high density polymer alone (compared to Fig. 10(a)). This result does suggest that the blend of polymers interact during crystallization as suggested by their large size and lack of small crystals that would be expected from the lower density polymer. However, the above results show that the turbidity is not clearly related to just the concentration of polymer and hence it is difficult to obtain a soluble or purge fraction of the polymer.

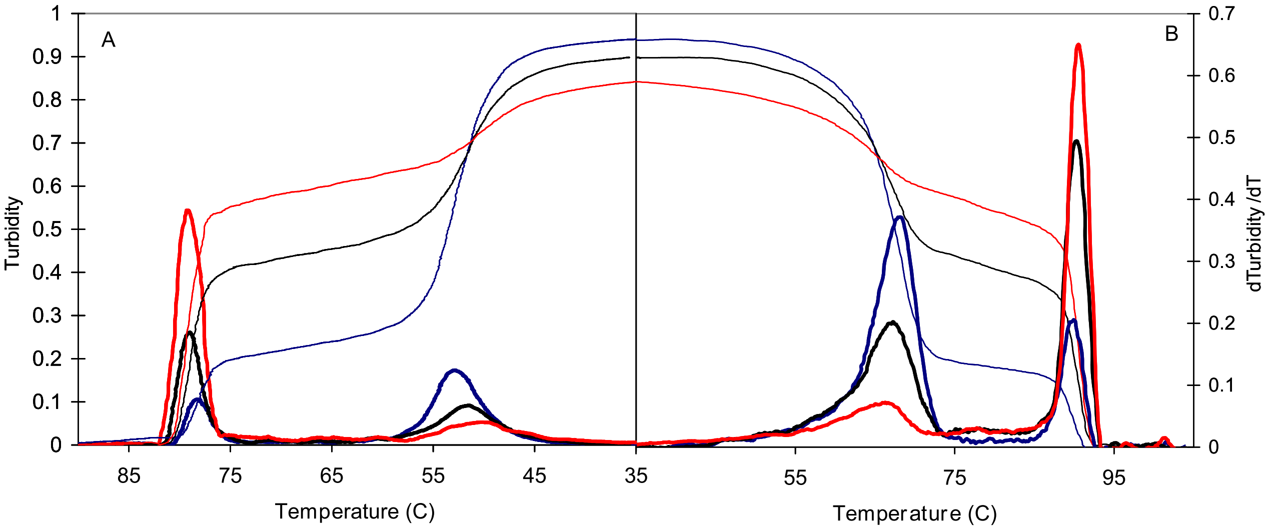
3.4. Blend study of low/high density polymers

Analyses with different blend compositions and different cooling rates were carried out in both TFA cooling and TFA heating.

Fig. 11(A) shows the resulting turbidity and SCBD profiles of low and high density polymer blends from TFA cooling analysis. As shown, the turbidity profiles change accordingly with different blend compositions between 25 and 75% of each component. The proportions of the higher density polymer and lower density polymer calculated from the TFA SCBD are quite consistent with the actual composition. One other thing to note in Fig. 11 is that the turbidity at 30 °C (at the end of the analysis) shows that the blends with the larger fraction of the lower density polymer have higher turbidity. At a given concentration, if all the polymer precipitated from solution, you might expect that the same final turbidity would be reached. If the lower density material did not completely fractionate, upon reaching the final temperature, a lower than expected turbidity would be observed to account for the higher portion that remains soluble. In these analyses, this was not observed. The difference may be linked to the sizes of the crystals formed. Fig. 11(B) shows the same blends during heating at a constant rate (0.7 °C/min) following the previous crystallization at 0.2 °C/min. From these profiles, the proportions of high density and low density polymers calculated from the TFA SCBD that were cooled at 0.2 °C/min and then heated at 0.7 °C/min show some differences with the actual composition. Despite these differences, the turbidity profiles of the dissolution of the polymer also relate to the SCBD of the polymer. The experiment has also been carried out at a faster cooling rate (0.7 °C/min) (results are not shown) but it was found that a faster cooling rate results in a more reliable weight fraction measurement. The quick cooling probably results in smaller crystals that are more uniform in size. Slow cooling may allow for larger and a wider range of crystal sizes which might account for the variation in the compositional estimates.

3.5. Measurement of TFA SCBD in dodecane

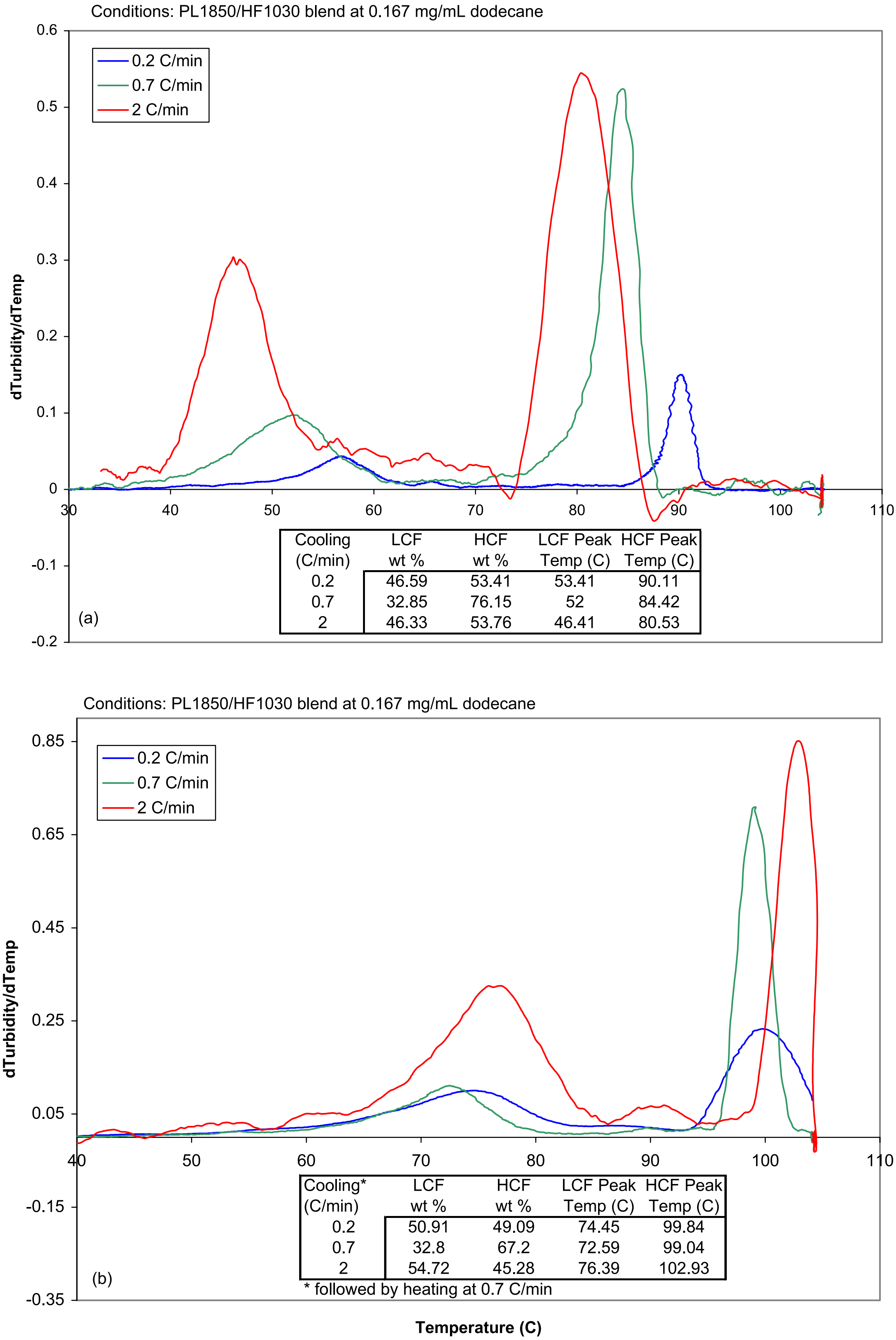
The simple equipment setup and operation of the TFA allows for the flexibility to perform crystallization experiments



Turbidity 0.2 C/min Cooling	75/25 LCF	HCF	50/50 LCF	HCF	25/75 LCF	HCF
Wt.(%)	74.5	25.5	49.4	50.6	27.5	72.5
Peak Temp C	52.9	78.3	51.7	79.1	50.2	79.3

Turbidity 0.7 C/min Heating	75/25 LCF	HCF	50/50 LCF	HCF	25/75 LCF	HCF
Wt.(%)	79.8	20.3	54.0	46.0	33.6	66.4
Peak Temp C	68.0	89.9	67.1	90.4	66.2	90.5

Fig. 11. TFA cooling and heating SCBDs of low and high density polymers with different blend ratios.



Cooling (C/min)	LCF wt %	HCF wt %	LCF Peak Temp (C)	HCF Peak Temp (C)
0.2	46.59	53.41	53.41	90.11
0.7	32.85	76.15	52	84.42
2	46.33	53.76	46.41	80.53

Cooling* (C/min)	LCF wt %	HCF wt %	LCF Peak Temp (C)	HCF Peak Temp (C)
0.2	50.91	49.09	74.45	99.84
0.7	32.8	67.2	72.59	99.04
2	54.72	45.28	76.39	102.93

* followed by heating at 0.7 C/min

Fig. 12. (a) TFA cooling SCBDs of low/high density blends measured in dodecane at different cooling rates. (b) TFA heating SCBDs of low/high density blends measured in dodecane at different cooling rates and heated at a constant rate.

in different solvents. This is a distinct advantage over other techniques such as CRYSTAF and TREF that are centered around the use of 1,2,4-trichlorobenzene for its high temperature use and dissolution ability of polyolefins. TFA experiments carried out in dodecane solvent were able to fractionate these high crystalline fractions, if present, and also measure their corresponding short chain branching distributions. Dodecane, being an aliphatic solvent, is a poor solvent for polyolefins.

Fig. 12(a) and (b) shows the TFA SCBDs of the same 50/50 low/high density blends measured with dodecane as a solvent. It was found that 1/6th of the concentration (0.167 mg/mL) was required to obtain the same range of detector response as with TCB (1 mg/mL). Fig. 12(a) and (b) shows the SCBDs measured upon cooling at different rates (0.2–2 °C/min) followed by heating at 0.7 °C/min. Overall, the weight fractions estimated for the 50/50 blend were not as accurate as those measured in TCB. The peak temperatures measured during cooling and heating were approximately 8–9 °C higher than in TCB. However, it was demonstrated that SCBD information can be obtained upon rapid cooling at 2 °C/min. The fact that this experiment was successfully carried out in an aliphatic solvent is encouraging since the turbidity analysis may be performed rapidly and potentially, in an online or at-line measurement of reactor products which are dissolved in aliphatic solvents.

3.6. TFA SCBD analysis of complex SCBDs

To demonstrate the ability of TFA to characterize a resin with a complex SCBD, Fig. 13(a) and (b), shows a complex SCBD as measured by both CRYSTAF and TREF. In this resin, a lower density peak is observed at low crystallization temperatures, 47 °C in CRYSTAF and 70 °C in TREF. Higher density peaks are observed between 55 and 85 °C for CRYSTAF and 80–105 °C in TREF.

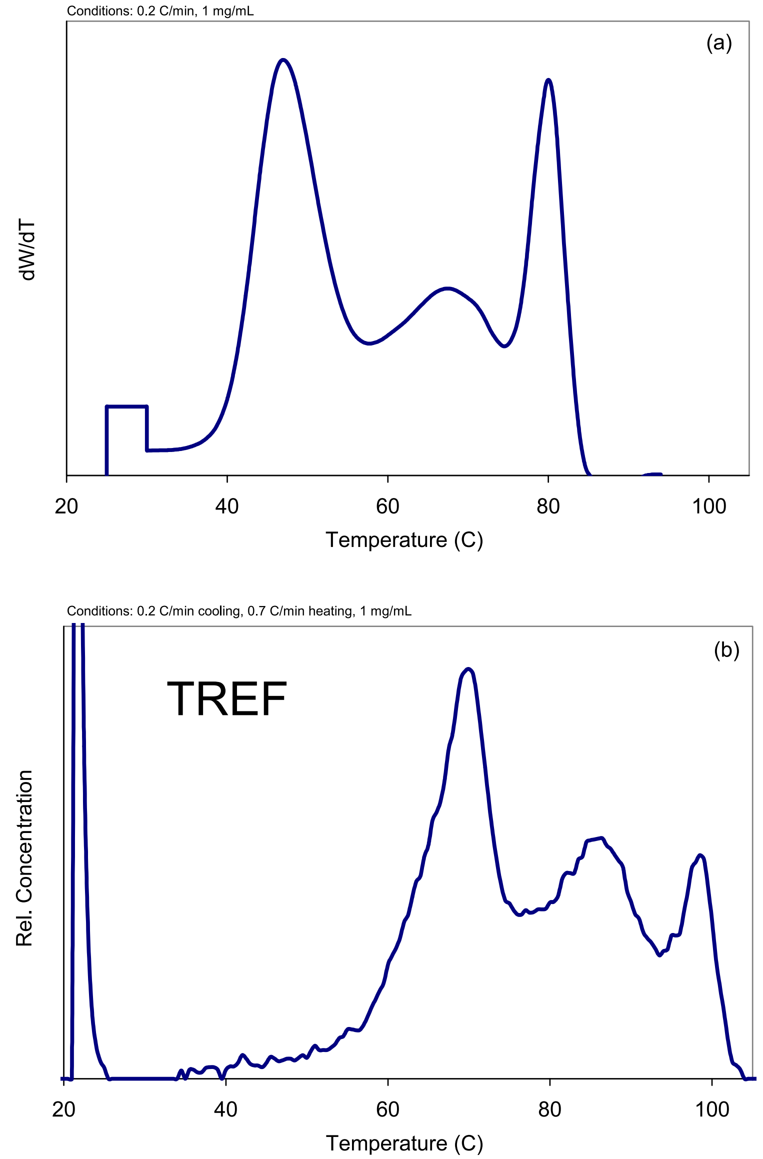


Fig. 13. (a) CRYSTAF SCBD of complex polymer. (b) TREF SCBD of complex polymer.

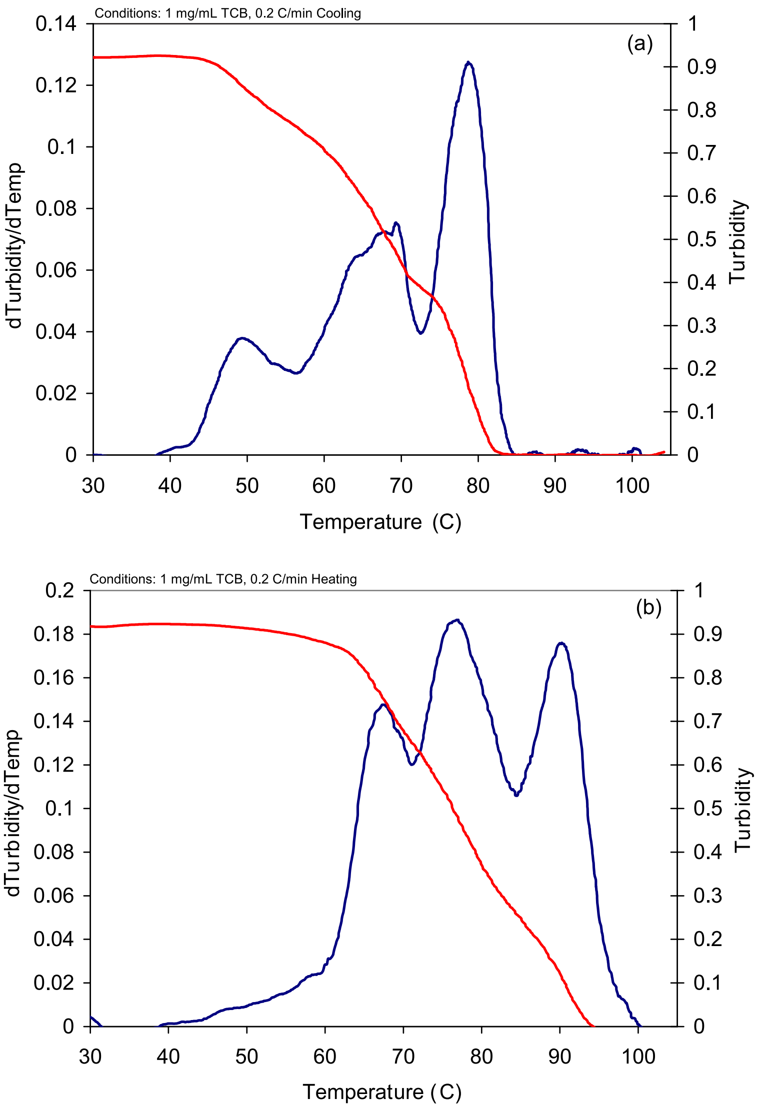


Fig. 14. (a) TFA cooling SCBD of complex polymer cooled at 0.2 °C/min. (b) TFA heating SCBD of complex polymer heated at 0.7 °C/min (after being cooled at 0.2 °C/min).

Fig. 14(a) and (b) shows the TFA results for the same polymer under heating and cooling conditions. As shown, TFA was able to capture the three distinct regions observed in CRYSTAF and TREF. However, the proportions of the measured fractions differ with the cooling and heating conditions. These different profiles probably result from the different crystallization conditions imposed by the different cooling and heating histories. Different cooling and heating histories would certainly influence the size and number of the resulting crystallites and affect the measured turbidity. More interestingly, why are different proportions obtained and what is the true SCBD of these products?

4. Conclusions

Turbidity analysis of ethylene/α-olefin copolymers by turbidity fractionation analysis can provide short chain branching distribution information that is similar to CRYSTAF and TREF. For the polyethylenes studied, thus far, the TFA results have provided accurate representations for polymers with broad and narrow SCBDs such as Ziegler-Natta LLDPE and homogeneous polymers catalyzed by single-site catalysts.

In a TFA experiment, the turbidity of a polymer solution is monitored while changing its temperature at a controlled rate. The resulting turbidity profile represents the precipitation or dissolution of the crystallized polymer at a given temperature. Although the mechanism for TFA is still in debate, it is believed that the crystallite number and size determine the turbidimetric response during crystallization or dissolution.

A TFA apparatus is simple to operate and is inexpensive when compared to the cost of operation and maintenance of other fractionation instruments. Given the flexibility of the instrument, experiments can be designed to help further the understanding of the fractionation and crystallization of polymers.

With the development of new and more differentiated products that are either tailored in-reactor or by catalyst means, TFA has great potential as a rapid screening tool or online/at-line measurement for characterizing the SCBD of products for product differentiation and quality control. DOW has also investigated this same turbidimetric approach for the high throughput screening of polymers from catalytic studies. The ability to rapidly measure the short chain branching distribution of polyolefins provides valuable insight into its catalytic origin which will lead to faster and improved catalyst and product development.

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