Fractionation of Metallocene-LLDPE Blends by High Temperature Thermal Gradient Interaction Chromatography

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by

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Outline

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  - CCD Characterization Techniques
  - Comparison Between CEF and HT-TGIC
- **Schematic Diagram of the Instrument**
- **Results**
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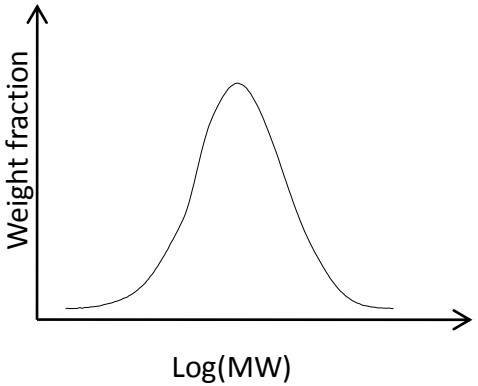
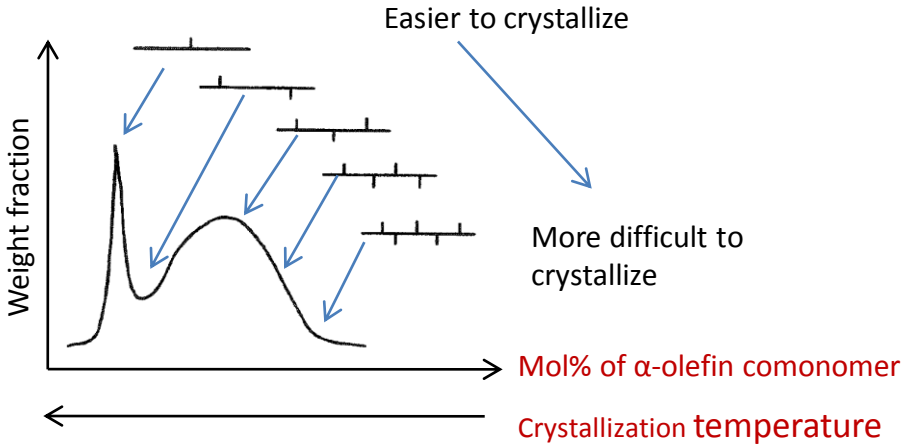
  - Blends
- **Conclusions**

Importance of CCD

- The end-use properties of LLDPEs depend not only on their average molecular weight and average comonomer content but also on their molecular weight distribution (MWD) and chemical composition distribution (CCD).
  - **MWD and CCD of LLDPE made with heterogeneous Ziegler-Natta catalysts**



Broad MWD



Broad and bimodal CCD

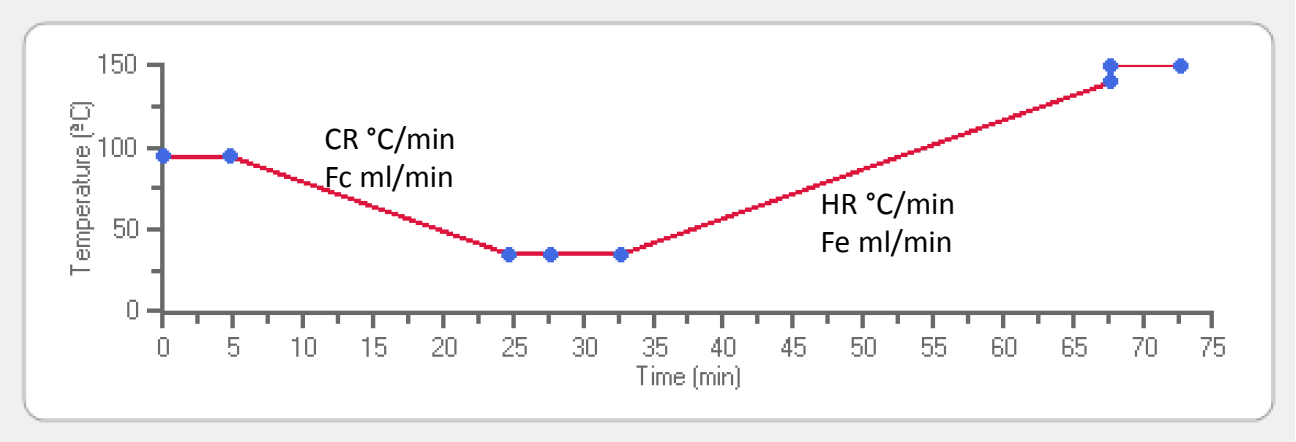
  - **Metallocene – LLDPEs have unimodal CCDs that depend on the comonomer content.**

CCD Characterization Techniques

- The CCD can be measured by different techniques:
  - Temperature Rising Elution Fractionation (TREF)
  - Crystallization Analysis Fractionation (CRYSTAF)
  - Crystallization Elution Fractionation (CEF)
  - High-Temperature Thermal Gradient Interaction Chromatography (HT-TGIC)

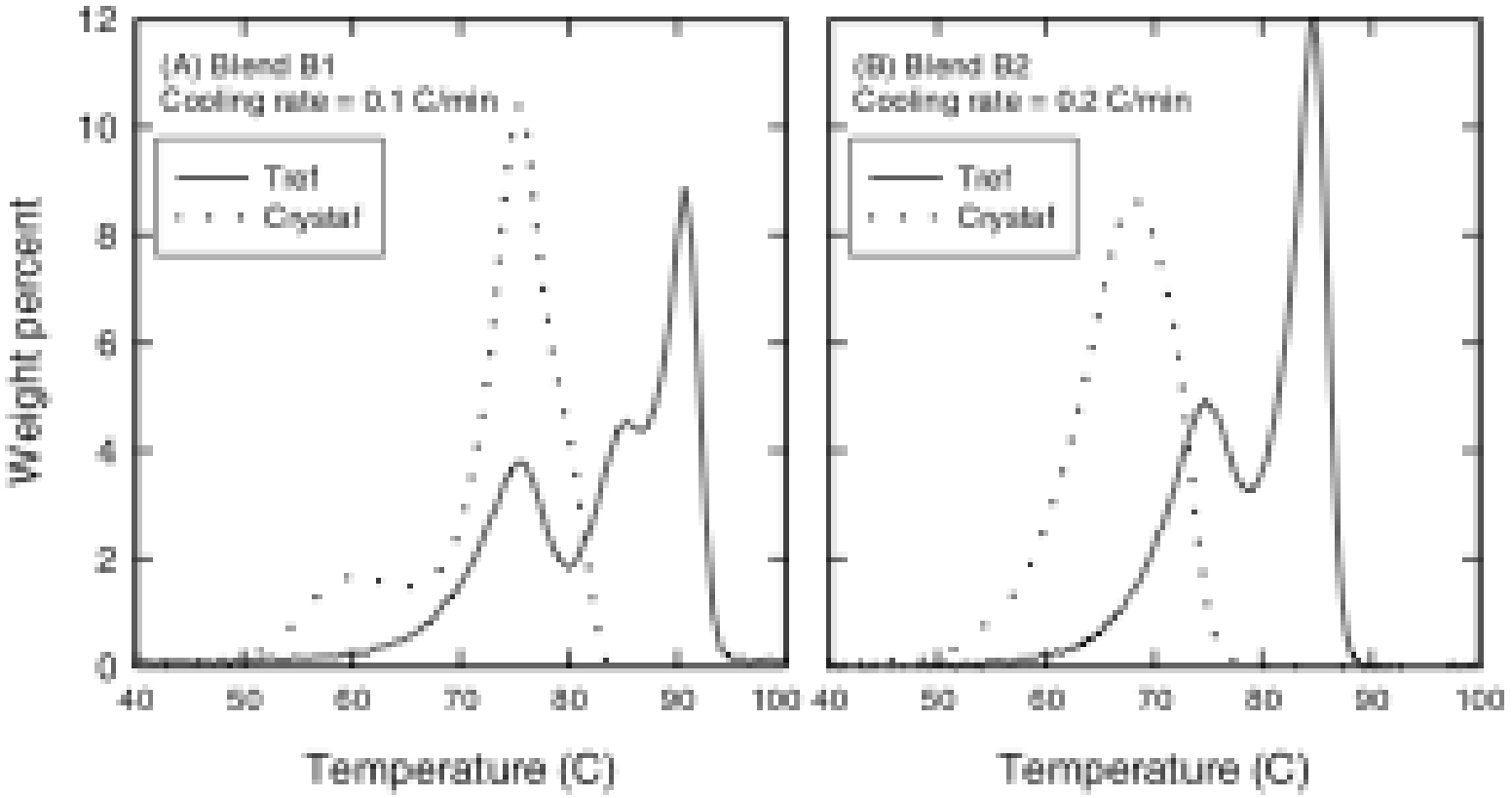
- In TREF, CRYSTAF, and CEF techniques, LLDPEs are fractionated according to their crystallinities.
- The crystallizability of LLDPE chains depends on the comonomer incorporation into the chains that results in chain irregularities.
- HT-TGIC uses the commercially available HYPERCARB® columns to separate the polymer chains based on their interaction with the porous graphitic carbon stationary phase in a temperature gradient mode.

Comparison Between CEF and HT-TGIC



- HT-TGIC is similar to temperature rising elution fractionation (TREF) and crystallization elution fractionation (CEF) in that it needs two temperature cycles: cooling and heating.
- The TGIC is free of cocrystallization effects that usually influence the TREF and CEF profiles. The HT-TGIC retention temperature, which is above the crystallization temperature, is proportional to the comonomer content in ethylene/1-alkene copolymers.

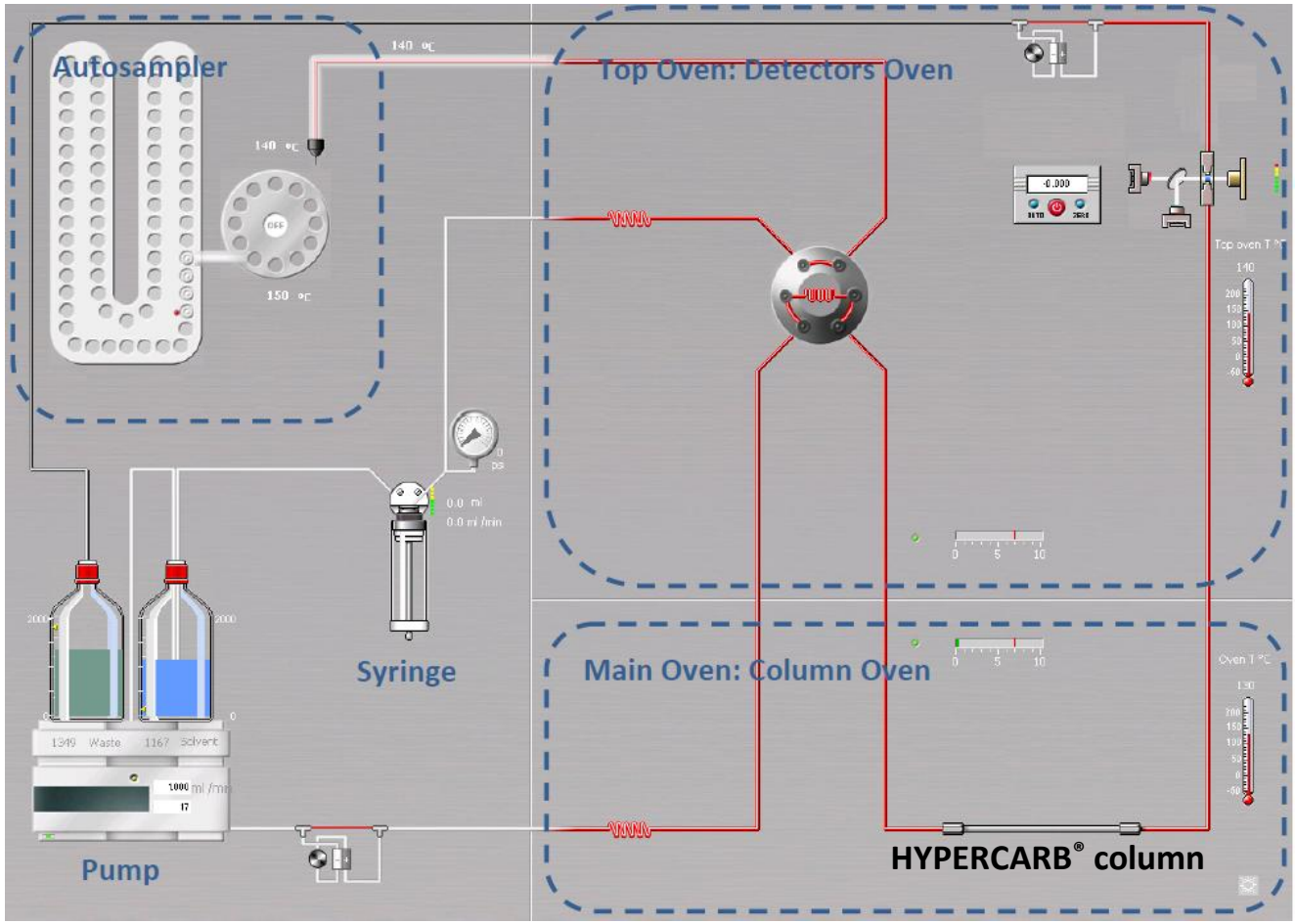
Cocrystallization Effects in TREF and CRYSTAF



Cocrystallization effects are less severe in TREF than in CRYSTAF, but they are not negligible

S Anantawaraskul, JBP Soares, PM Wood-Adams. Fractionation of semicrystalline polymers by crystallization analysis fractionation and temperature rising elution fractionation. *Adv Polym Sci* **2005**, *182*, 1-54.

Schematic Diagram of the CEF Apparatus



HYPERCARB column used in this study is: 10 cm length, 4.6 mm I.D, and 5 µm particle diameter

Polymer Samples

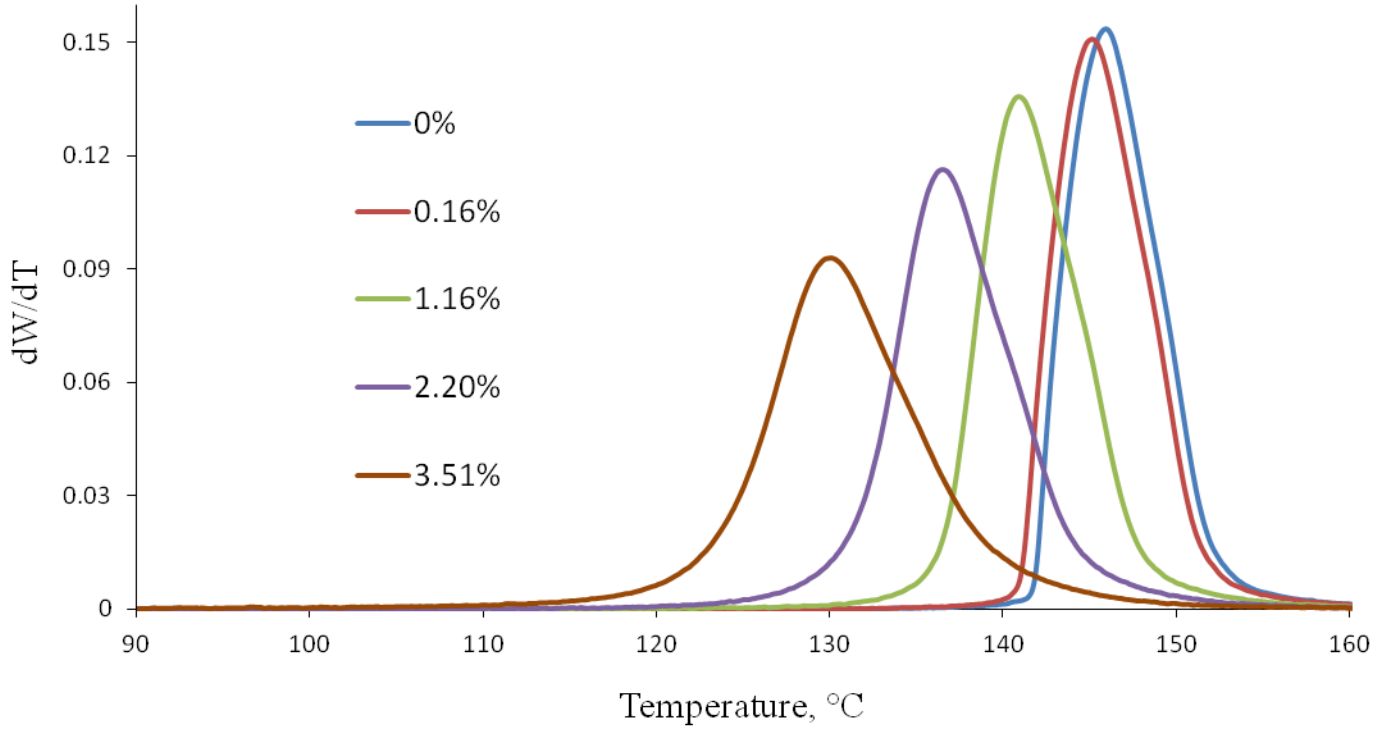
• In this study ethylene/1-octene copolymers were used to study the main factors affecting HT-TGIC analysis.

Sample	*Octene* mol %	M_n
m-1	0	46,600
m-2	0	19,000
m-3	0.16	48,161
m-4	1.16	47,000
m-5	2.2	47,700
m-6	3.51	49,800

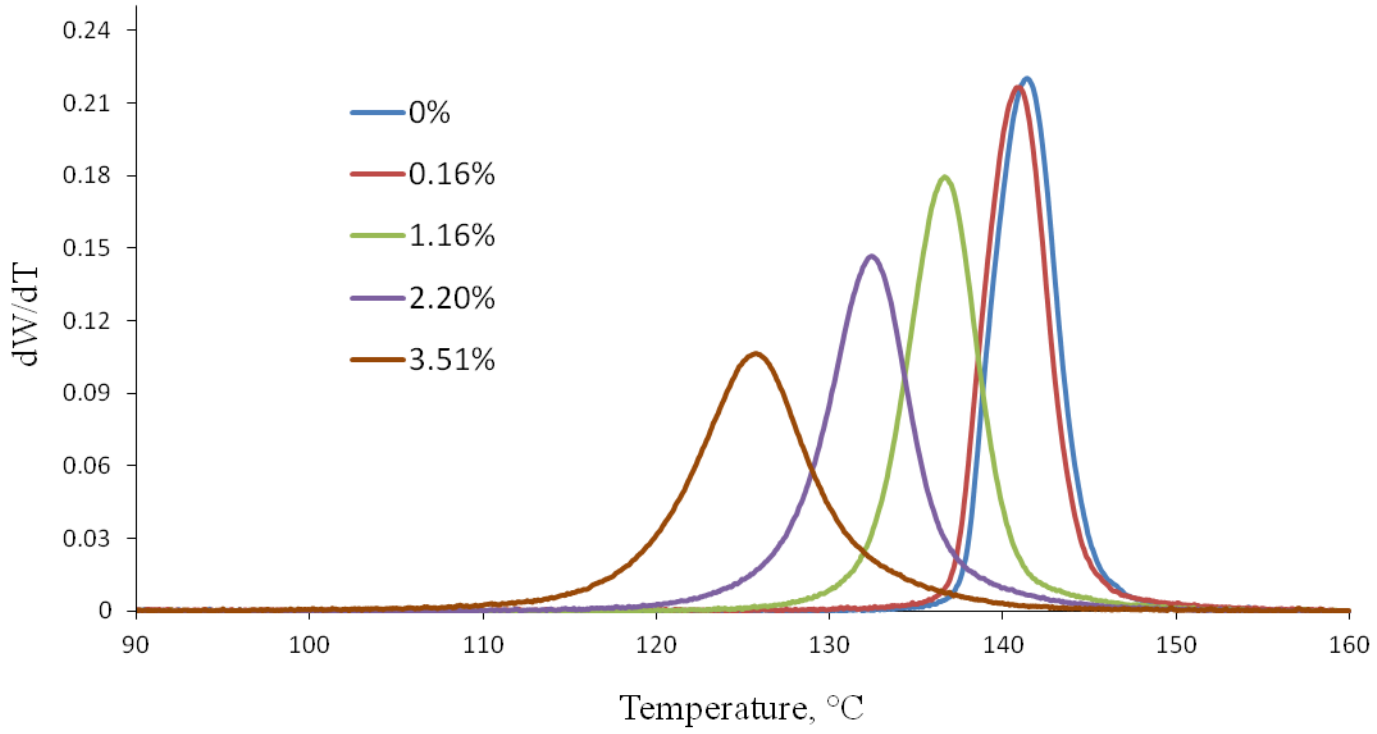
• These samples have similar number and weight average molecular weights to study the effect of comonomer content on TGIC chromatograms.

HT-TGIC Results of Individual Samples

CR = 5 °C/min – HR = 3 °C/min – Fe = 0.5 ml/min – ODCB solvent



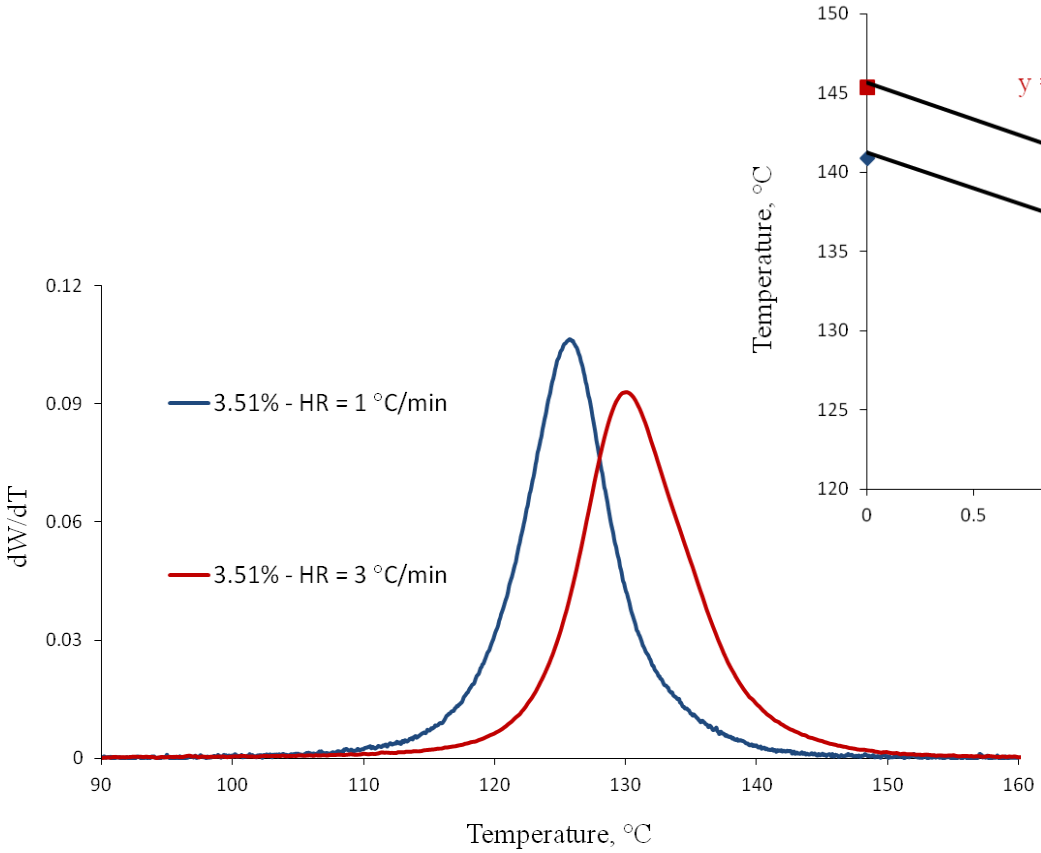
Effect of Heating Rate

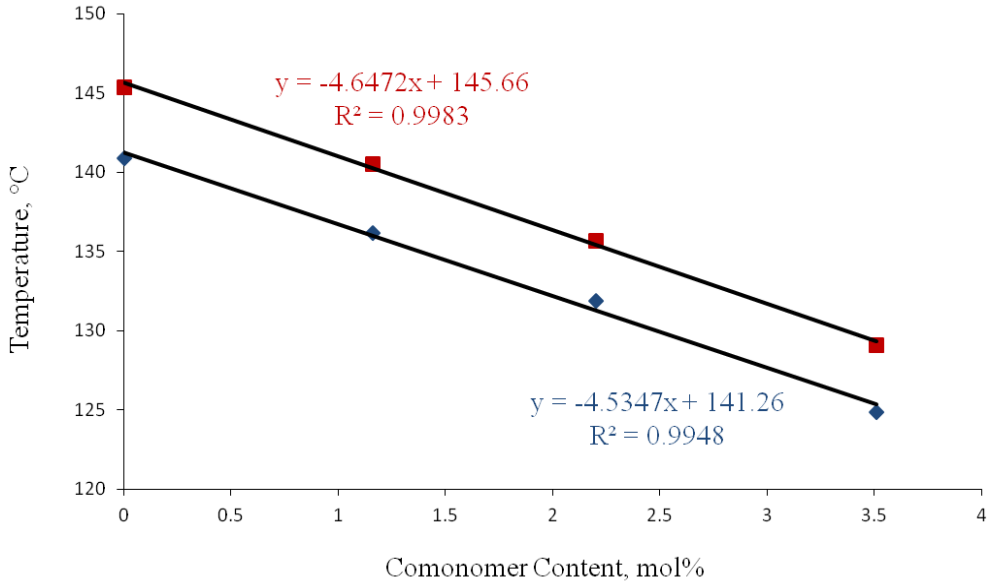


CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – ODCB solvent

Effect of Heating Rate (cont.)

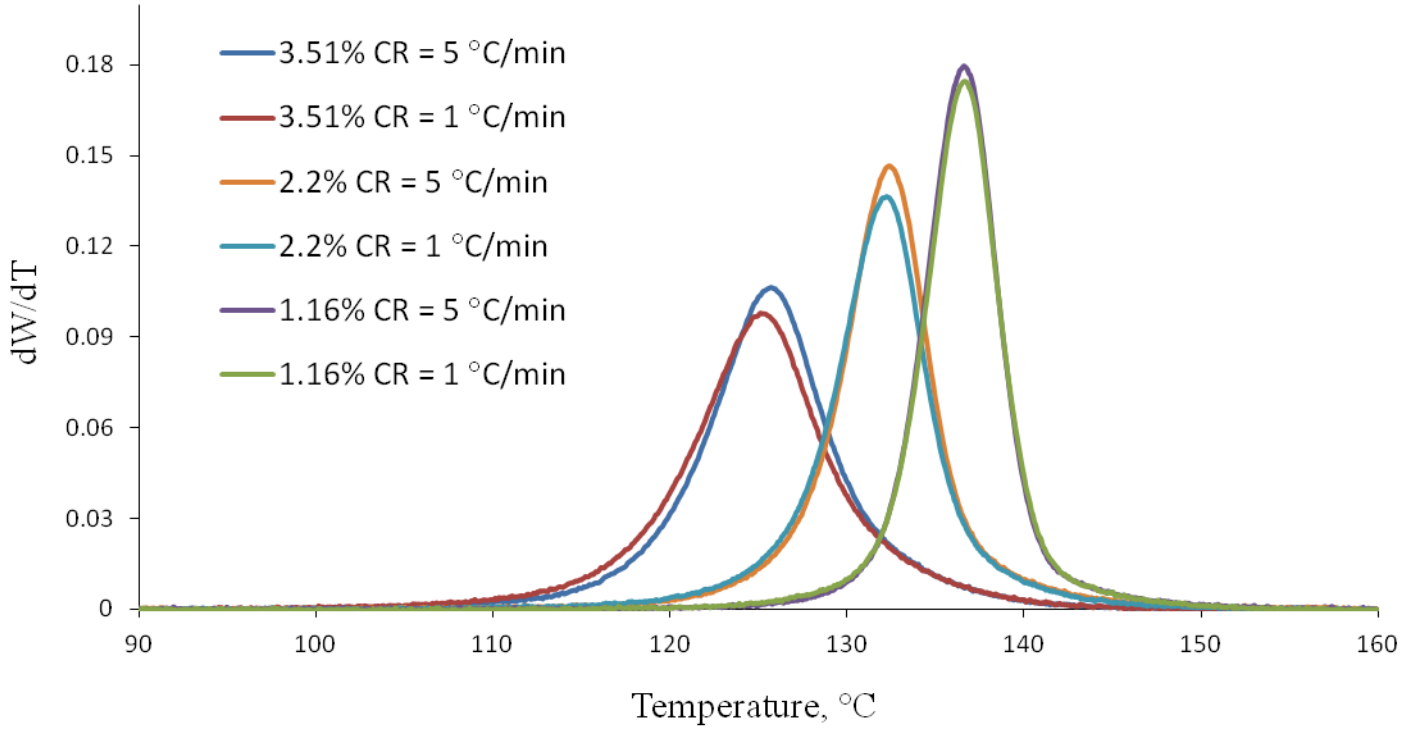
Calibration Curve at **HR = 3** and **HR = 1** °C/min





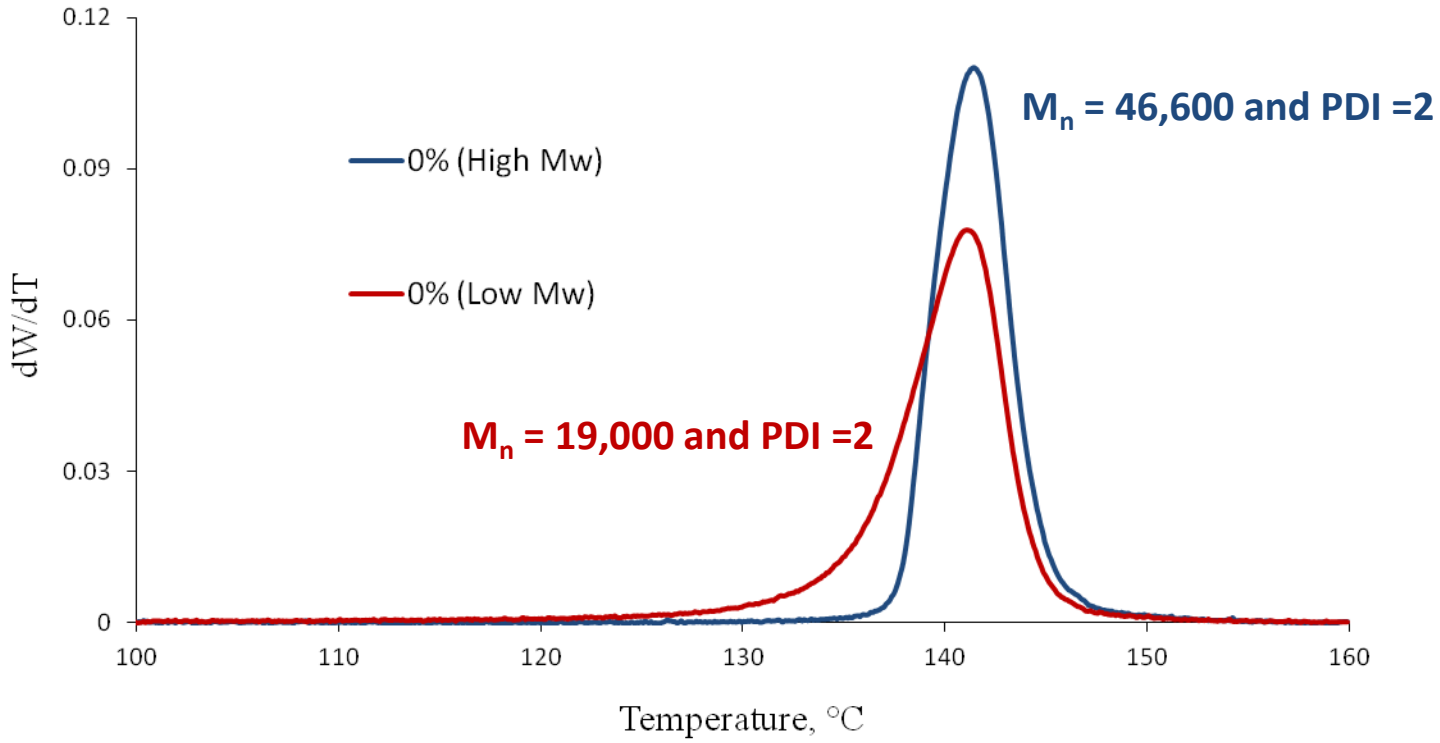
CR = 5 °C/min – Fe = 0.5 ml/min – ODCB solvent

Effect of Cooling Rate



HR = 1 °C/min – Fe = 0.5 ml/min – ODCB solvent

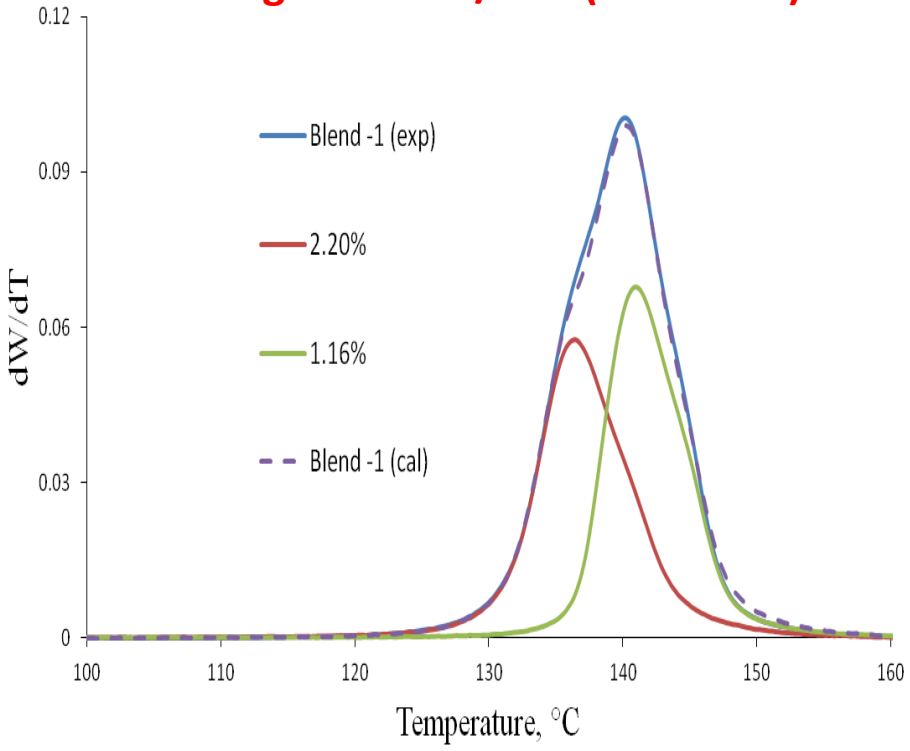
Effect of Molecular Weight



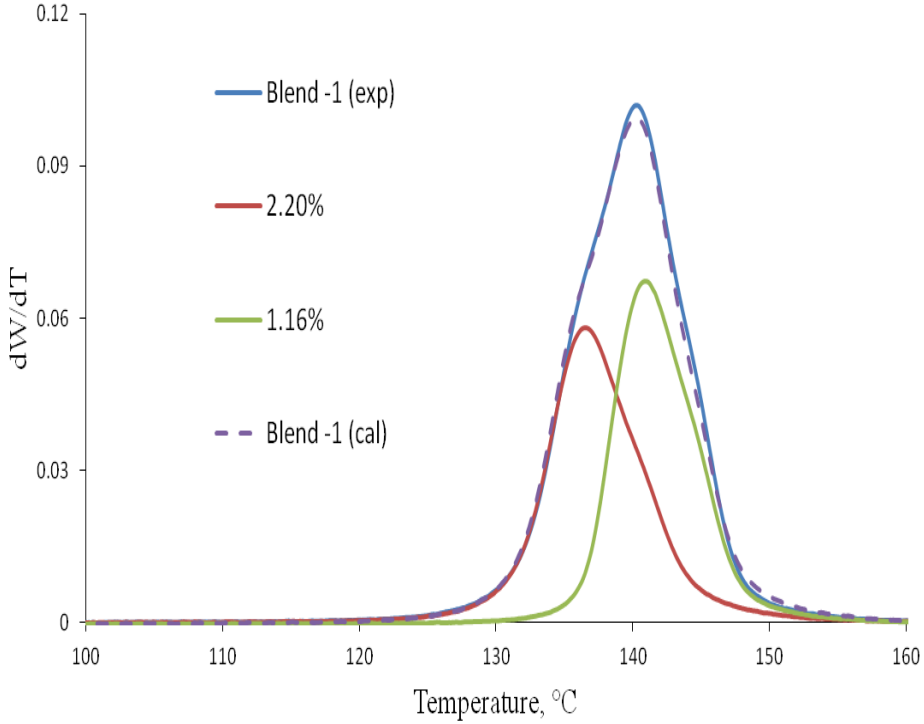
CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – ODCB solvent

HT-TGIC of Blend-1: Cooling Cycle

Cooling Rate 5 °C/min (155-35 °C)

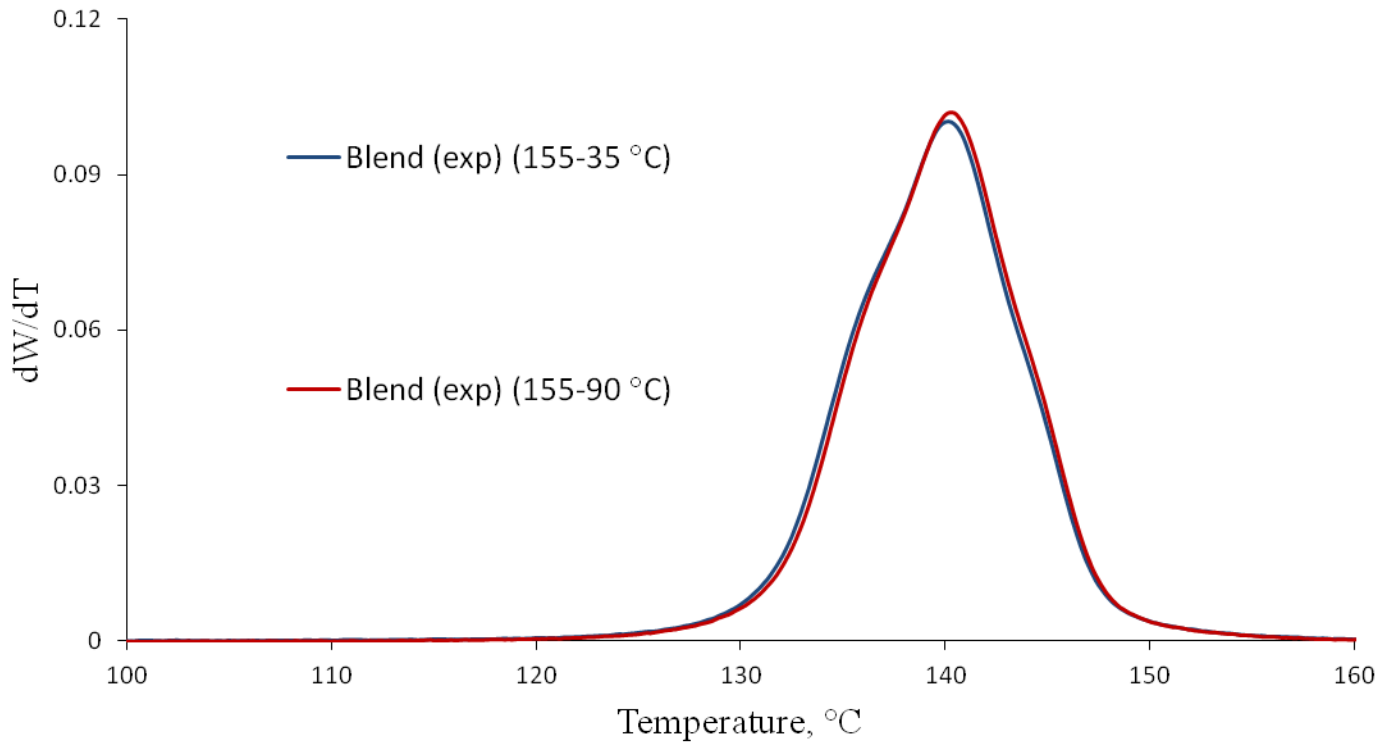


Cooling Rate 5 °C/min (155-90 °C)



HR = 3 °C/min – Fe = 0.5 ml/min – ODCB solvent

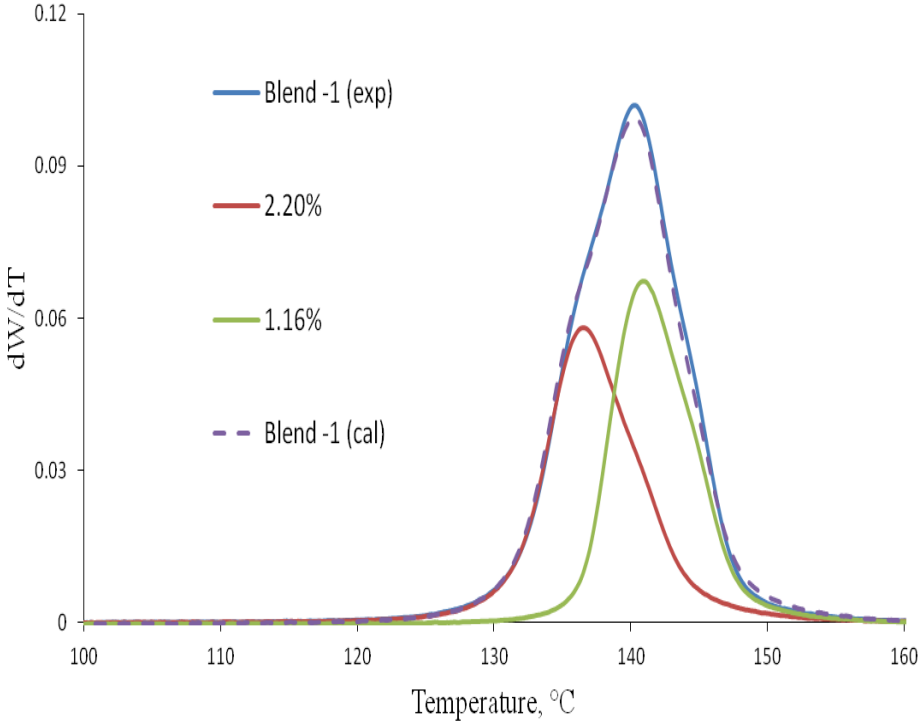
HT-TGIC of Blend-1: Cooling Cycle (cont.)



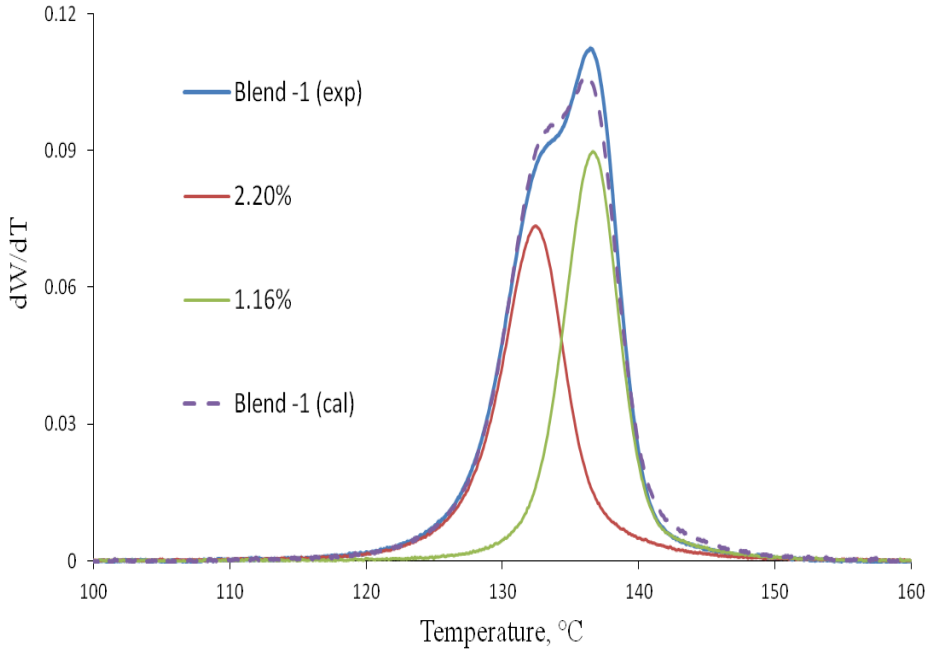
CR = 5 °C/min – HR = 3 °C/min – Fe = 0.5 ml/min – ODCB Solvent

HT-TGIC of Blend-1: Effect of Heating Rate

Heating Rate 3 °C/min



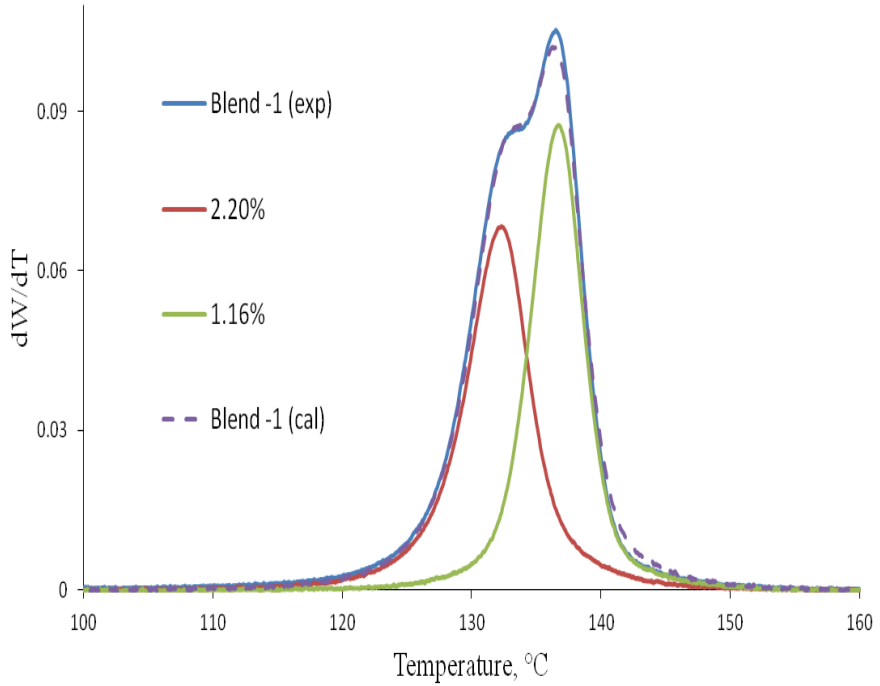
Heating Rate 1 °C/min



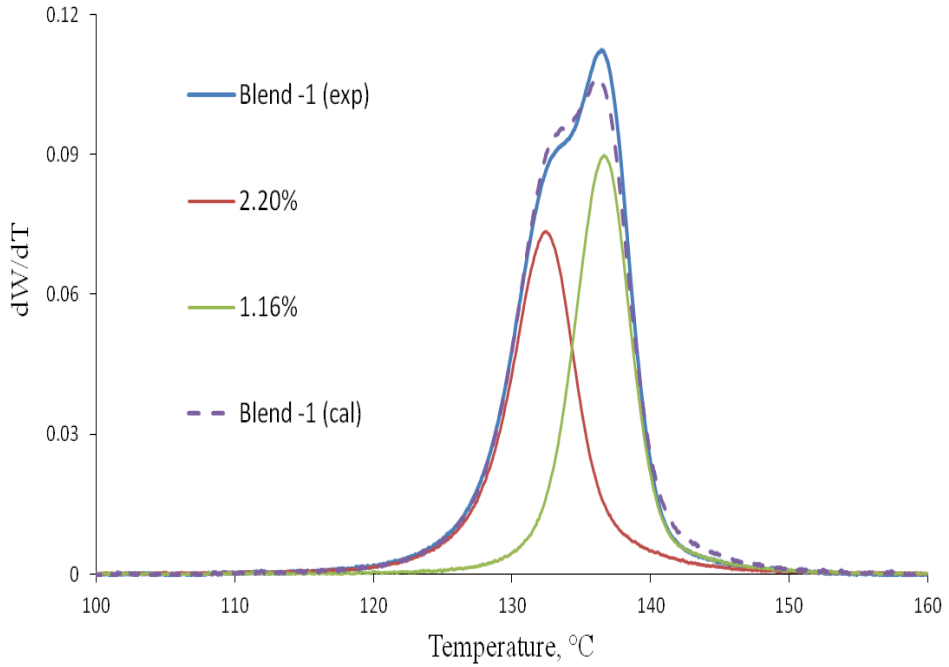
CR = 5 °C/min – Fe = 0.5 ml/min – ODCB Solvent

HT-TGIC of Blend-1: Effect of Cooling Rate

Cooling Rate 1 °C/min (155-90 °C)



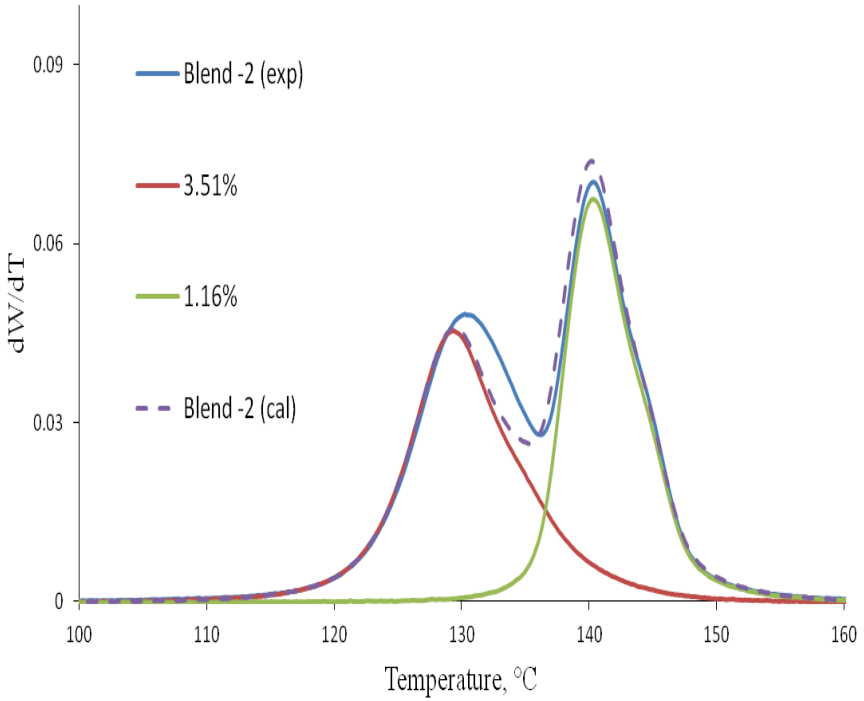
Cooling Rate 5 °C/min (155-90 °C)



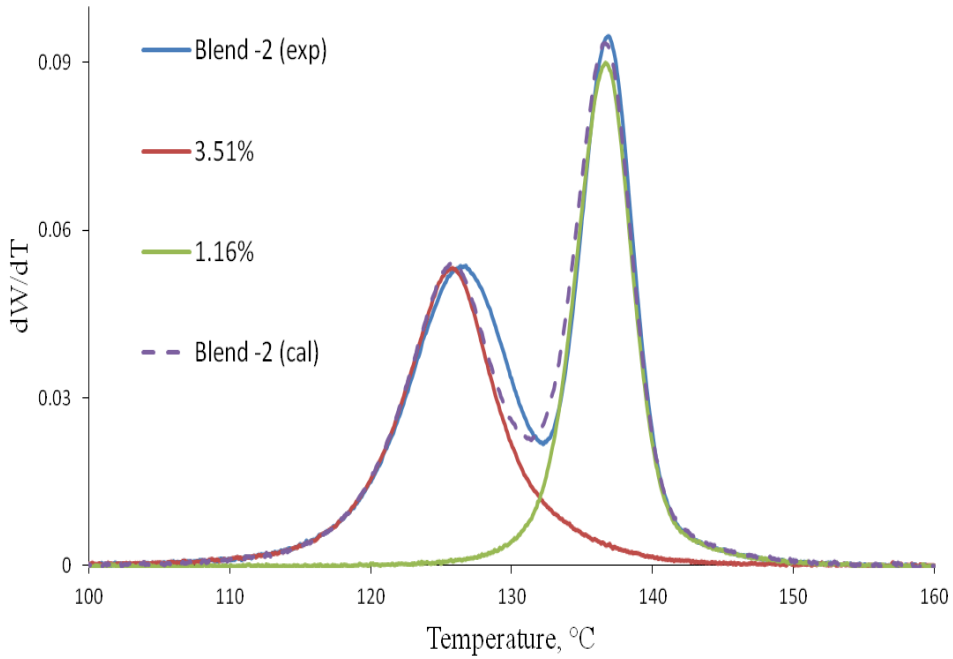
HR = 1 °C/min – Fe = 0.5 ml/min – ODCB Solvent

HT-TGIC of Blend-2: Effect of Heating Rate

Heating Rate 3 °C/min

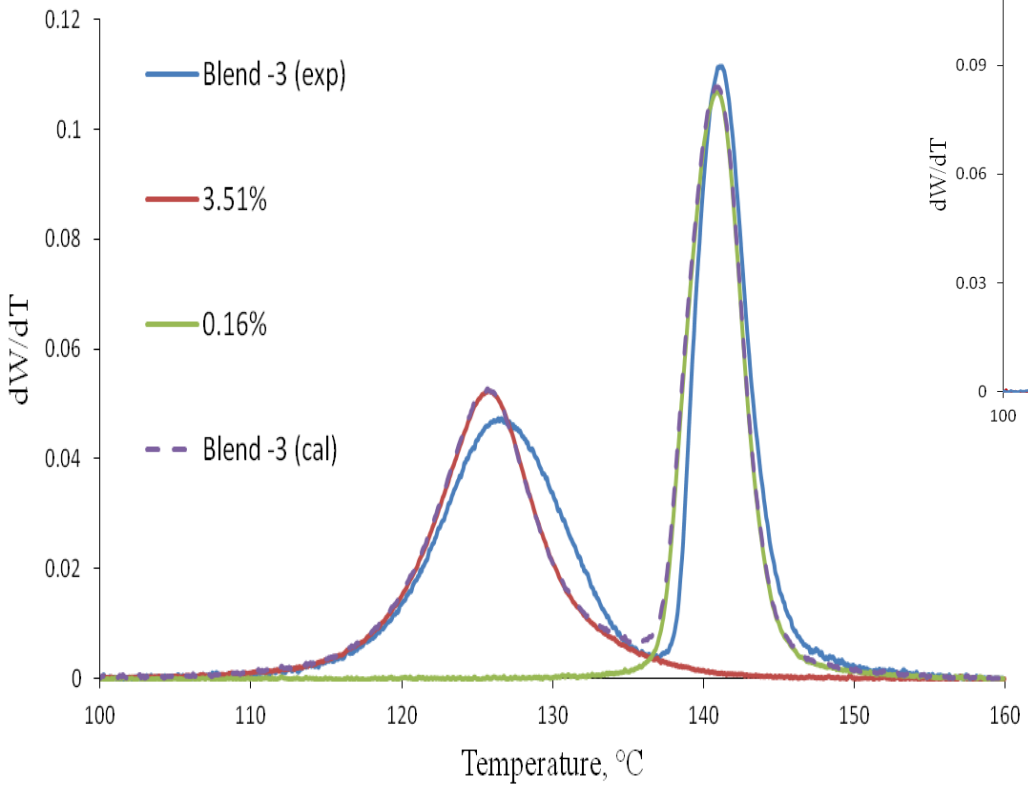


Heating Rate 1 °C/min

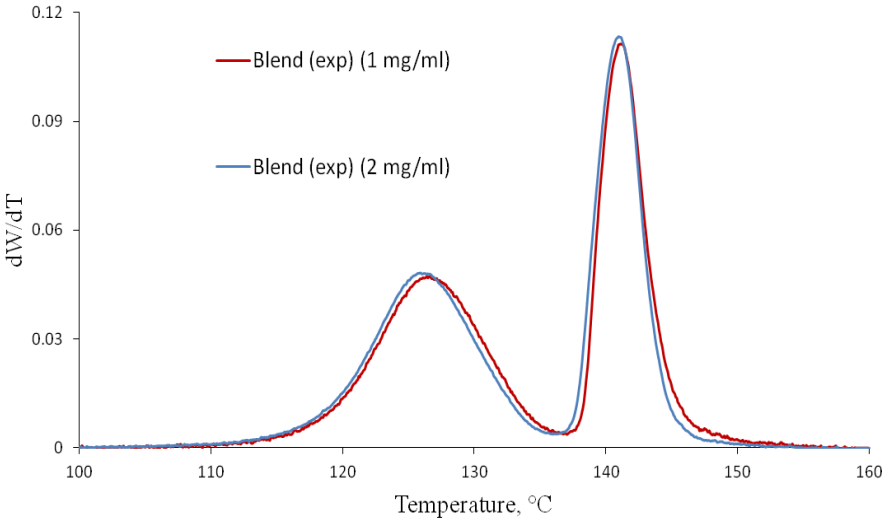


CR = 5 °C/min – Fe = 0.5 ml/min ODCB Solvent

HT-TGIC of Blend-3



(Effect of Sample Concentration)

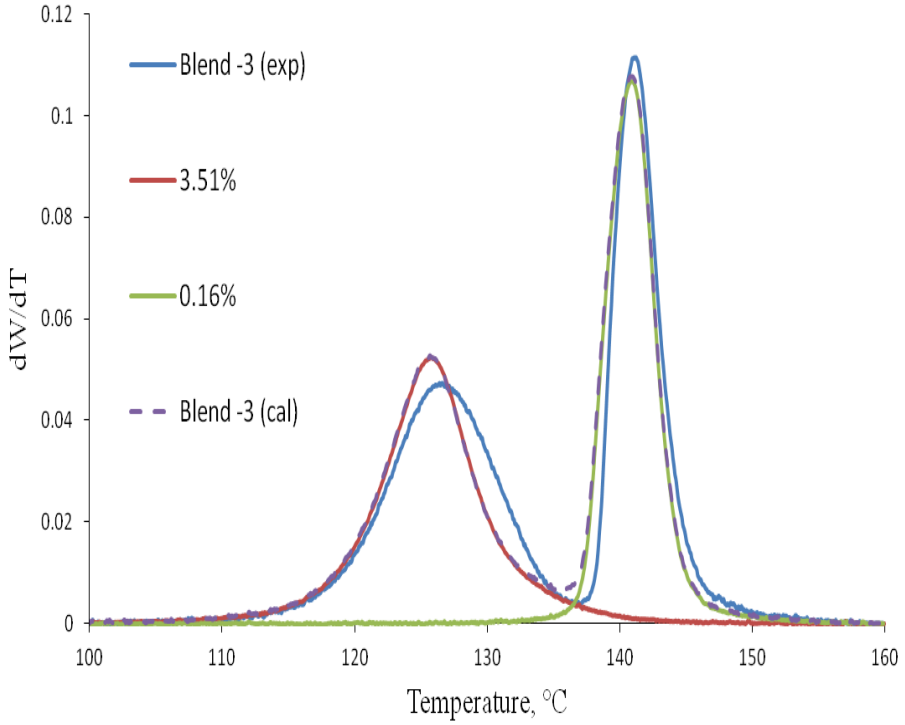


CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min

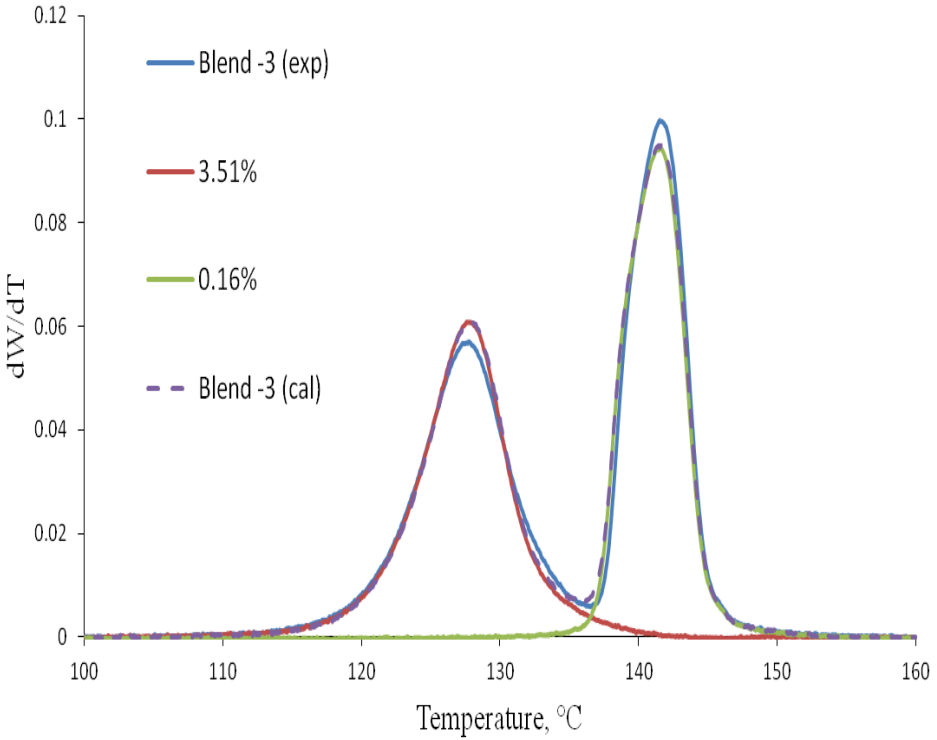
CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – ODCB Solvent

HT-TGIC of Blend-3: Effect of Sample Size

(Injection Volume = 400 µL)



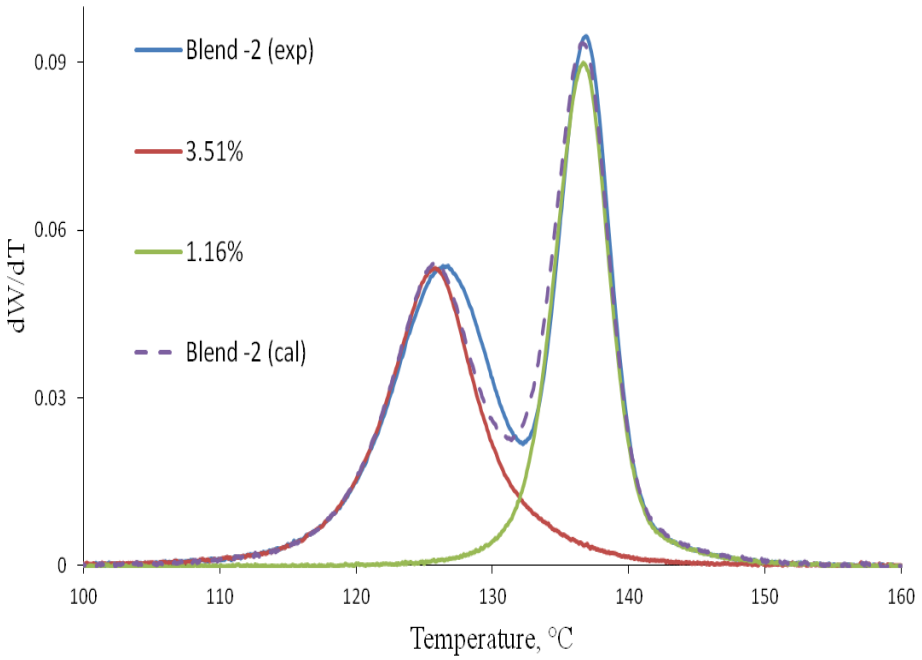
(Injection Volume = 100 µL)



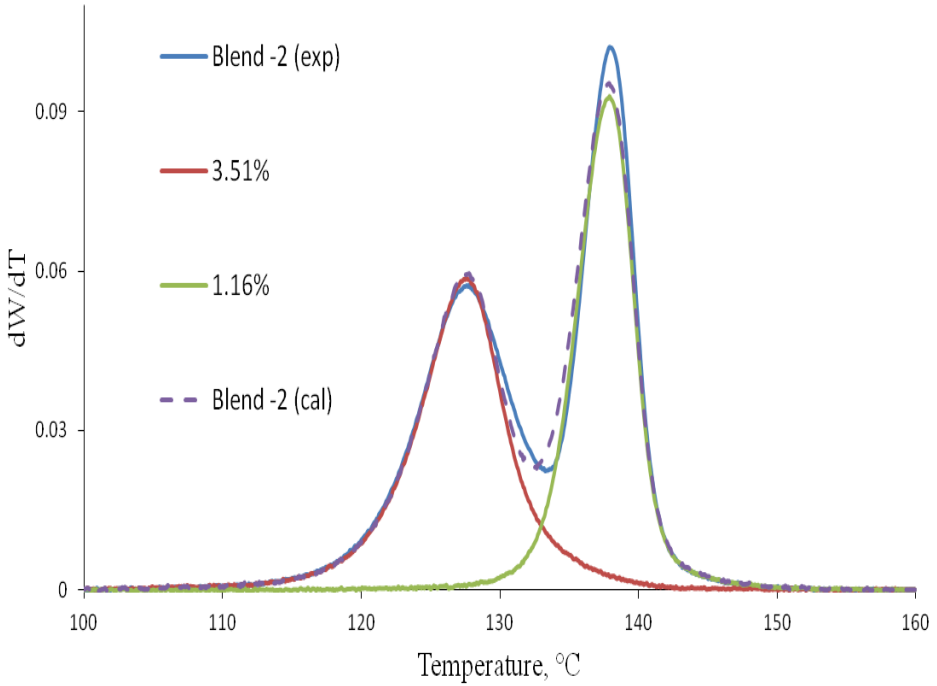
CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – ODCB Solvent

HT-TGIC of Blend-2: Effect of Sample Size

(Injection Volume = 400 µL)



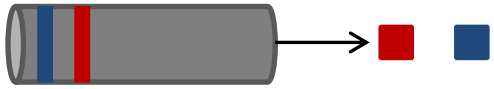
(Injection Volume = 100 µL)

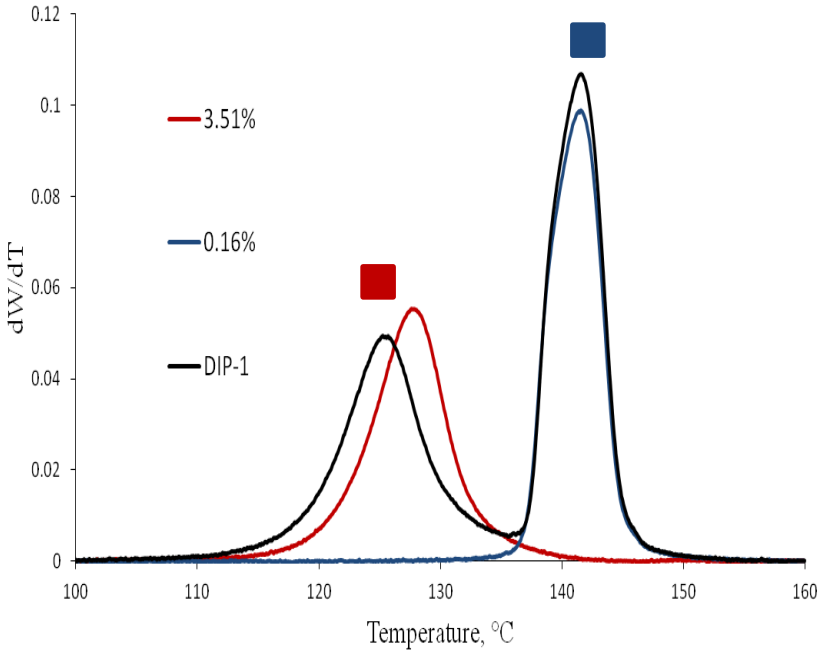


CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – ODCB Solvent

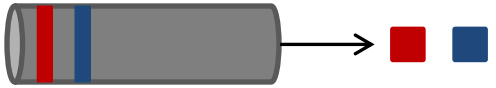
HT-TGIC of Blend-3

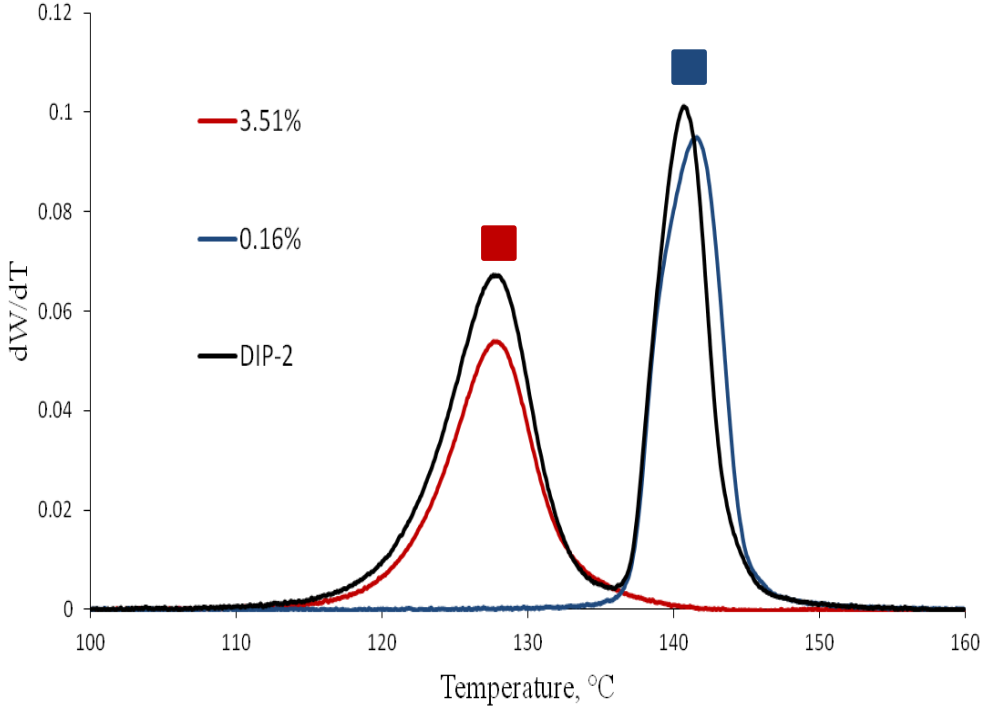
(Different Injection Points -1)





(Different Injection Points -2)

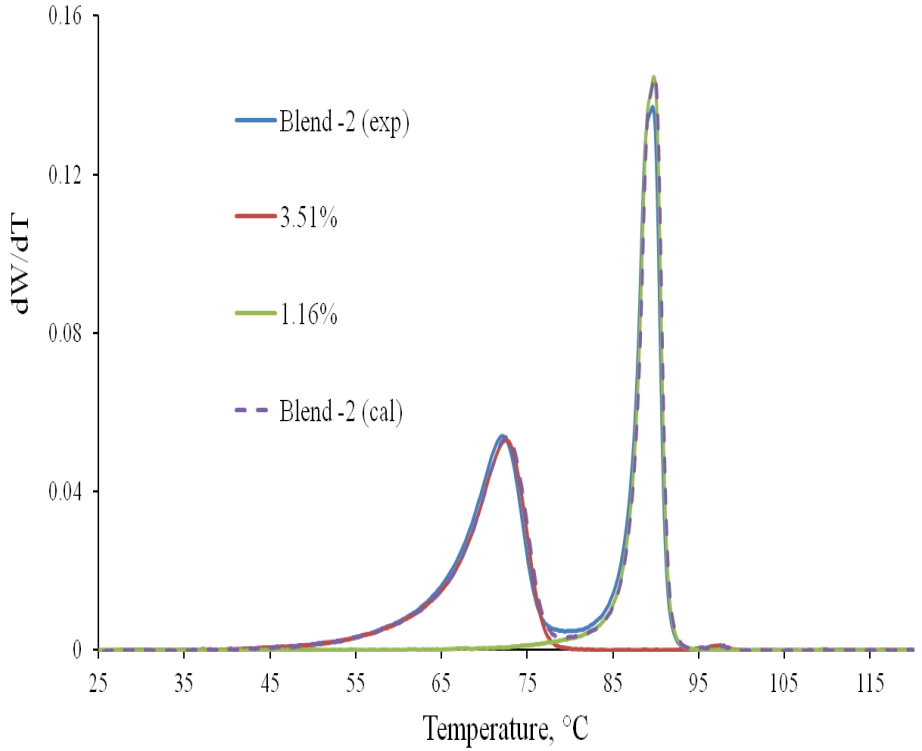




CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – ODCB Solvent

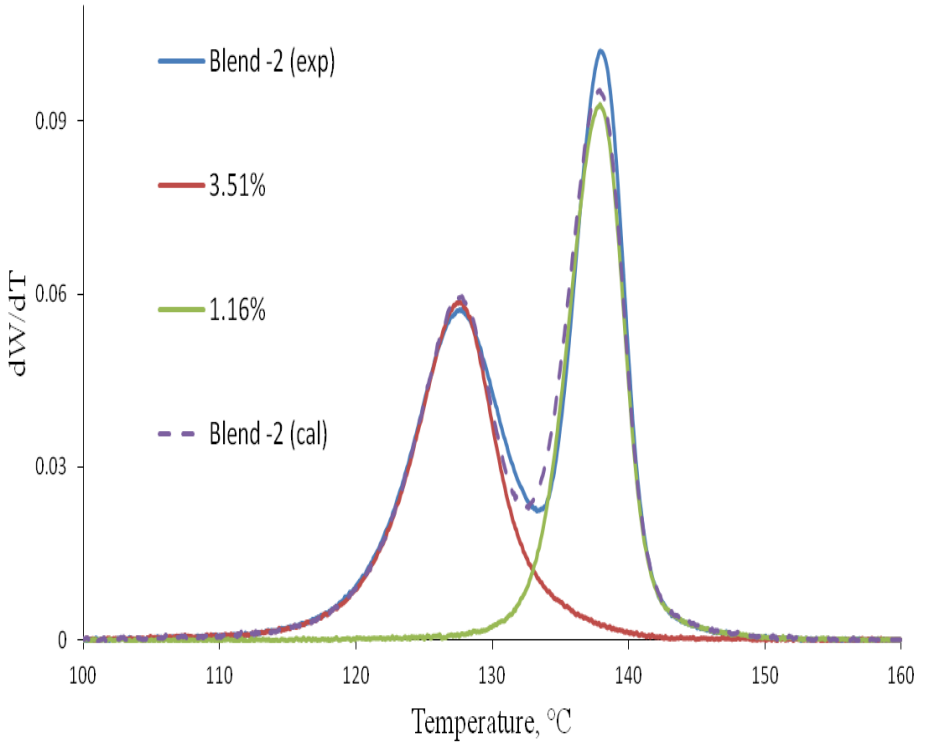
HT-TGIC of Blend-2: Comparison with CEF

CEF results



CR = 1 °C/min – HR = 3 °C/min – Fe = 1 ml/min

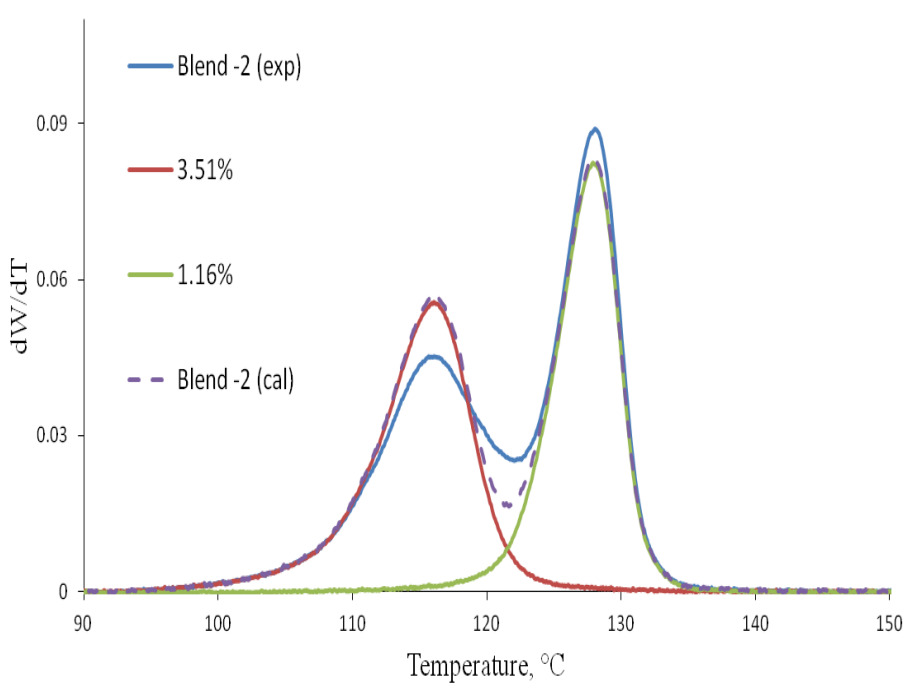
HT-TGIC results



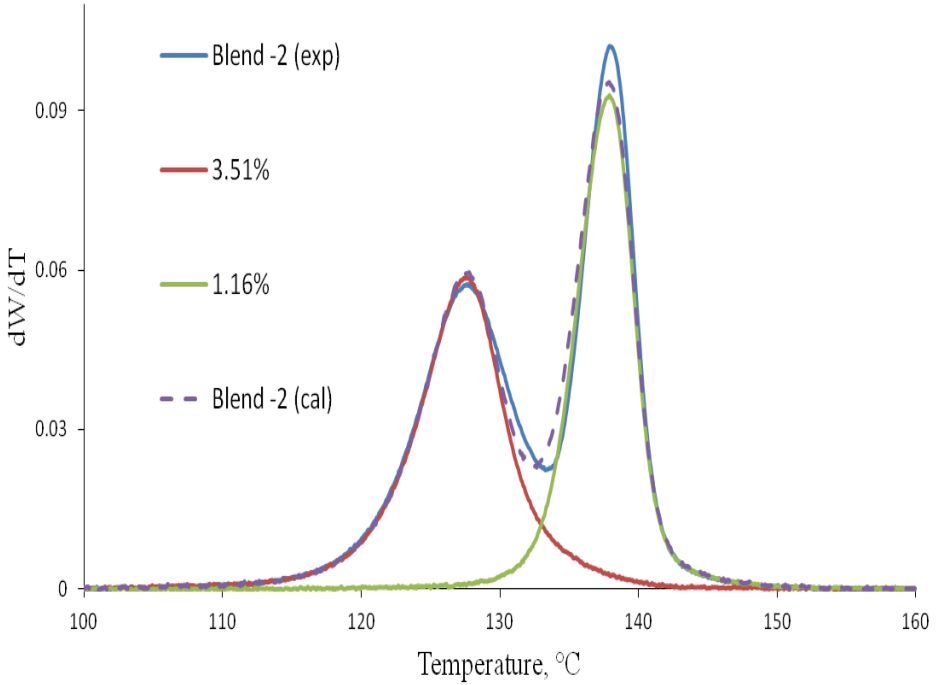
CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min

HT-TGIC of Blend-2: Effect of Solvent Type

(Solvent: TCB)



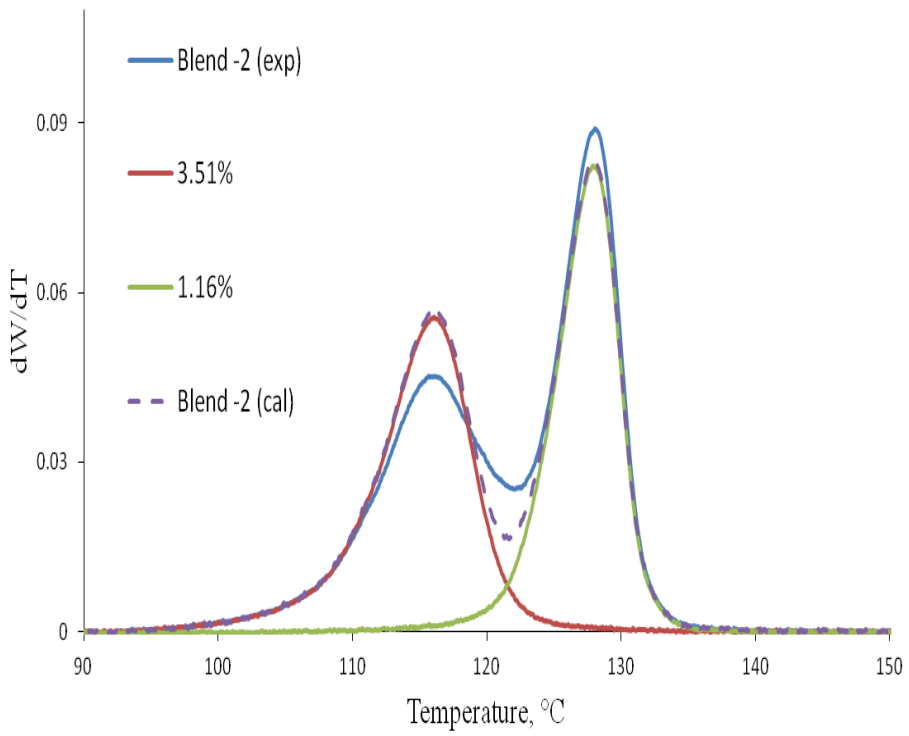
(Solvent: ODCB)



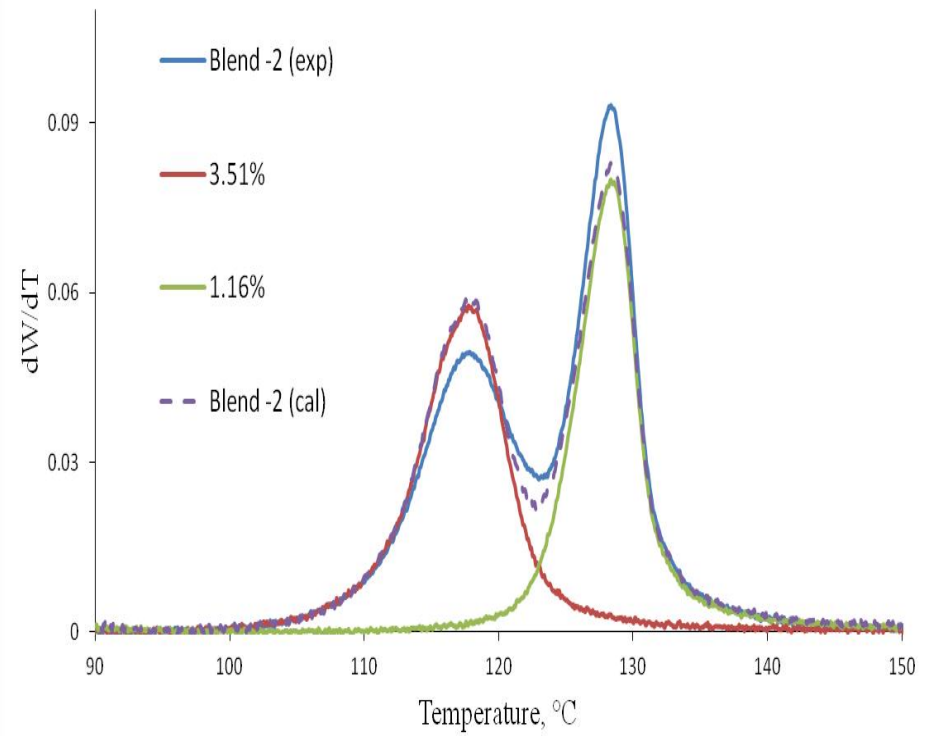
CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – IV = 100µL

HT-TGIC of Blend-2: Effect of Solvent Type

(Solvent: TCB)



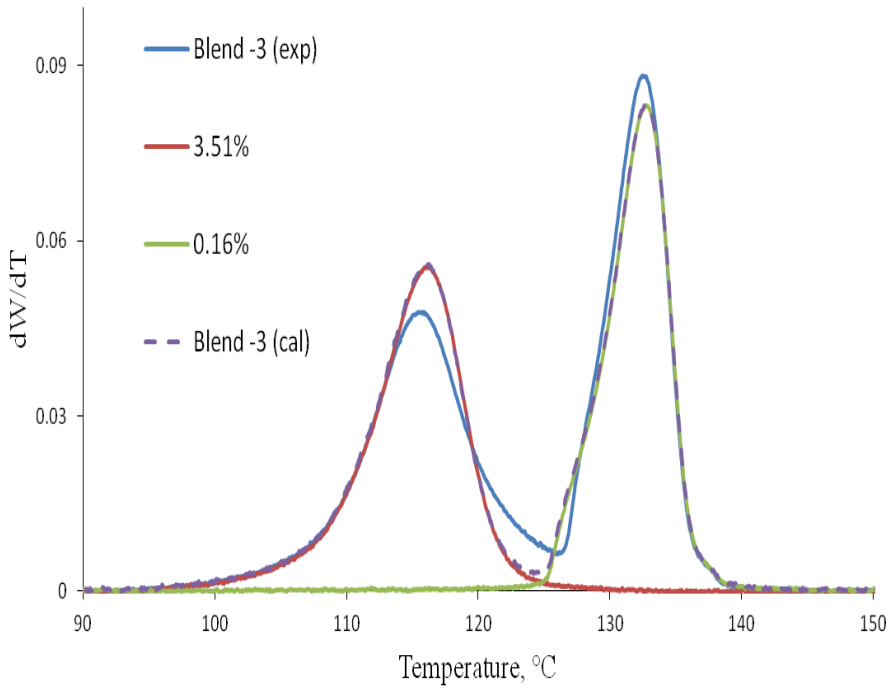
(Solvent: CN)



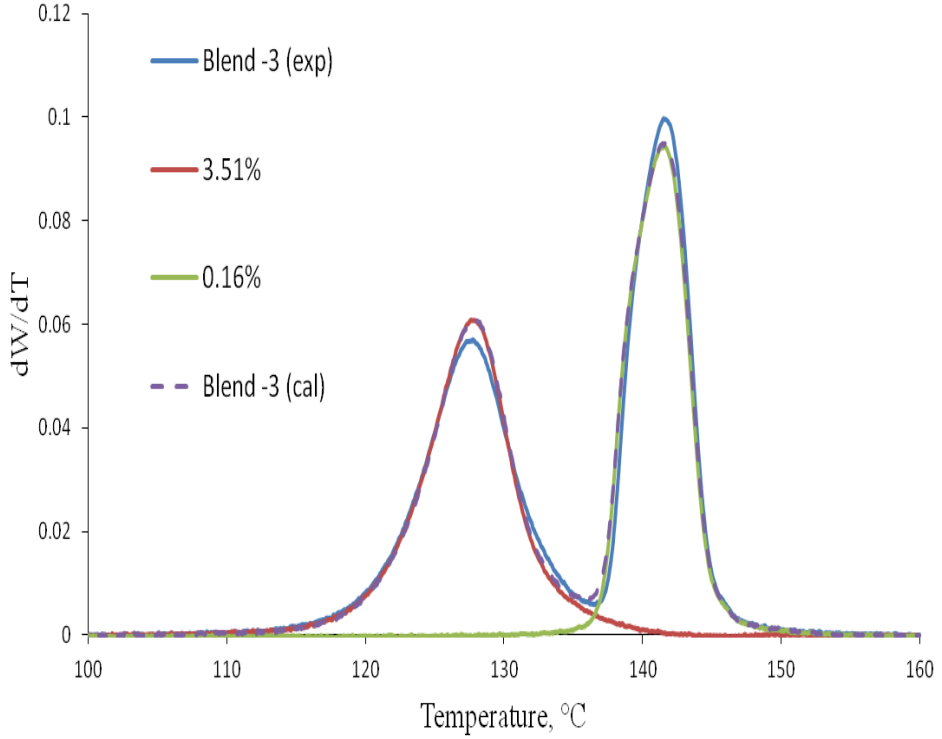
CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – IV = 100µL

HT-TGIC of Blend-3: Effect of Solvent Type

(Solvent: TCB)



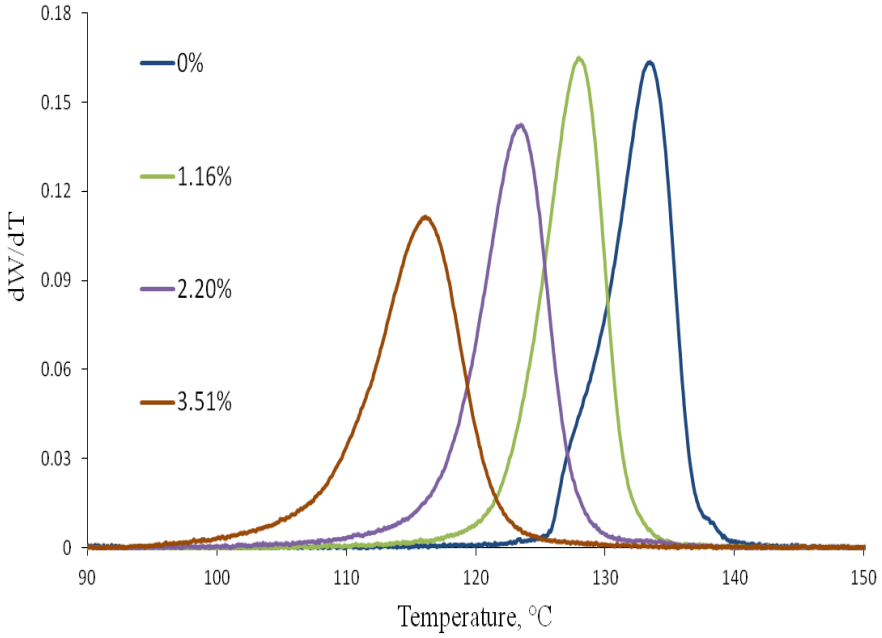
(Solvent: ODCB)



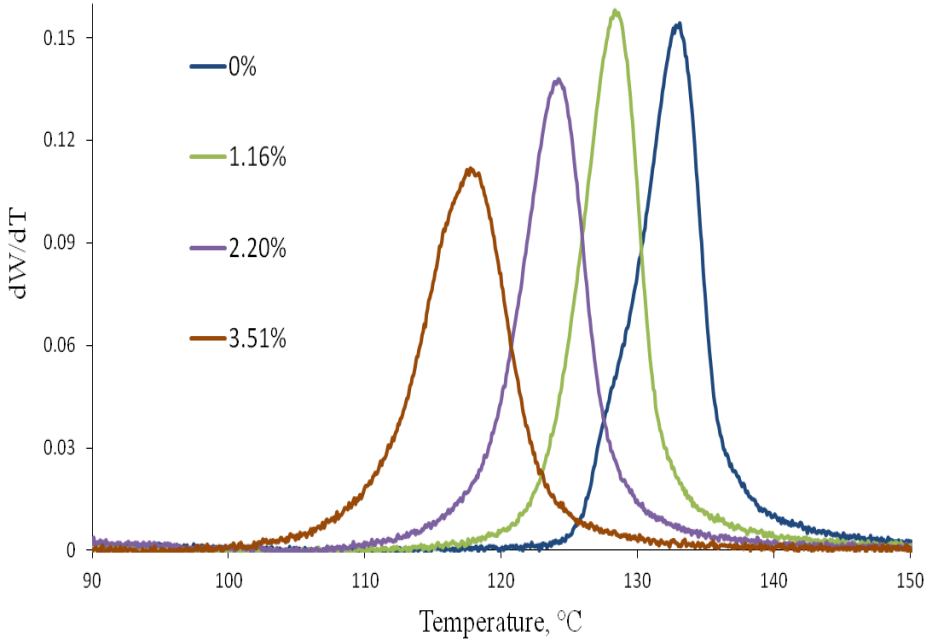
CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – IV = 100µL

HT-TGIC of Individual Samples: Effect of Solvent Type

(Solvent: TCB)



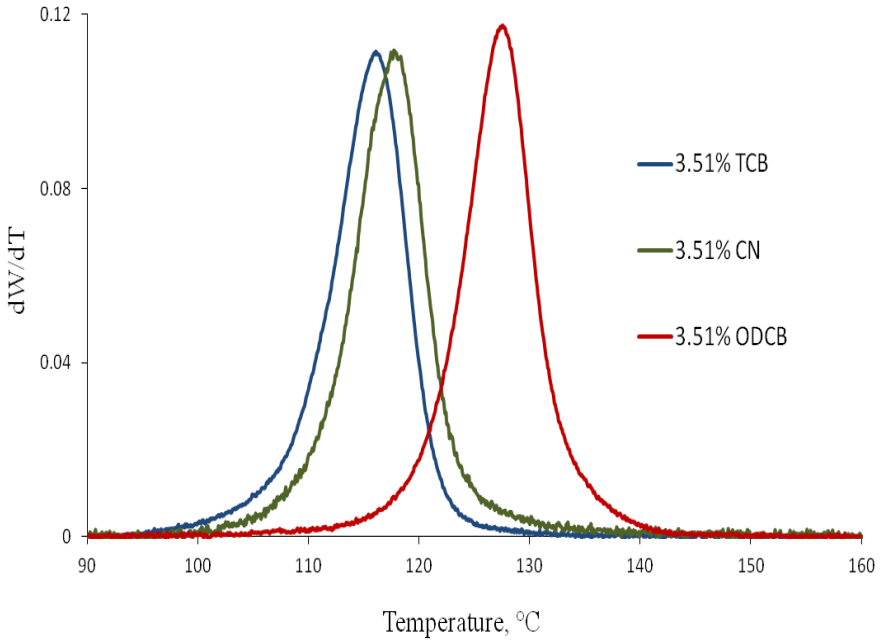
(Solvent: ODCB)



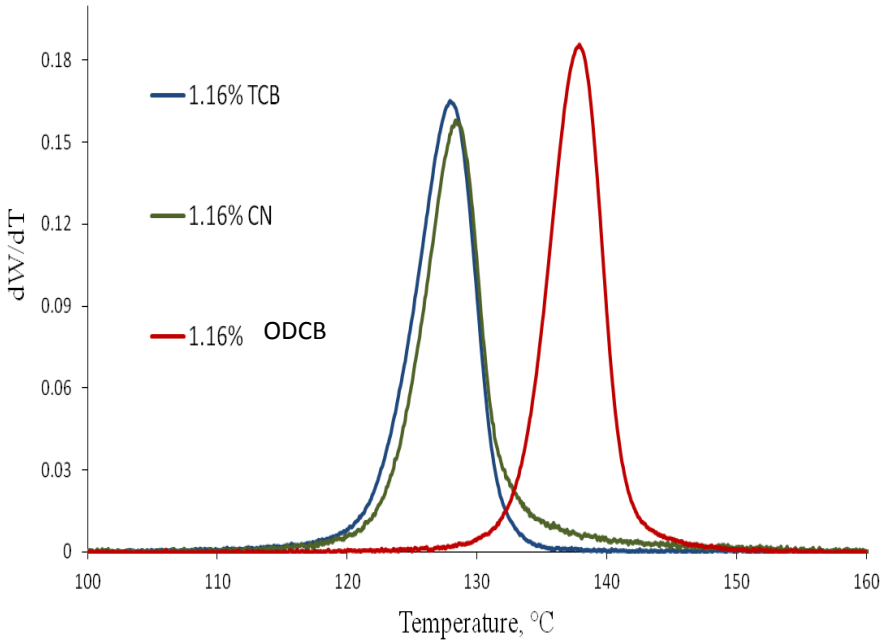
CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – IV = 100µL

HT-TGIC of Individual Samples: Effect of Solvent Type

(TCB/ CN/ ODCB : 3.51% CC sample)



(TCB/ CN/ ODCB : 1.16% CC sample)



CR = 5 °C/min – HR = 1 °C/min – Fe = 0.5 ml/min – IV = 100µL

Conclusions

- Several LLDPE samples have been analyzed by the HT-TGIC: this new technique was used to analyze the individual samples and their blends.
- The operational conditions of HT-TGIC have been studied systematically. The main objective was to study the effect of cooling rate, heating rate, sample size, and solvent type.
- The results show that cooling rate does not have a significant effect on the TGIC results of the blends, as expected since this technique does not fractionate the polyolefins according to their crystallinities.
- The results indicate that sample size, heating rate during the elution cycle, and solvent type are the most important parameters that may affect the chromatograms of polyolefins by this new technique.
- Orthodichlorobenzene (ODCB) was the best solvent for analysis of the blends in this study.
- Unlike CEF, TGIC analysis is free of cocrystallization effects, but it suffers from co-adsorption or co-elution effects. The results show that these effects can be minimized by the proper selection of sample size and solvent type.

Acknowledgments

- **The Dow Chemical Company (USA)**
- **Polymer Char (Spain)**
- **King Saud University (Riyadh, Saudi Arabia)**