Supporting Information for

Melting of Polymer NanoCrystals: A Comparison Between Experiments and Simulation

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Experimental

1. Nanoparticles synthesis procedures.

A surfactant mixture containing Tween 80 (or SDS) and hexanol was dissolved in nanopure water. The surfactant concentration was fixed at 4.8 wt%. The alkane was added to the solution which was then mixed with a homogenizer (Ultraturax, speed = 5000 rev/min).This work was repeated several times, changing nature of the organic phase ($C_{24}H_{50}$, $C_{25}H_{52}$, $C_{38}H_{78}$, $C_{58}H_{118}$), the amount of alkane and temperature of synthesis of nanoparticles. By changing these parameters, it was possible to obtain nanoparticles of different sizes for each alkane chains (see table 1, Supporting Information).

2. Characterization

2.1 DSC

Melting points were measured by modulated differential scanning calorimetry (DSC) using a Mettler Toledo DSC823e (TOPEM 15 modulation) equipped with an FRS5 sample cell, a sample robot, a Julabo FT400 intracooler and an HRS7 sensor. Samples were heated from 20 ^{o}C to 140 ^{o}C at a rate of 2 ^{o}C/min and data were analyzed using the STAR software. The amplitude of TOPEM modulation was 0.025K, using switching times 20 comprised between 15 and 30 seconds. All reported values are for samples which have been slowly cooled from the melt at a rate of 2 ^{o}C/min. This heating and cooling treatment was repeated three times. The results presented are for the second or third heating scans, which, for a given sample, were identical within experimental precision. Chains of pure alkanes were analyzed in standard aluminium cups (aluminium standard 40 µl). The colloidal solutions were analysis in sealed tank (Medium Pressure/Vitron 120µl).

2.2 High-Sensitivity Differential Scanning Calorimetry (HS-DSC) :

HS-DSC measurements were performed on a VP-DSC microcalorimeter (MicroCal Inc.) at an external pressure of ca. 25 psi. The cell volume was 0.517 mL. The heating and cooling rate was 1 °C/min. The suspensions were then filtered on 0.45 µm PVDF filter and degassed at 25 °C for 20 min. Once introduced in the instrument, the colloidal solutions were equilibrated at 20 °C for 30 minutes before initiation of the heating process. For each measurement, the sample was heated from 20 to 80 °C, maintained at 80 °C for 2 minutes and cooled to 20 °C. This heating and cooling treatment was repeated three times. The results presented are for the second or third heating scans, which, for a given sample, were identical within experimental precision. Data were corrected for instrument response time to take into account the effect of scan rate on the data collected. For each solution, the excess heat capacity curve was constructed by subtraction of water vs water scan from the sample vs water scan.

Table 1. Synthesis conditions and size of alkane nanoparticles

Entry	Type of alkane	Amount of				Temperature[d] (°C)	Particle size (nm)[e]
		Surfactant (mg)	Cosurfactant[c] (mg)	Water (g)	Alkane (mg)		
1	$C_{24}H_{50}$	380[a]	100	9.52	50	55	40
2	$C_{25}H_{52}$	380[a]	100	9.52	56	60	60
3	$C_{38}H_{78}$	80[b]	400	9.52	10	85	25
4	$C_{38}H_{78}$	80[b]	400	9.52	20	85	70
5	$C_{38}H_{78}$	420[a]	60	9.52	20	85	400
6	$C_{38}H_{78}$	480[b]	0	9.52	20	85	175
7	$C_{58}H_{118}$	480[a]	0	9.52	20	100	170

[a] The surfactant used is Tween 80.

[b] The surfactant used is SDS.

[c] The cosurfactant used in all solution is the hexanol.

[d] Temperature of the solution during the mixing.

[d] Diameter determined by DLS at 20°C.

DSC:

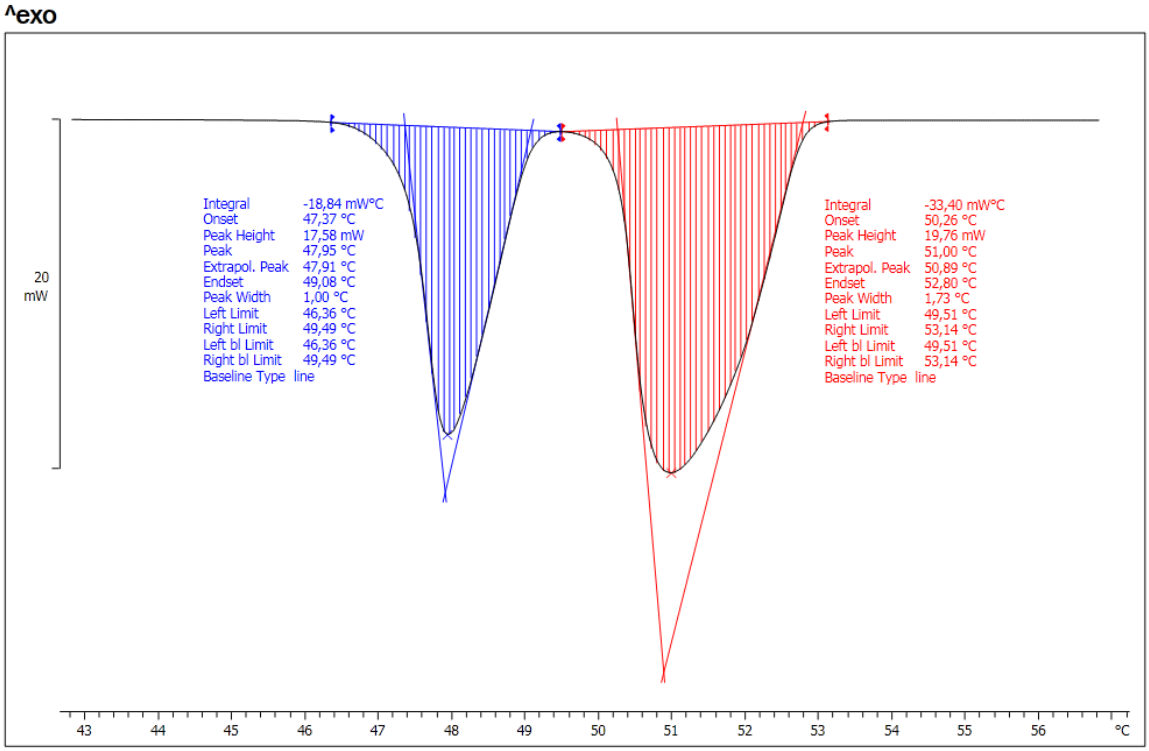

Figure 1. DSC thermogram of pure $C_{24}H_{50}$ (not nanoparticle). The first peak (blue) is a specific transition related to the presence of a rotator phase for C24 alkanes [1]. The second peak (red) is the melting point.

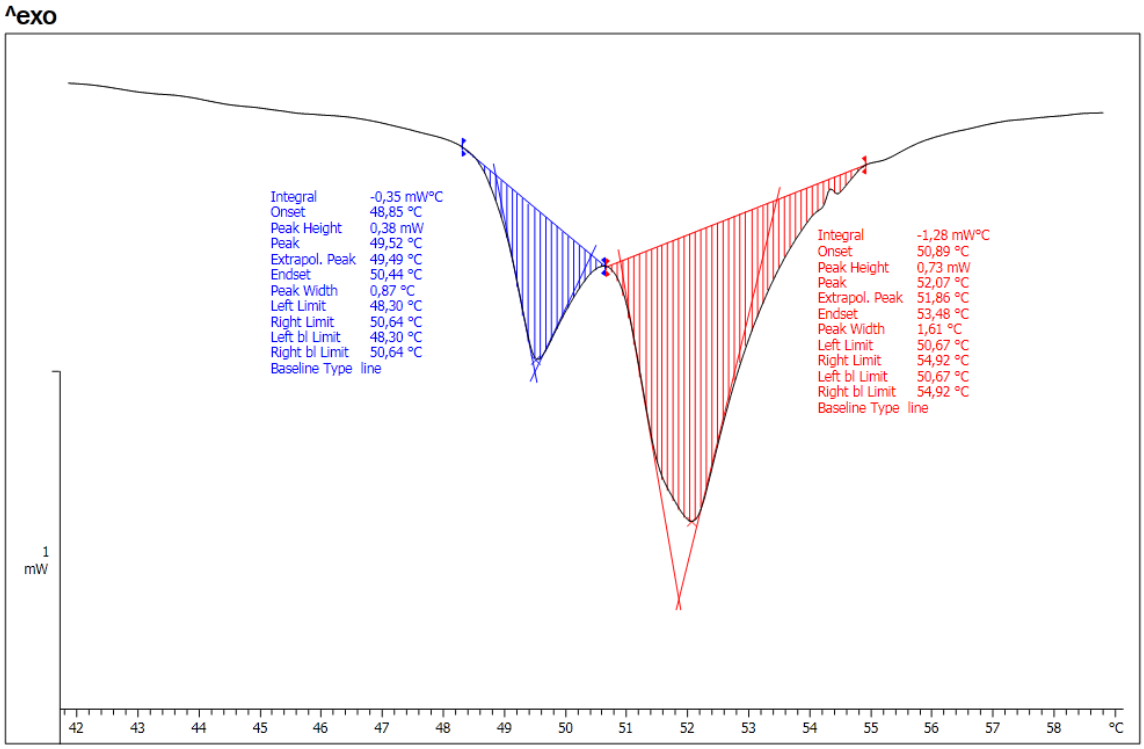

Figure 2. DSC thermogram for entry 1. See comment in Figure 1 for the presence of 2 peaks

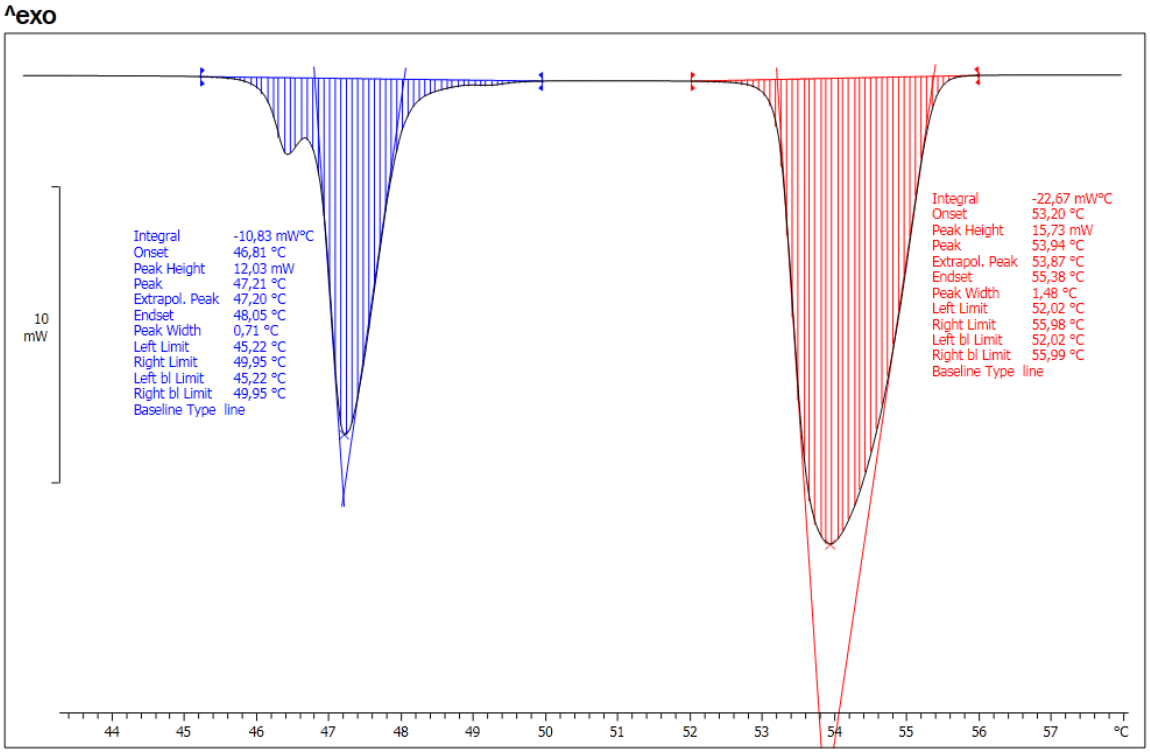

Figure 3. DSC thermogram for for $C_{25}H_{52}$ in bulk. See comment in Figure 1 for the presence of 2 peaks

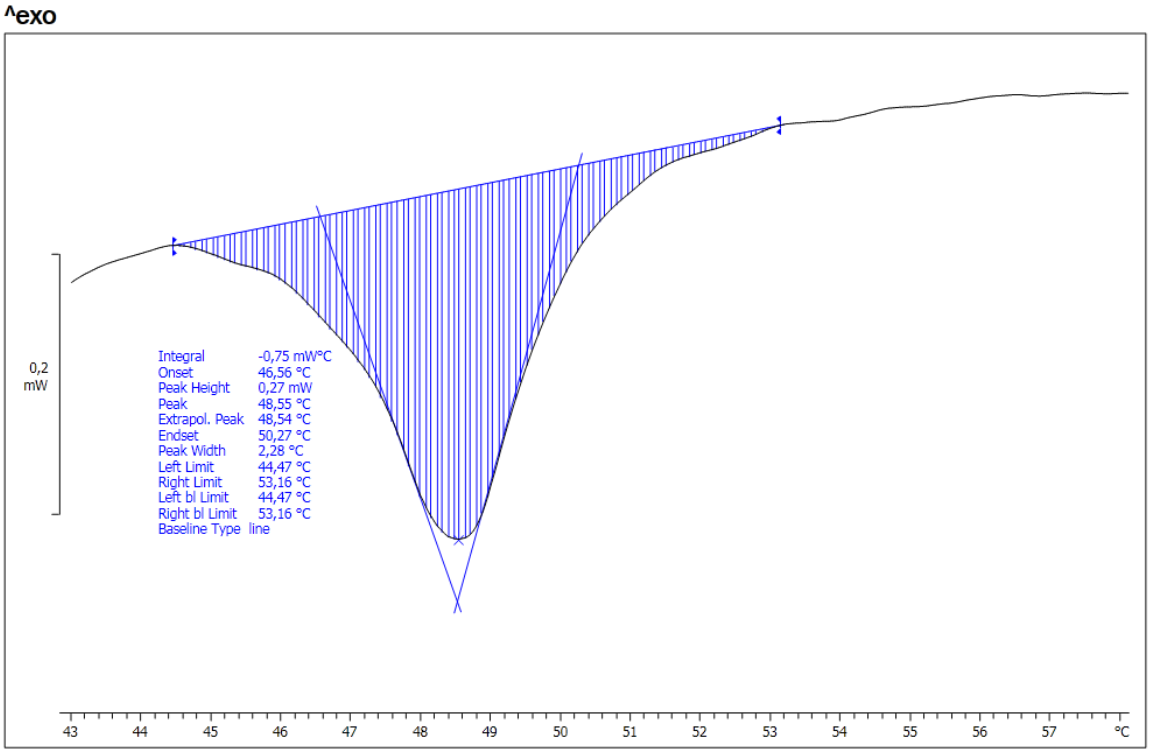

Figure 4. DSC thermogram for entry 2.

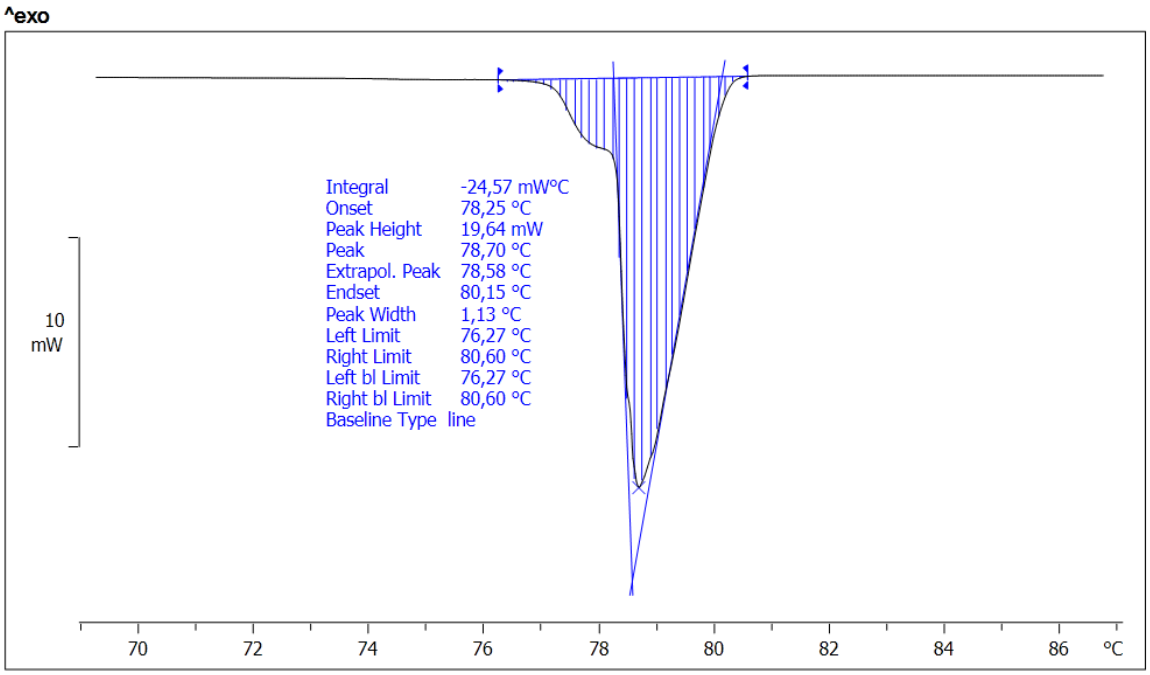

Figure 5. DSC thermogram for pure $C_{38}H_{78}$ in bulk (not nanoparticle).

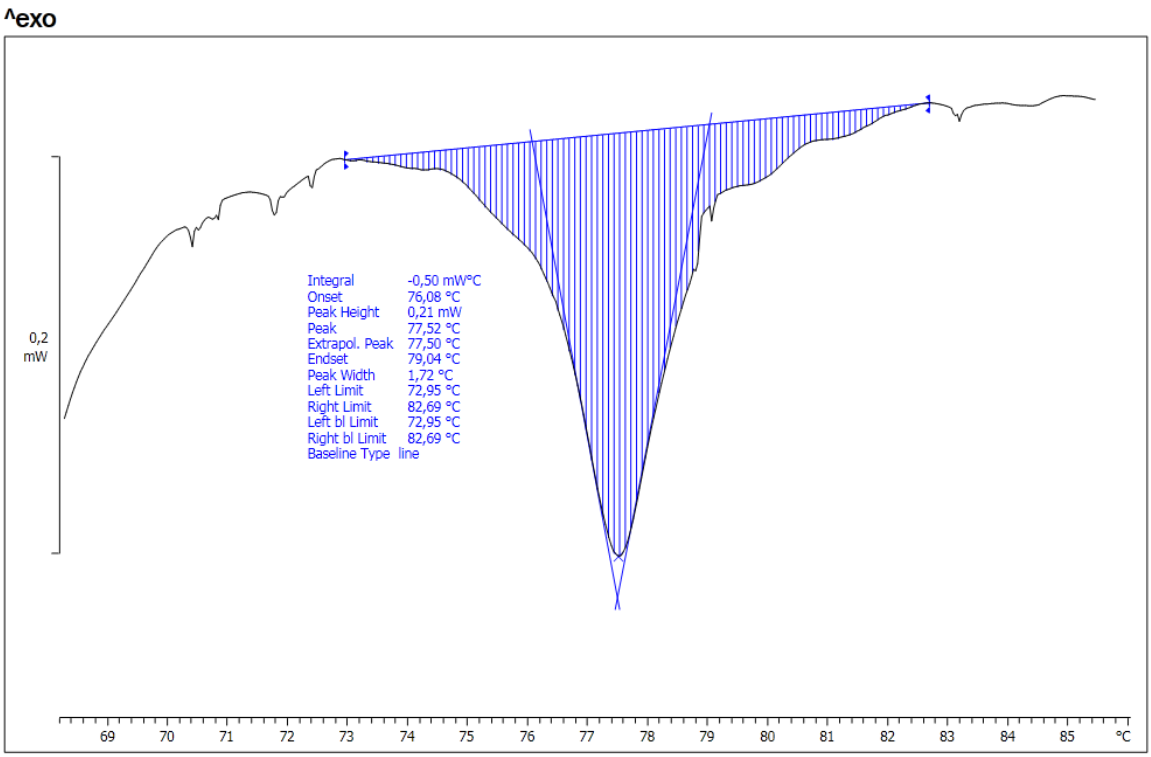

Figure 6. DSC thermogram for entry 3.

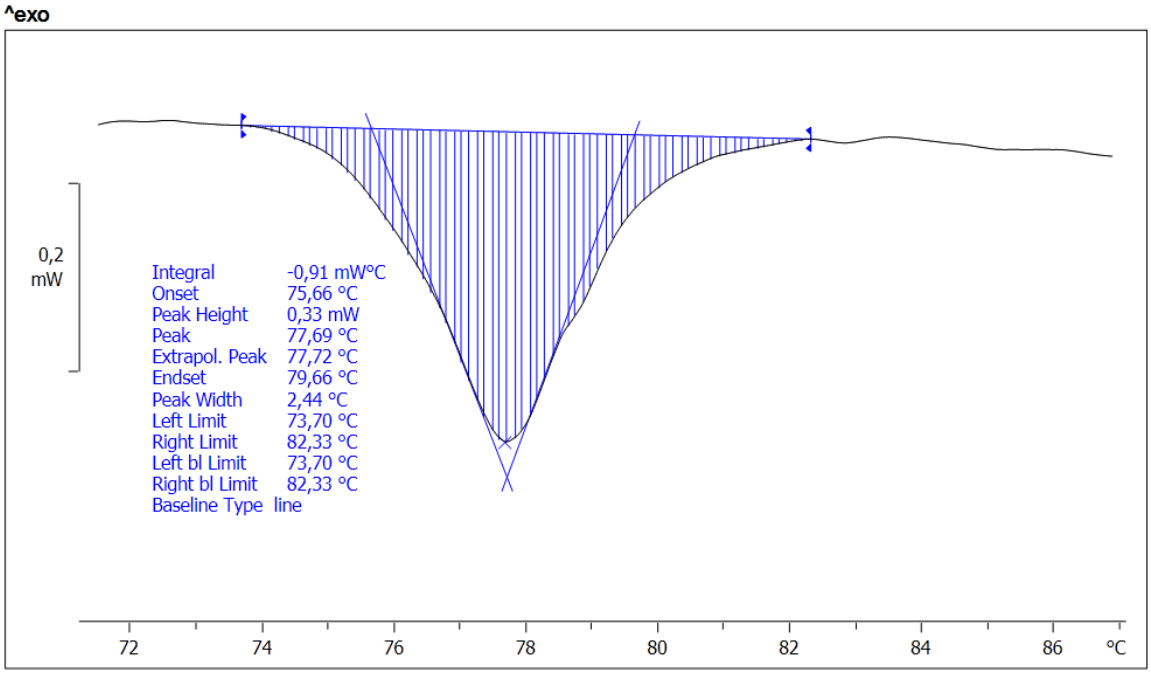

Figure 7. DSC thermogram for entry 4.

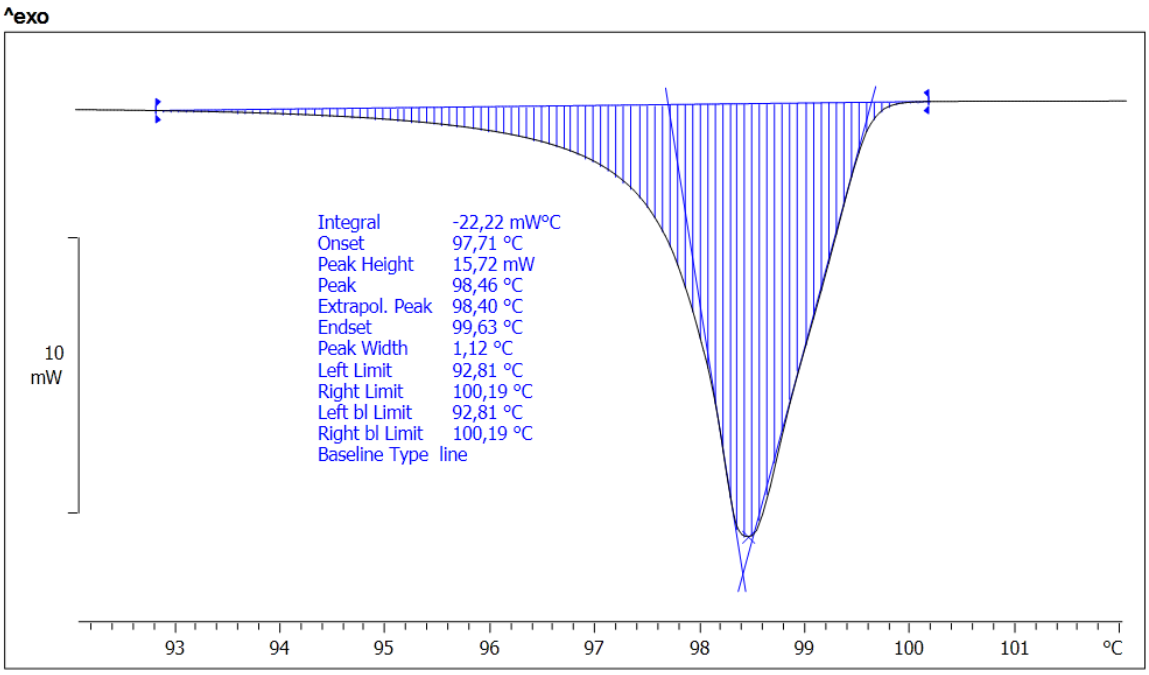

Figure 8. DSC thermogram for $C_{58}H_{118}$ in bulk.

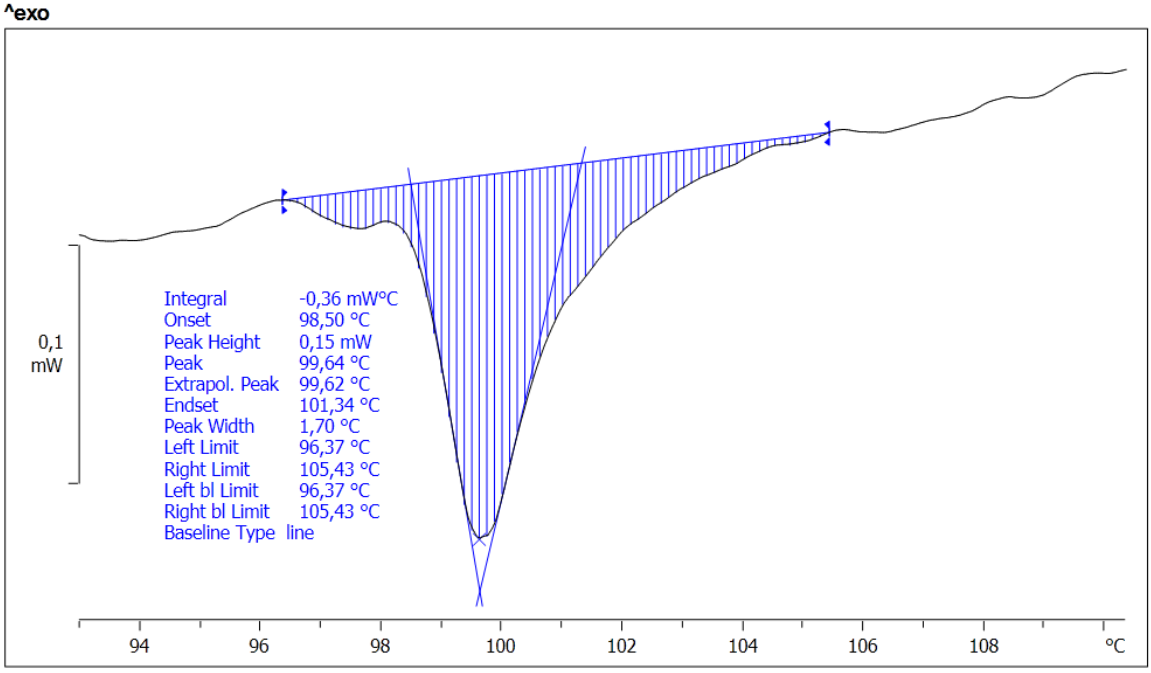

Figure 9. DSC thermogram for entry 7.

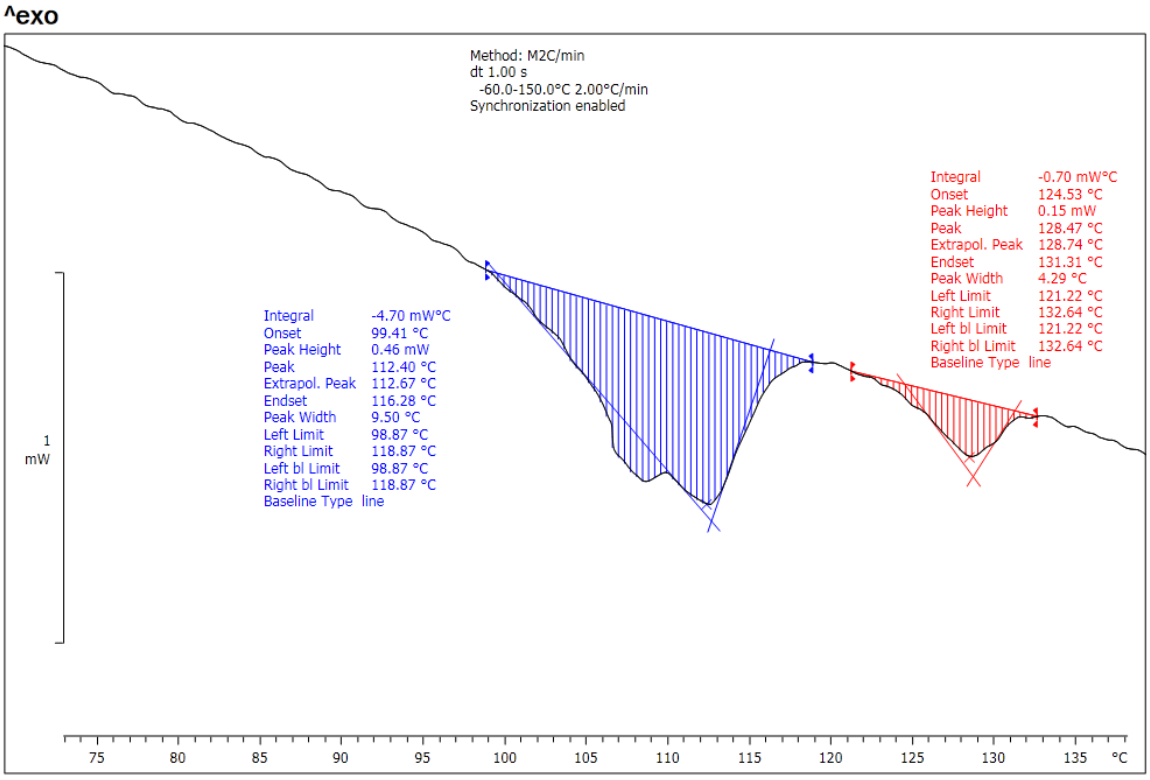

Figure 10. DSC thermogram e for a random copolymer of ethylene/*tert*butylacrylate with 2.4% of TBA.

HS-DSC :

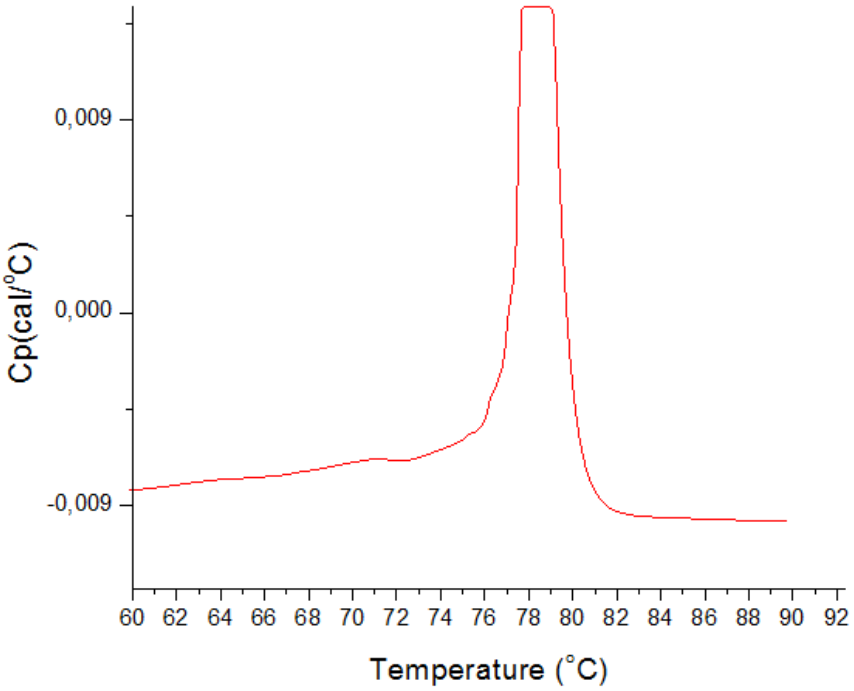

Figure 11. DSC thermogram for entry 5.

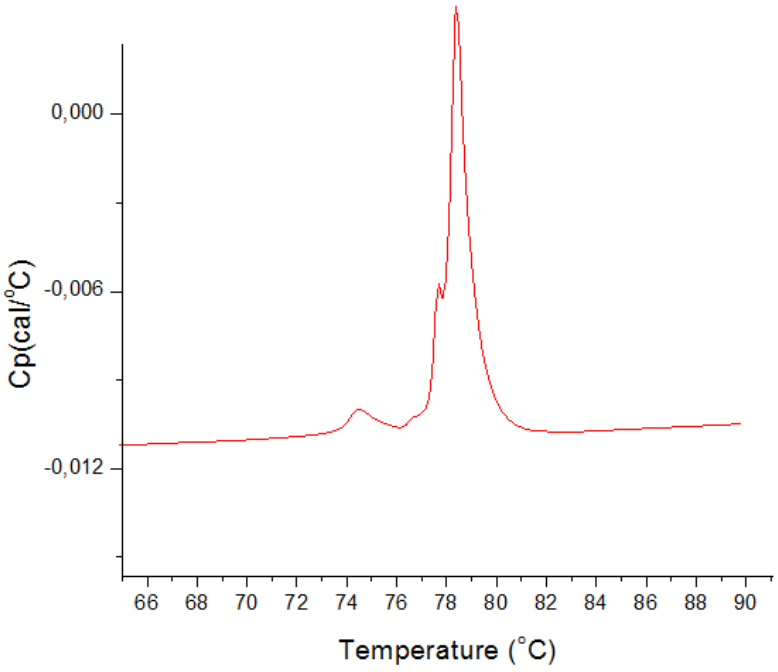

Figure 12. DSC thermogram for entry 6.

References :

[1] Montenegro R., Landfester K., Langmuir, **2003**, 19 (15), 5996-6003