Effect of SSS and SOS on crystallisation in model fat blends

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Introduction

- Drive to reduce *trans* fats in the diet
  - *Trans* required to supply solid fat
  - Alternative is saturated
- Challenge to retain functionality without compromising on saturated fat levels
- Need to optimise triglyceride composition
  - E.g. SOS has $^{2}/_{3}$ the saturates of SSS yet both provide similar solid at room temperature

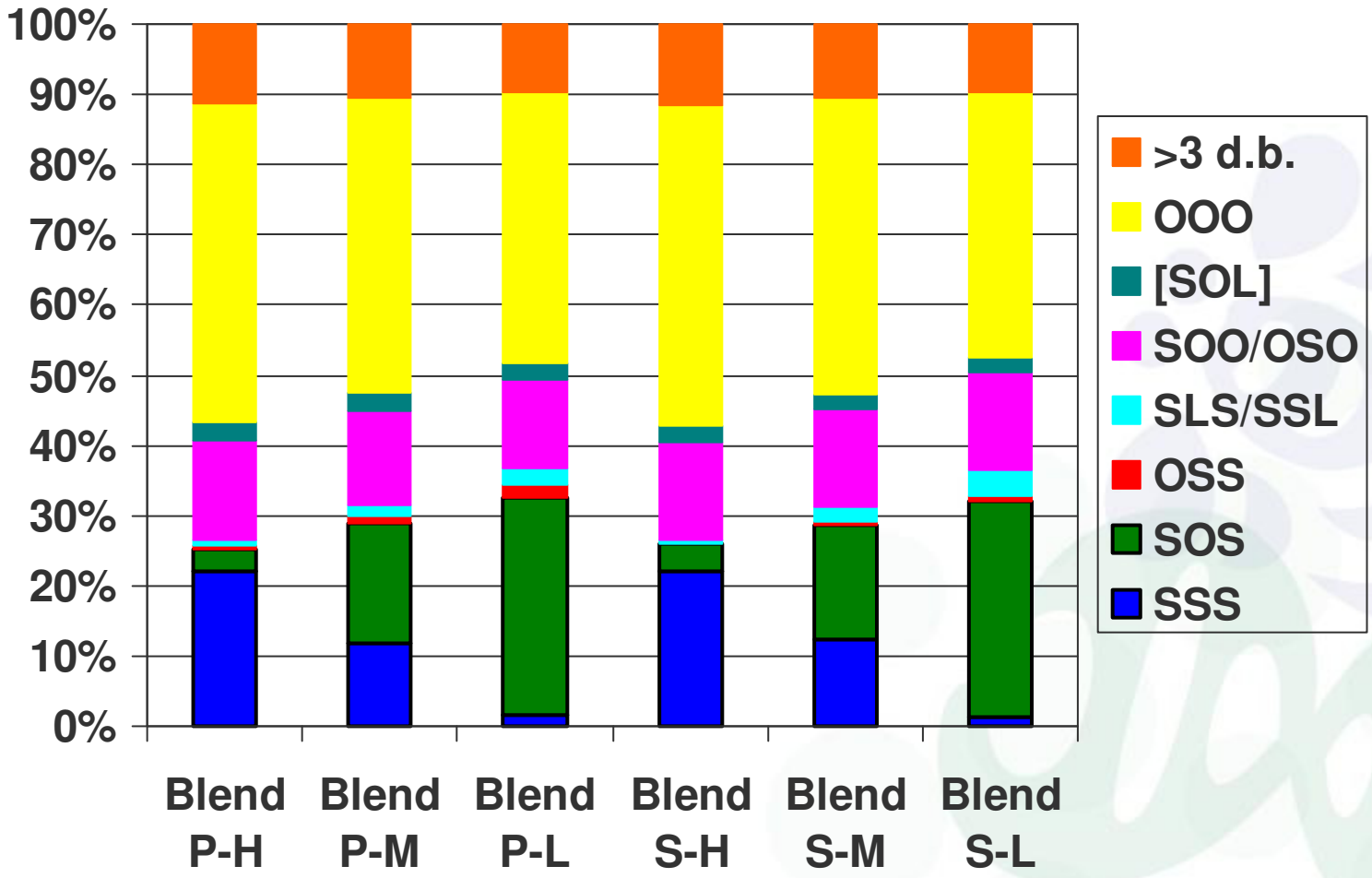
Approach

- Blends formulated to compare effect of:
  - SSS and SOS level
  - Saturate type: Stearic (C18) or Palmitic (C16)
  - At constant overall saturated fat level – 30%

- Blend components:
  - Palm stearin PPP
  - Palm mid fraction POP
  - Fully hydrogenated soybean oil StStSt
  - Shea stearin StOSt
  - High oleic sunflower oil OOO

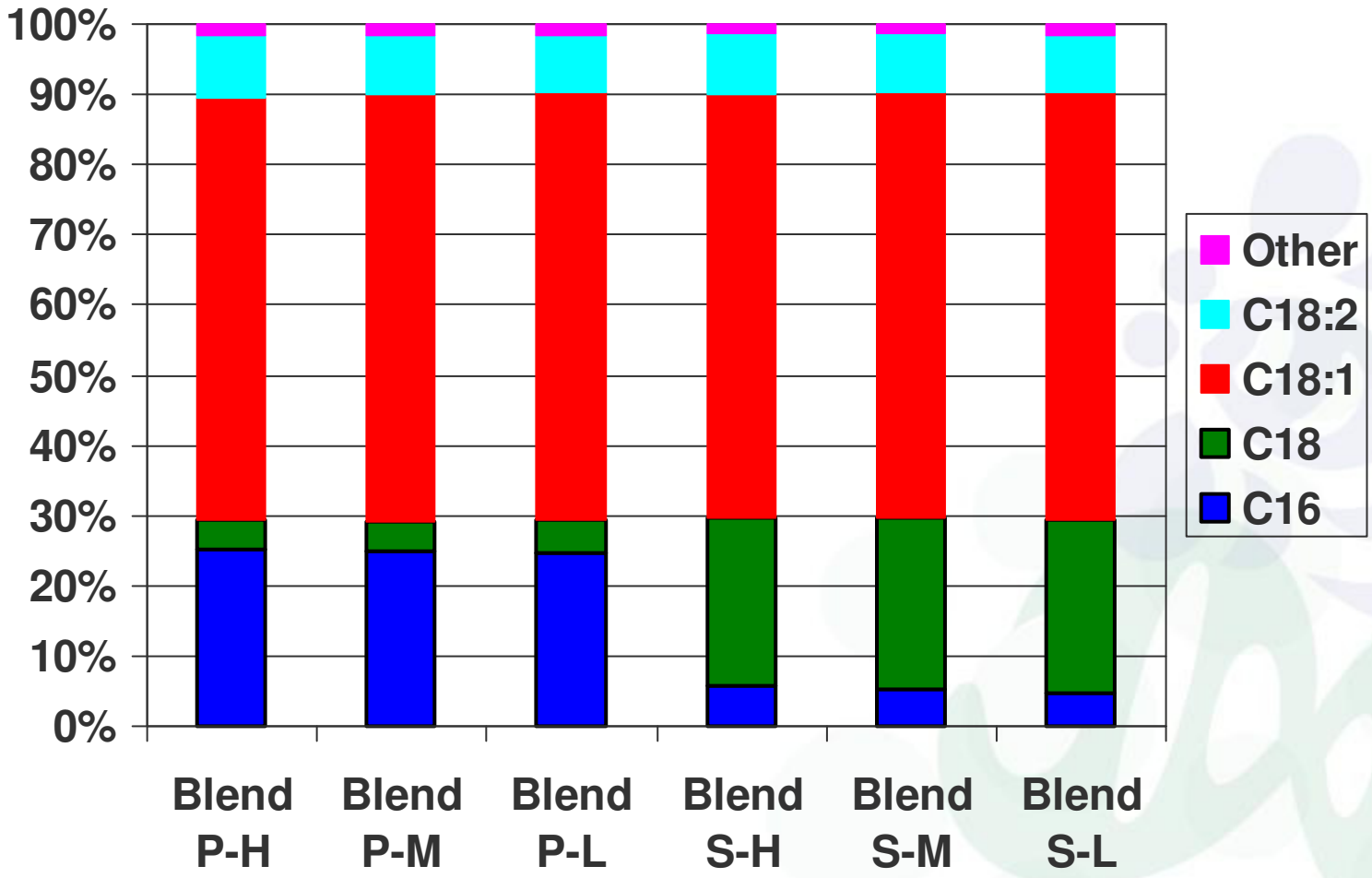
S = saturated, O = oleic, P = palmitic, St = stearic

Triglyceride Composition



S = saturated, O = oleic, L = linoleic

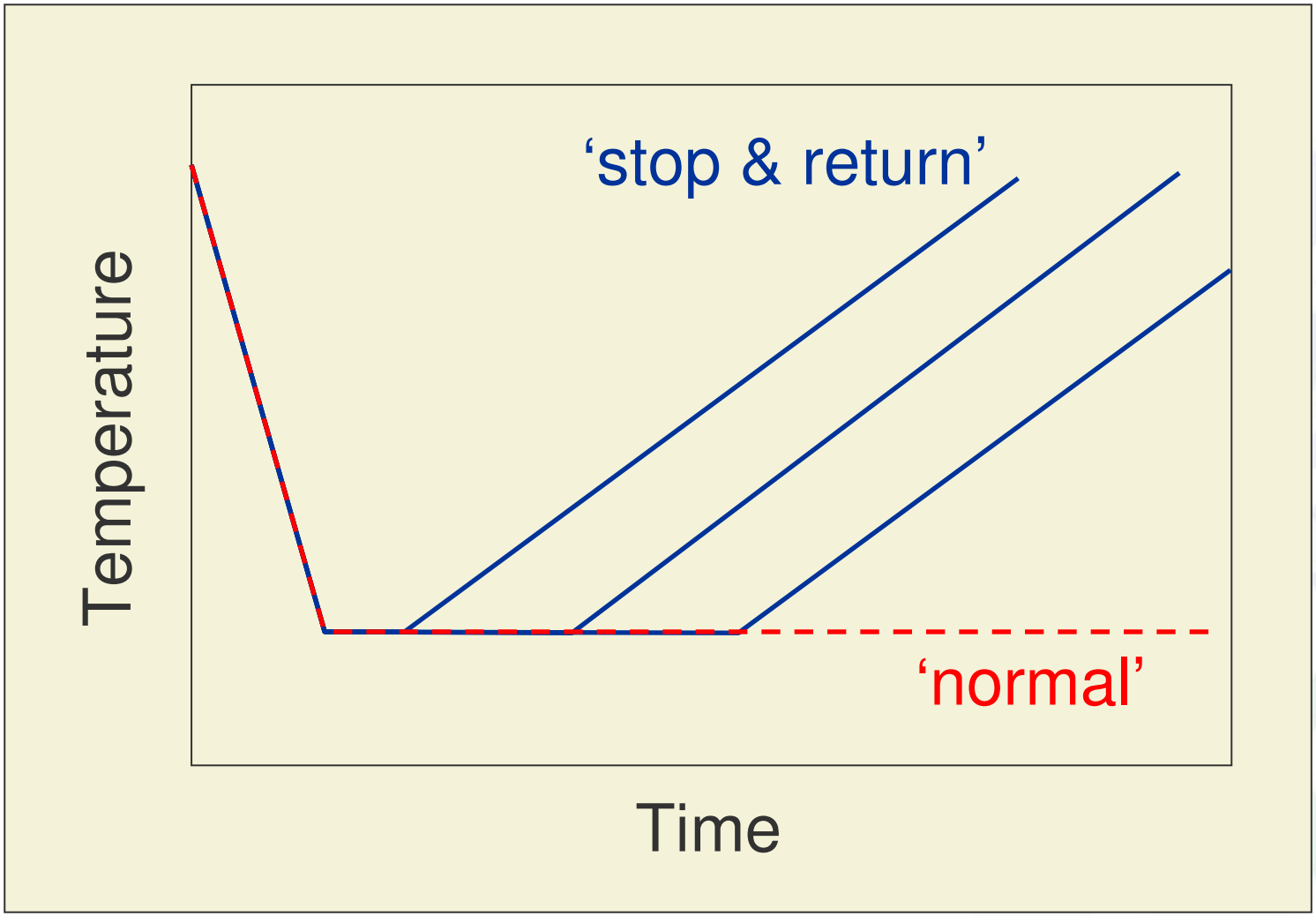
Fatty Acid Composition



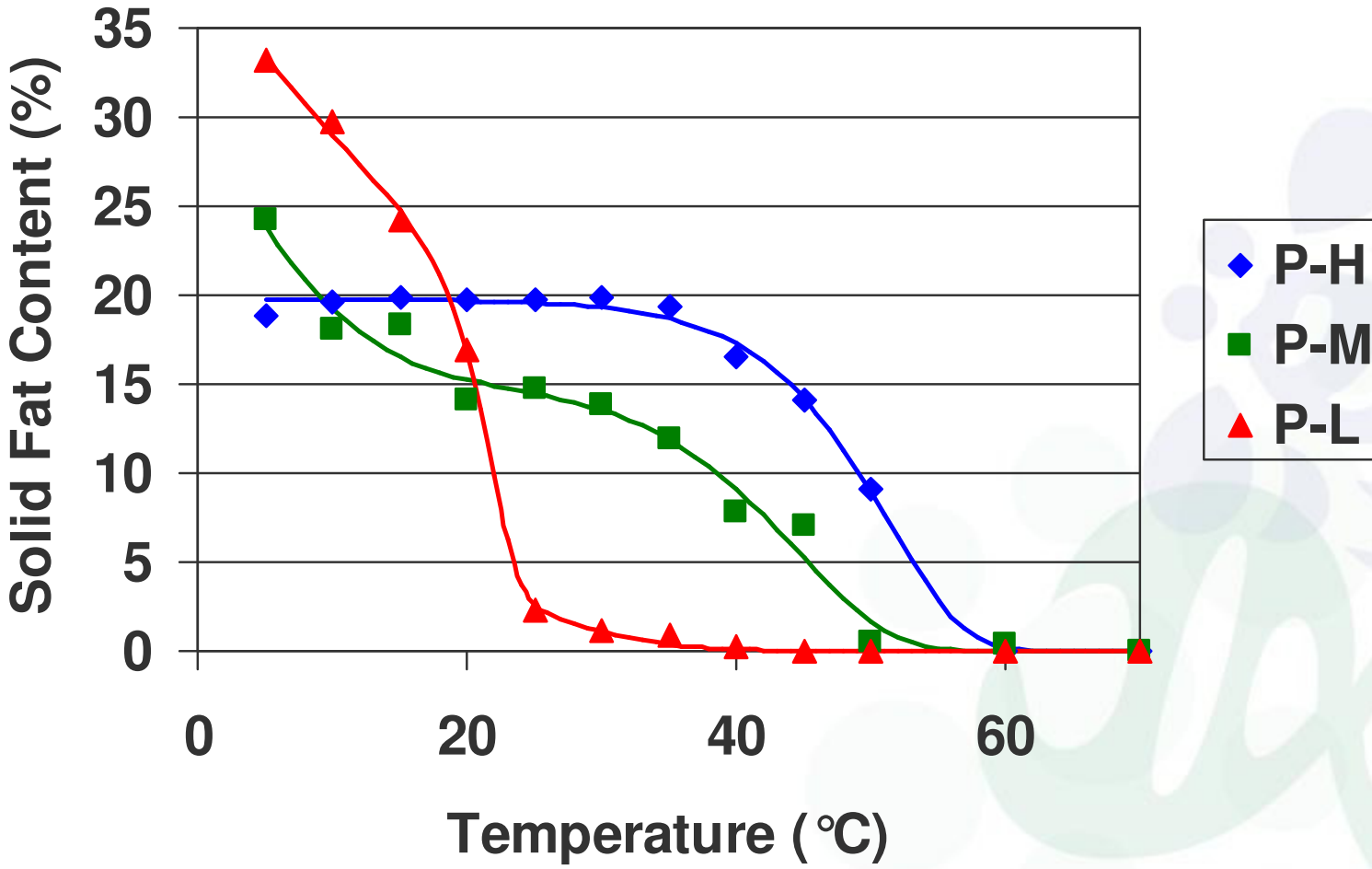
Measurements

- Solid Fat Content by pNMR
  - Serially tempered (IUAC 2.150)
- Isothermal crystallisation by DSC at 15°C & 20°C
  - ‘normal’
  - ‘stop-and-return’
- Crystal structure/morphology by light microscopy at 15°C and 20°C

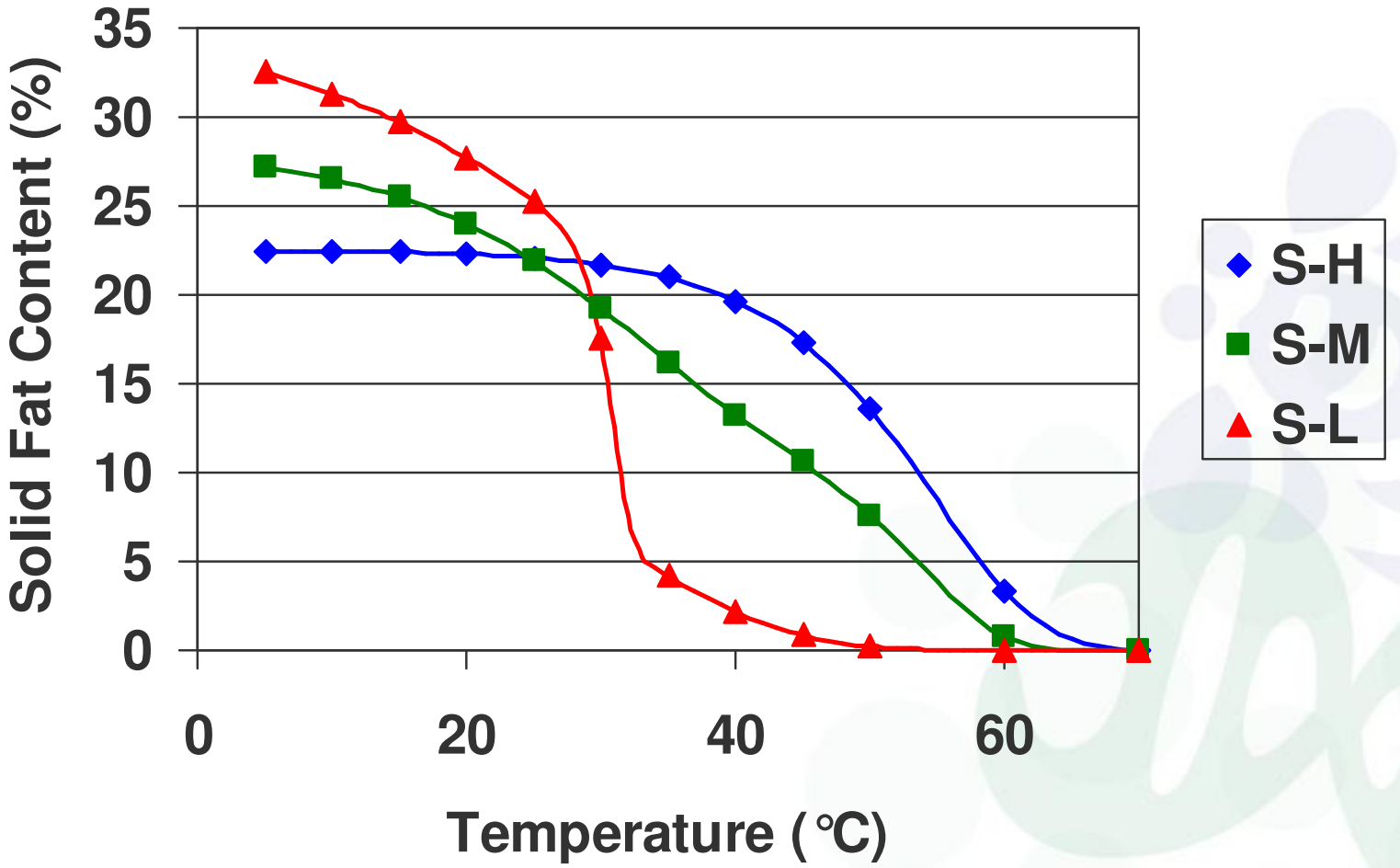
Isothermal DSC Normal vs Stop & Return



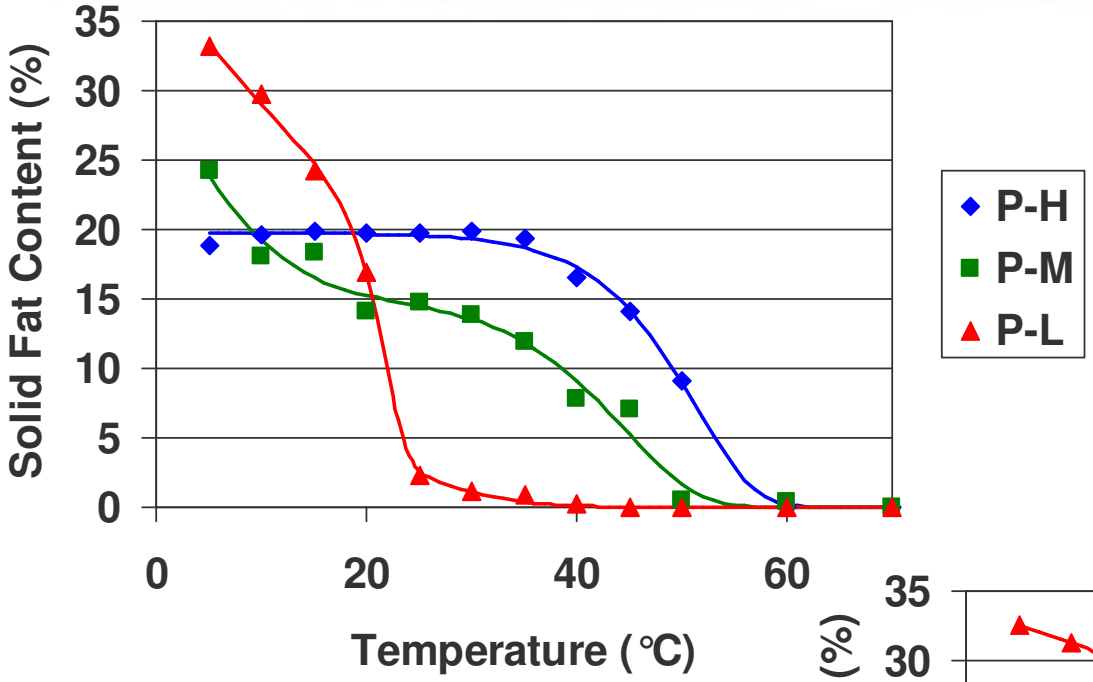
Effect of PPP/POP on SFC

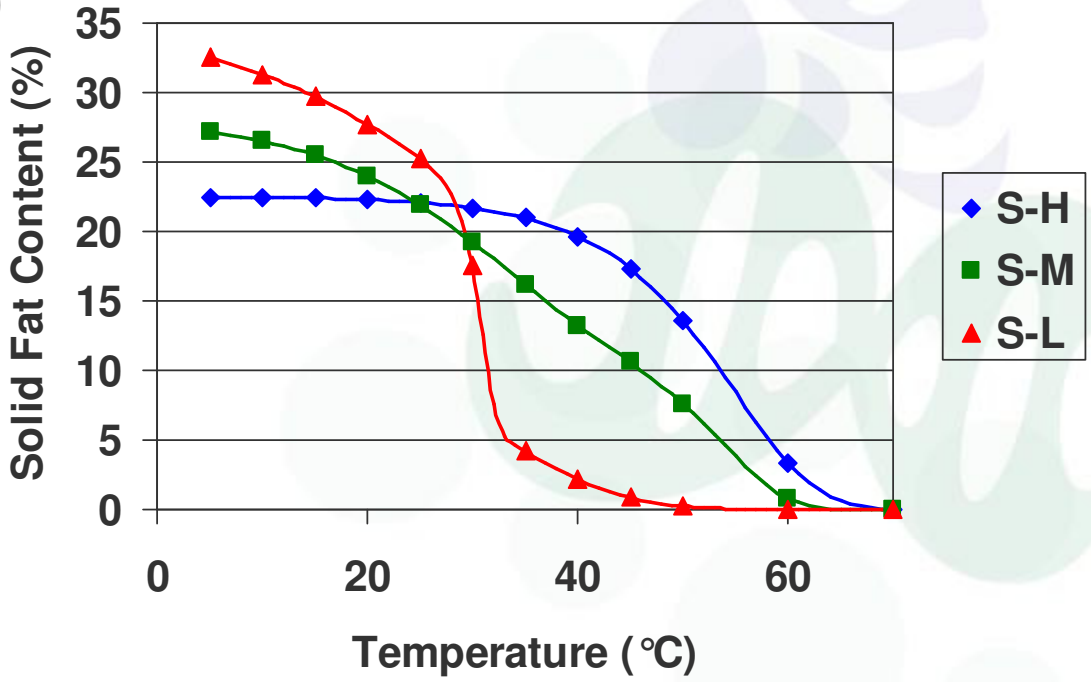


Effect of StStSt/StOSt on SFC



Comparison of P with St by SFC





Solid Fat Content

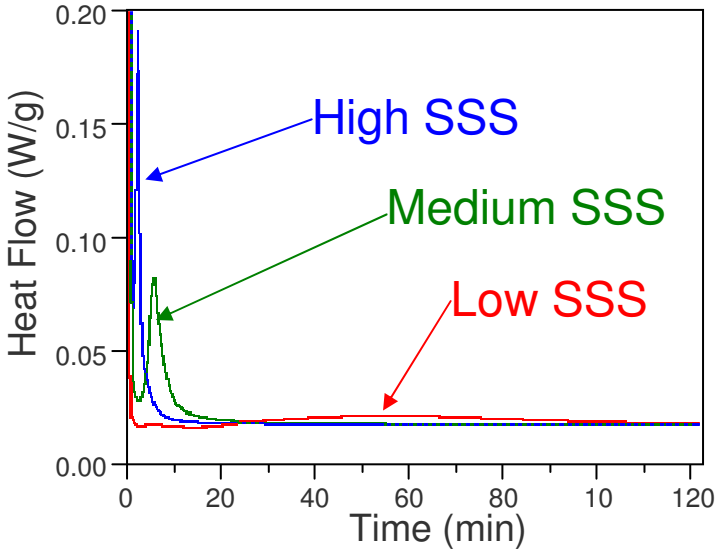
- SSS gives rise to higher SFC at high T but lower at low T
  - SSS provides solid at high T
  - Both SSS & SOS provide solid at low T
  - For same saturated fat, 1% SSS can be replaced with 1.5% SOS
- Final melting point increases with SSS
- “Cross-over” point is higher for St blends than for P
  - St TAG have higher melting points than P TAG
- Overall, SFC slightly higher for St blends
  - Lower solubility of St TAG in liquid oil compared to P TAG

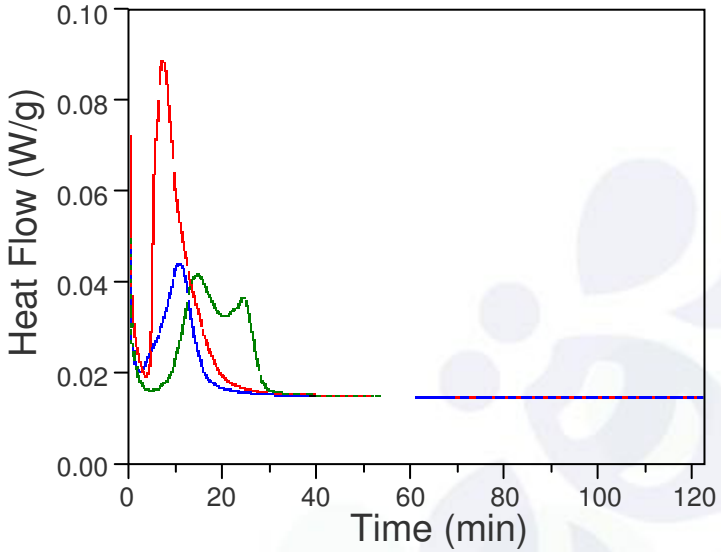
Isothermal DSC

Palmitic Blends

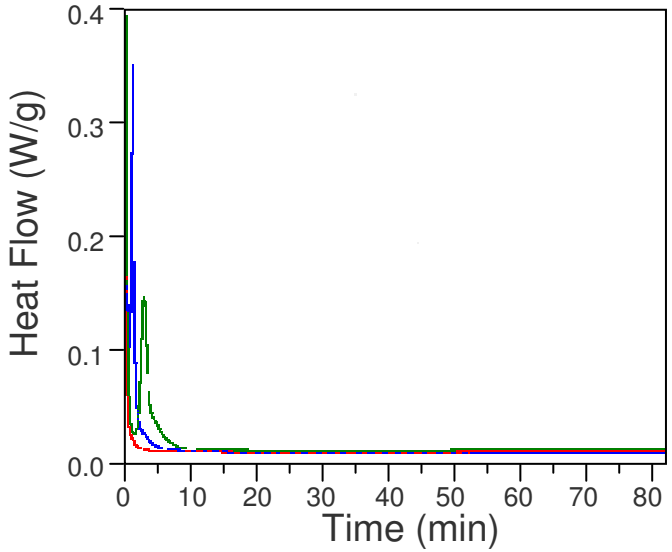
Stearic Blends

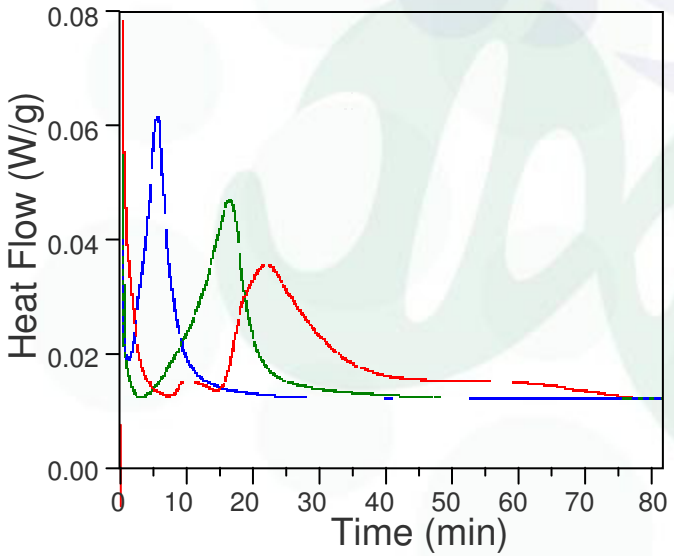
15℃



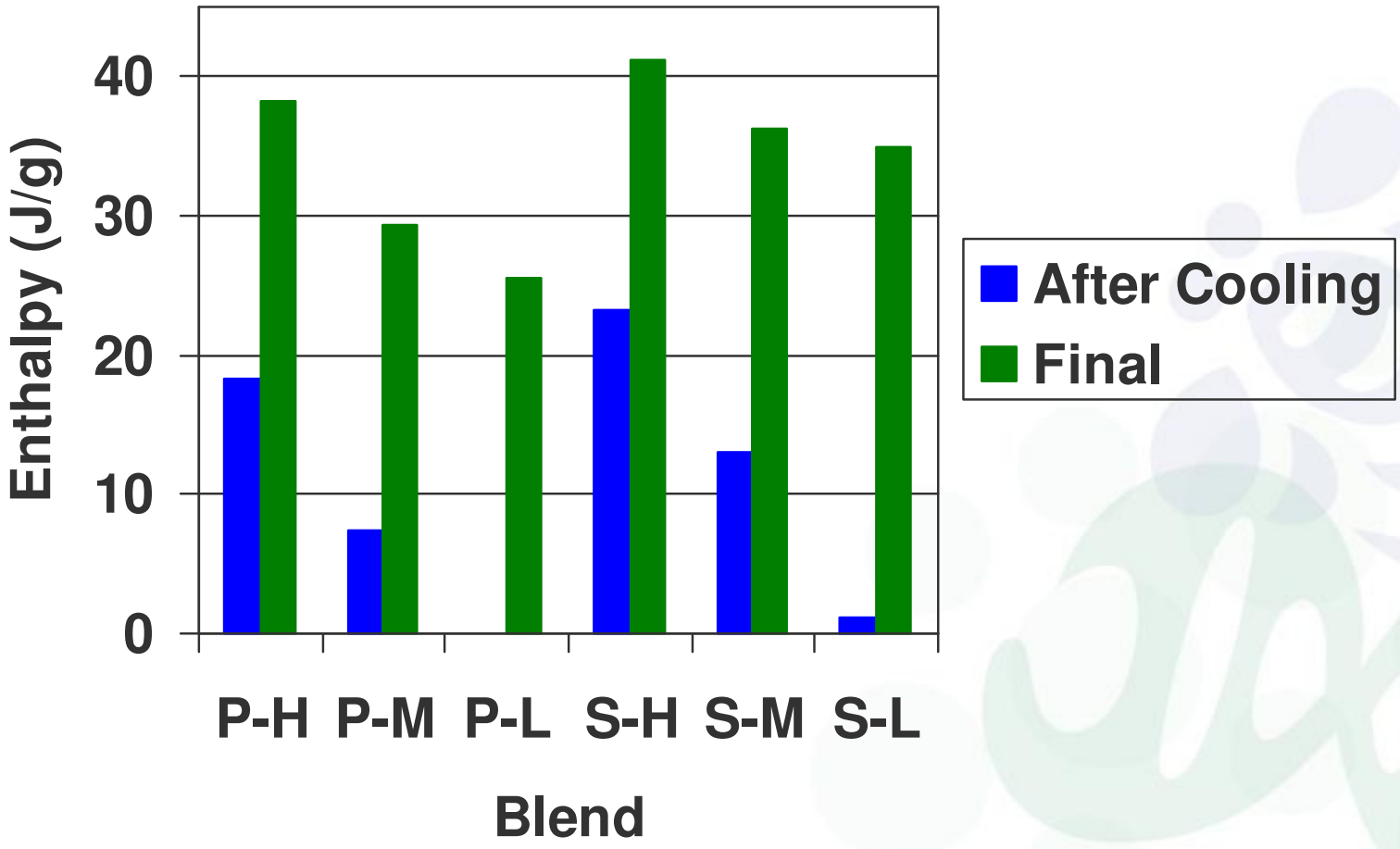


20℃

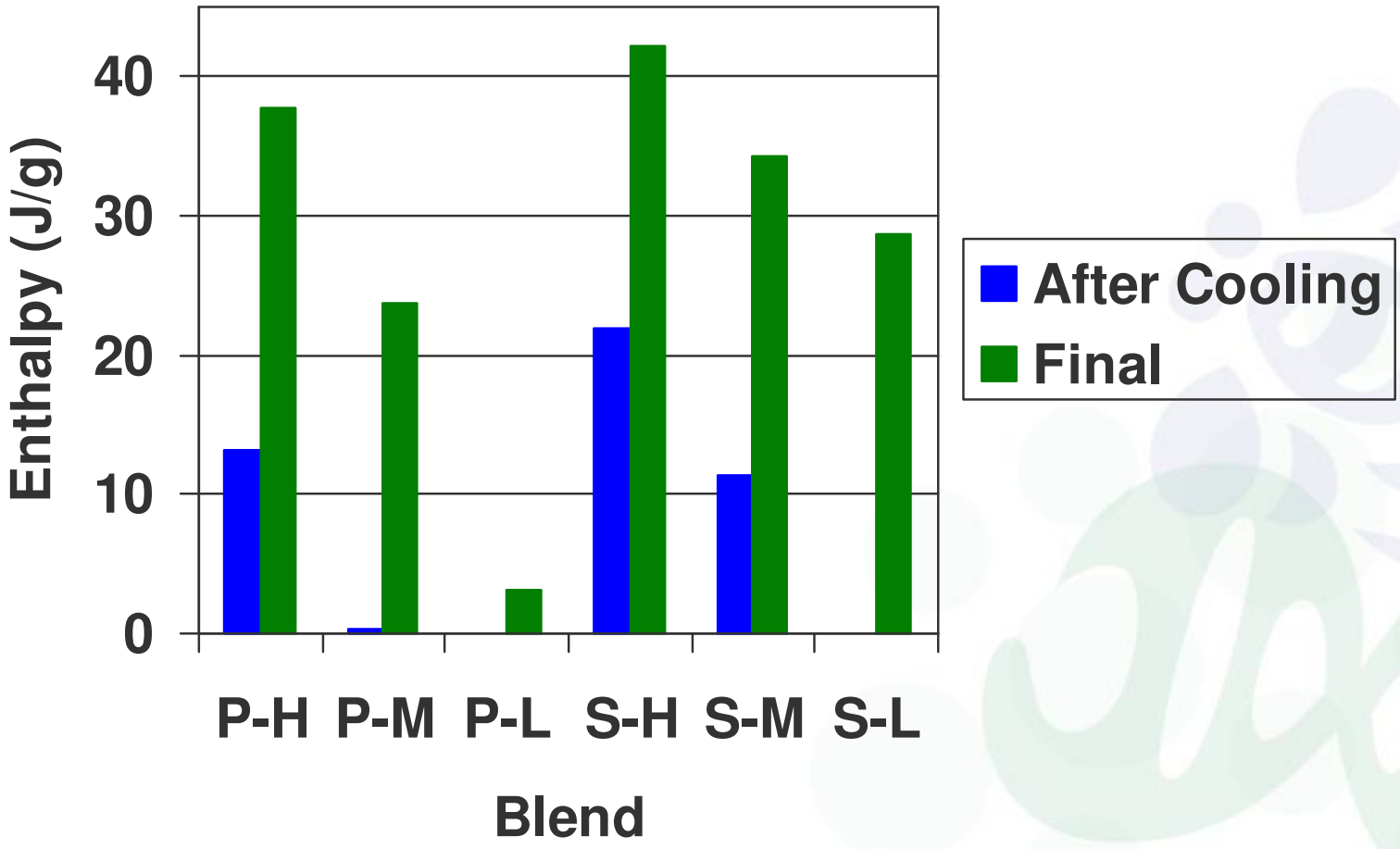




Peak areas at 15°C



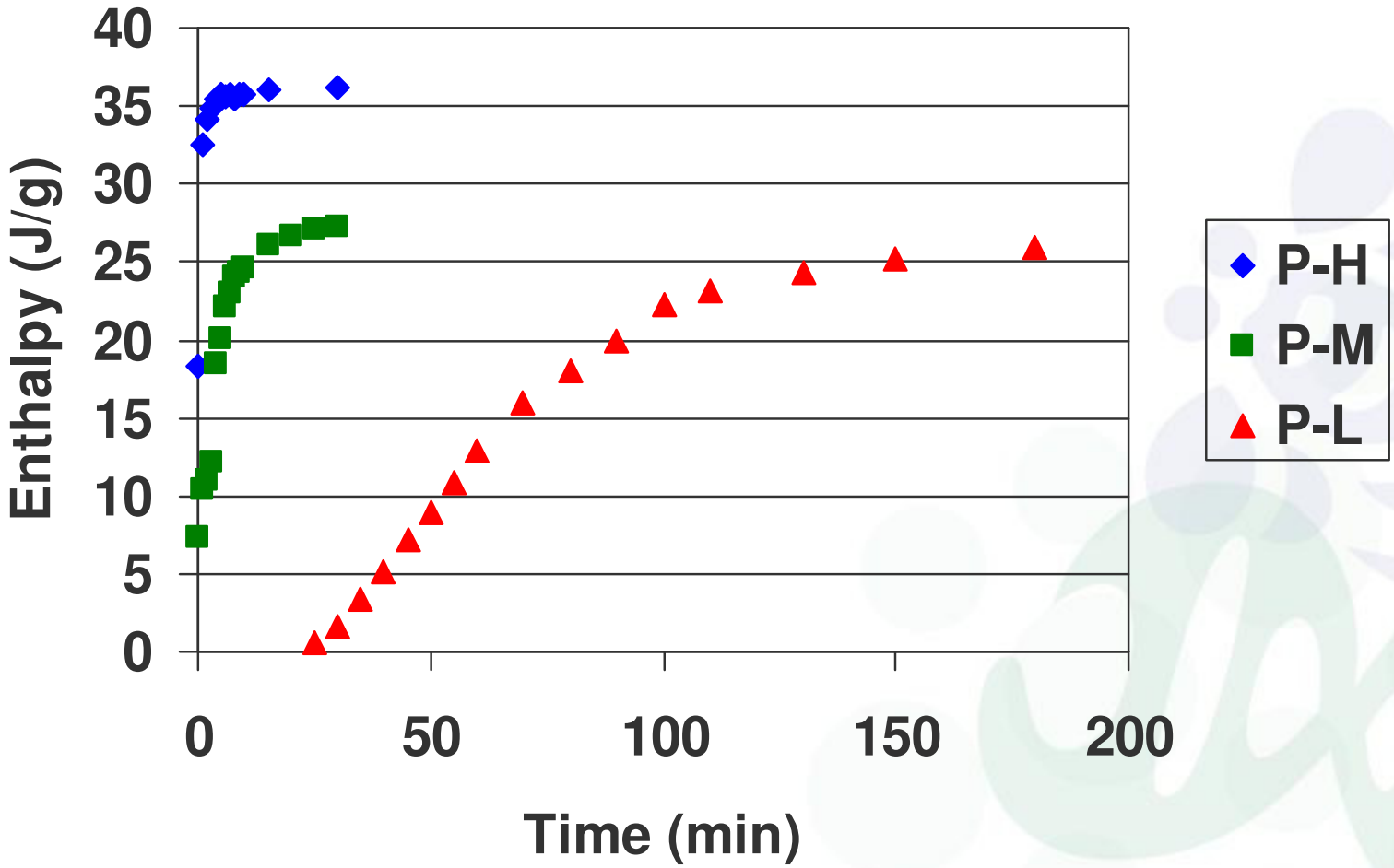
Peak areas at 20°C



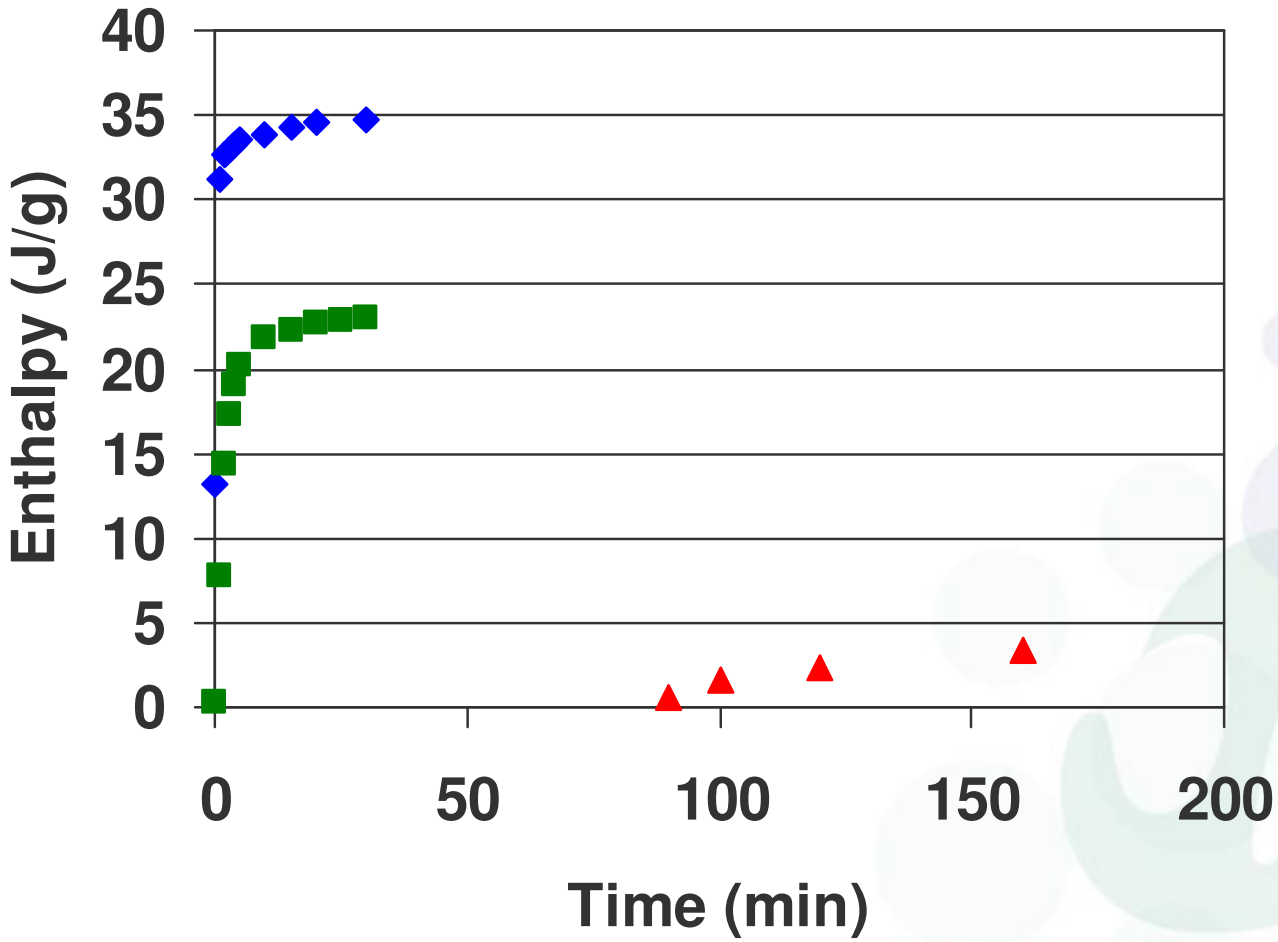
Isothermal DSC

- SSS acts as a seeding agent for SOS crystallisation
  - PPP more effective than StStSt
  - P blends crystallised faster than St blends
    - Despite lower undercooling
- P blends behave similarly at 15℃ & 20℃
  - Higher PPP leads to faster crystallisation
- St blends show differences between 15℃ & 20℃
  - Similar behaviour to P at 20℃
  - S-L fastest and S-M slowest at 15℃
- Evident that crystallisation begins before reaching isothermal temperature

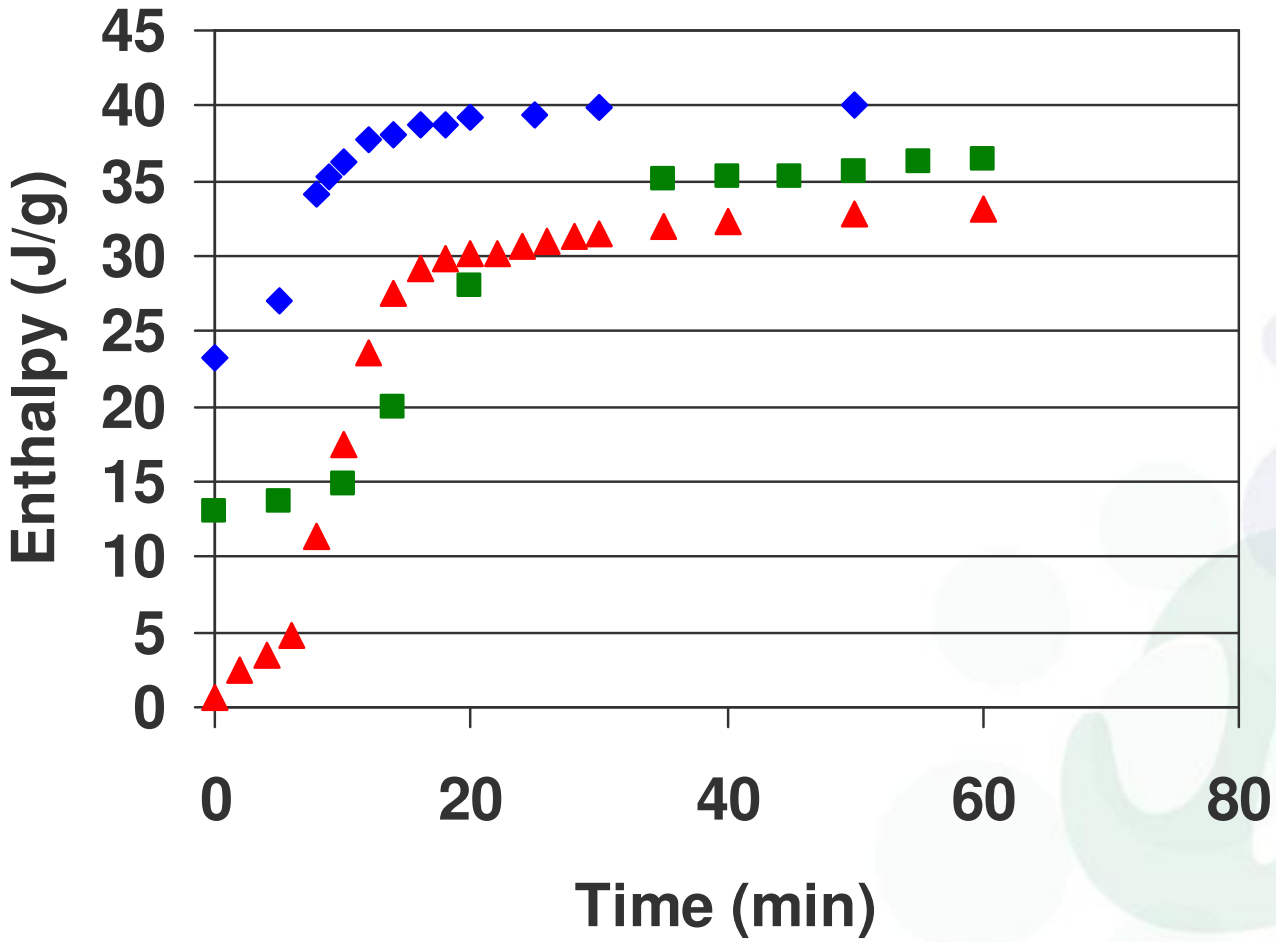
PPP/POP by S&R at 15℃



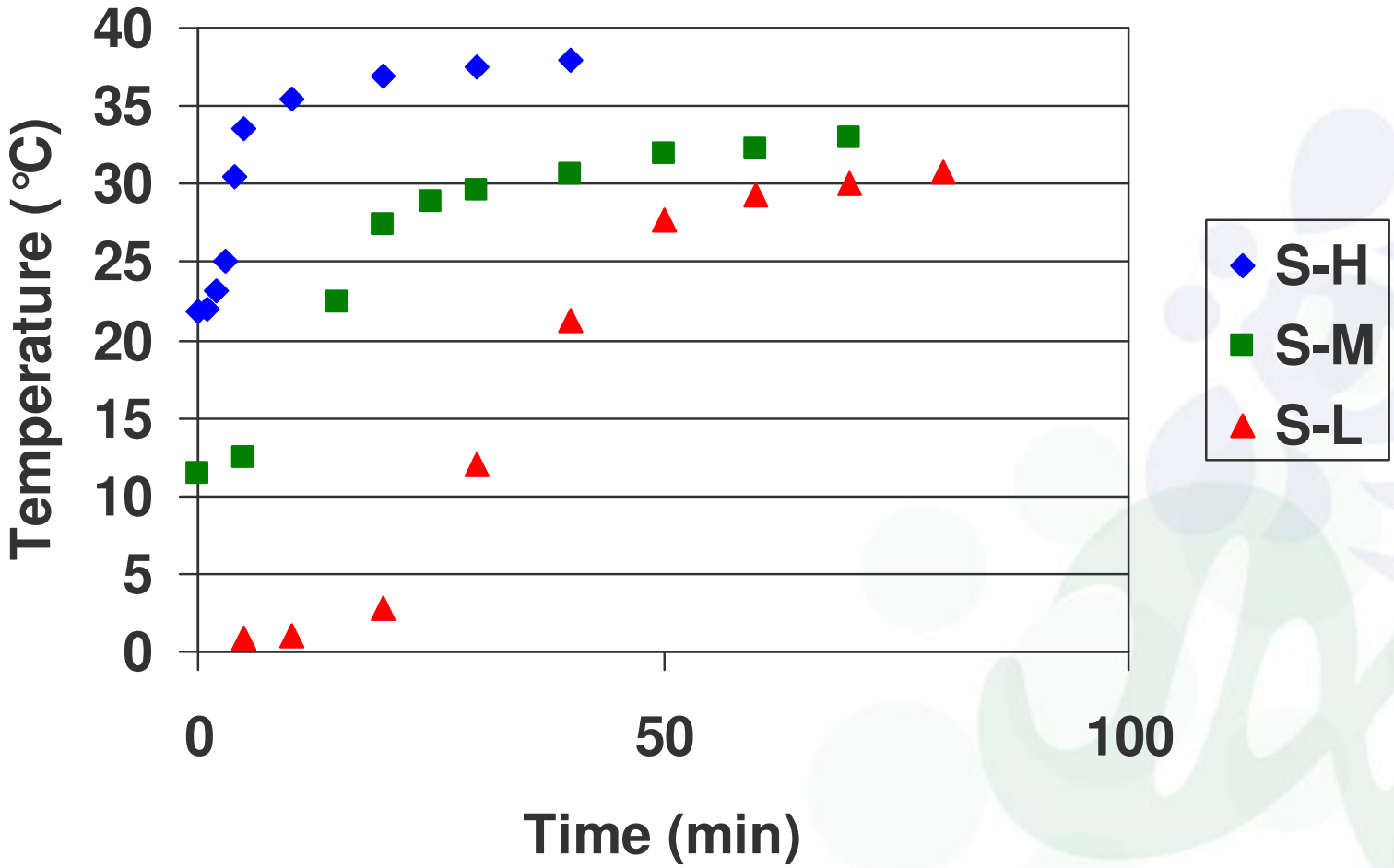
PPP/POP by S&R at 20℃



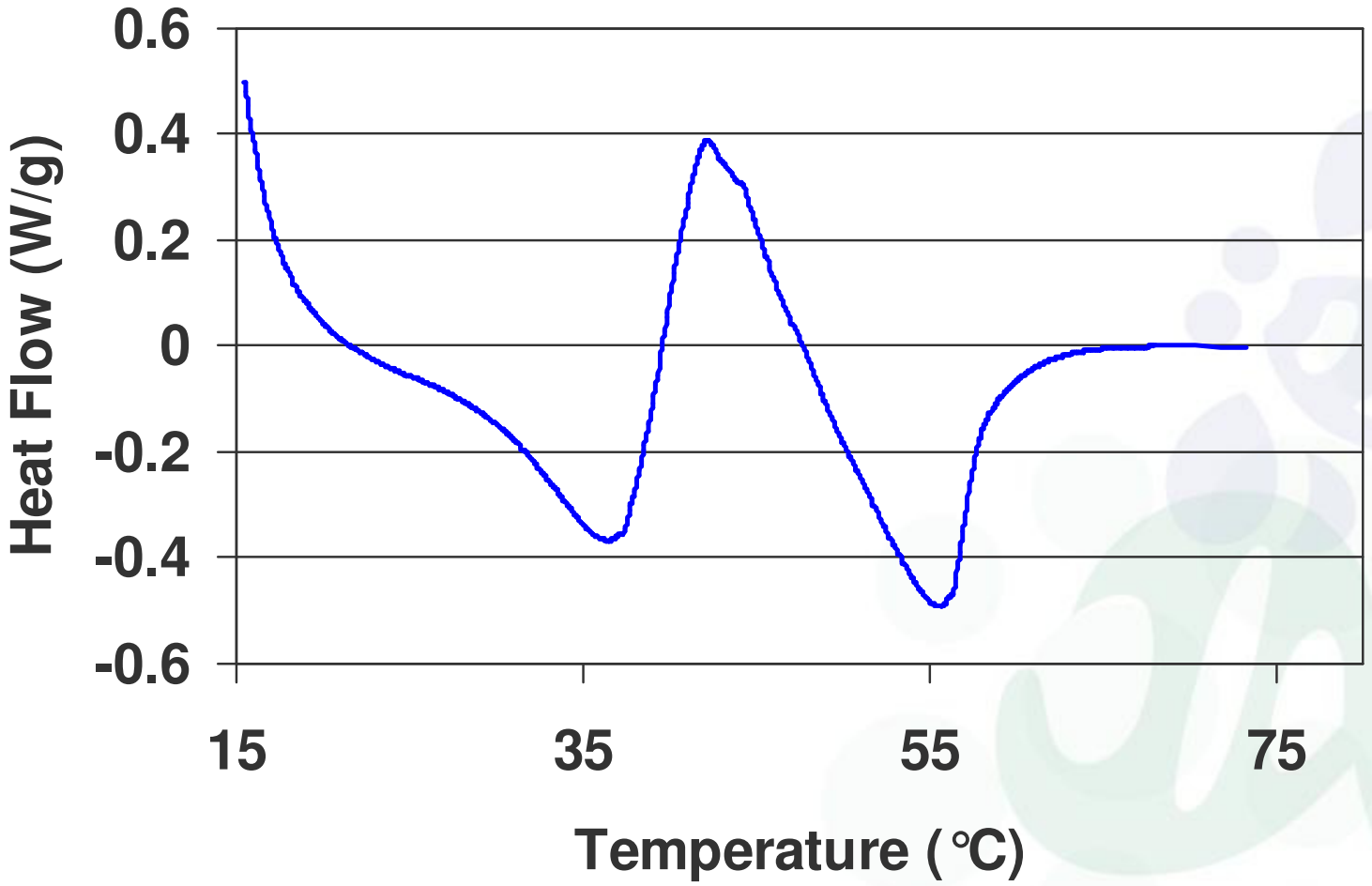
StStSt/StOSt by S&R at 15℃



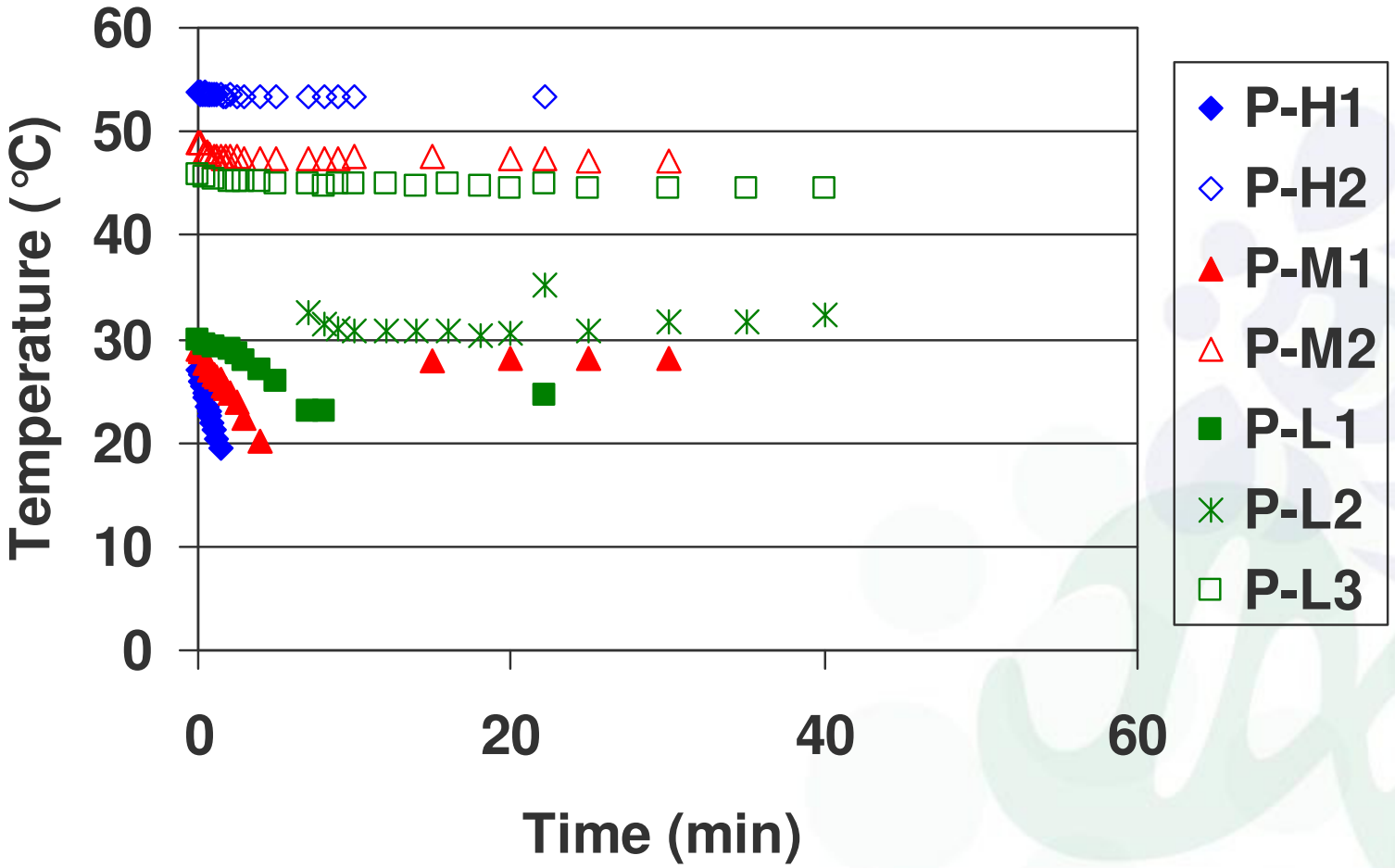
StStSt/StOSt by S&R at 20℃



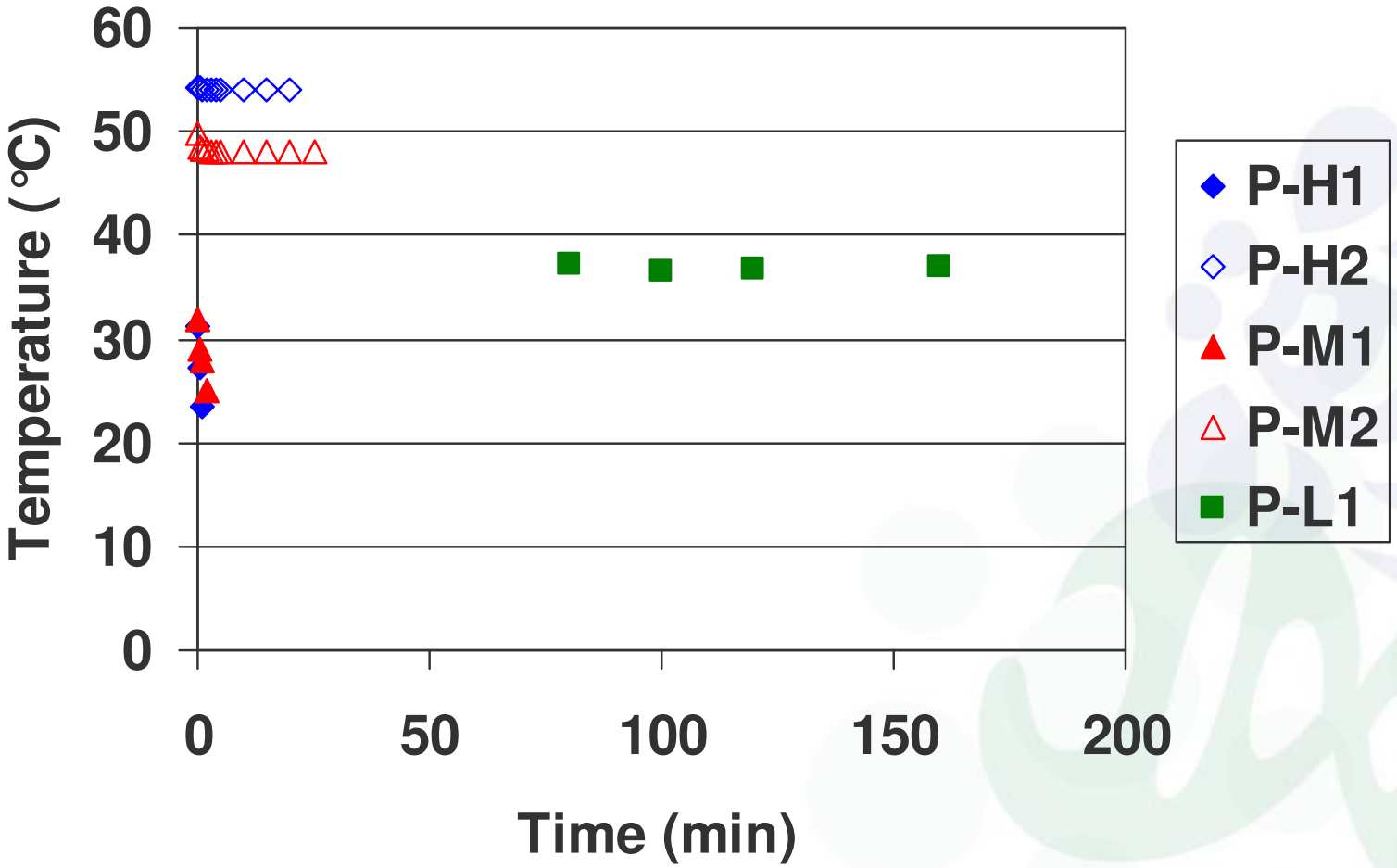
Example: Blend S-M S&R, 10min, 15°C



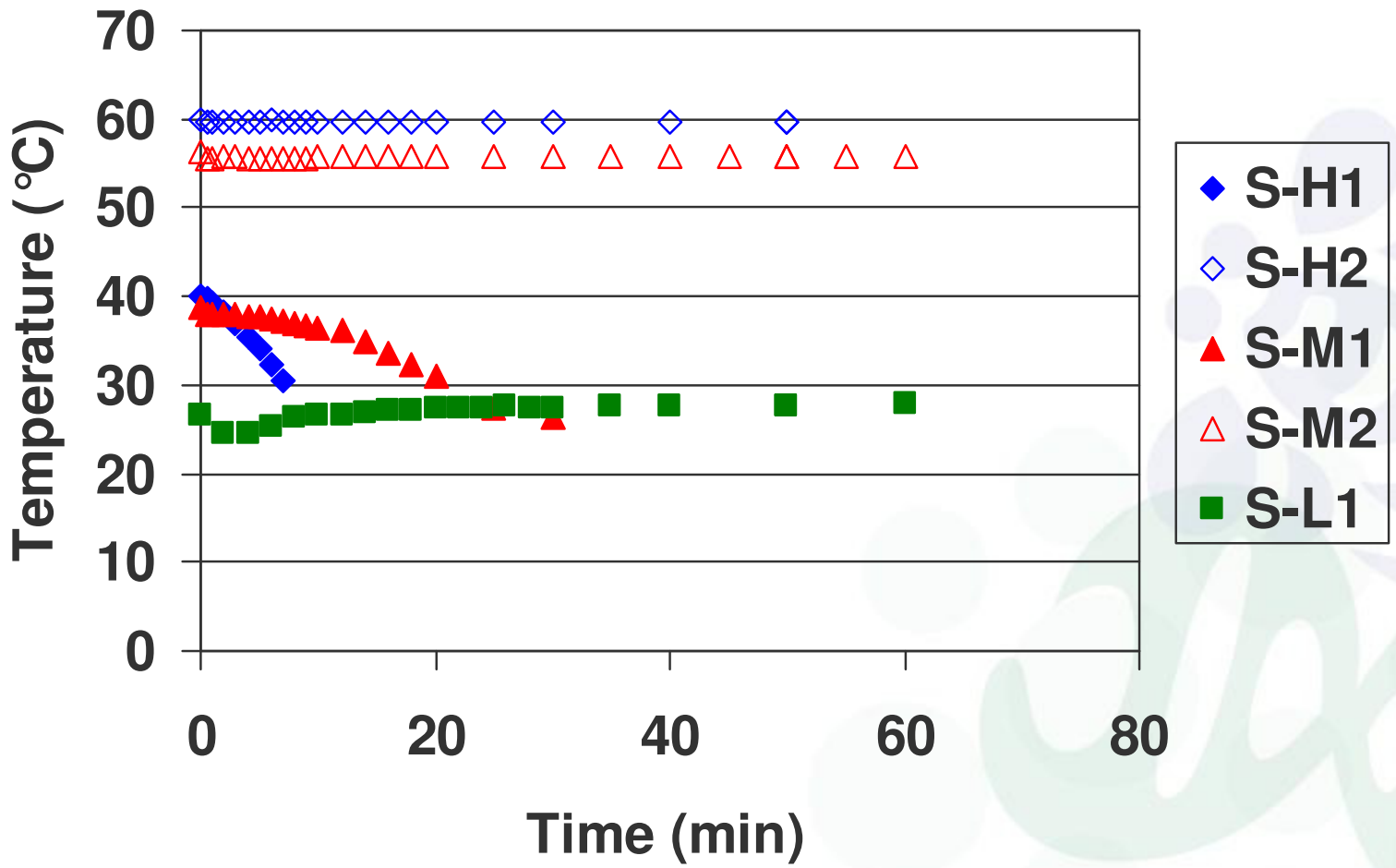
PPP/POP peak evolution at 15°C



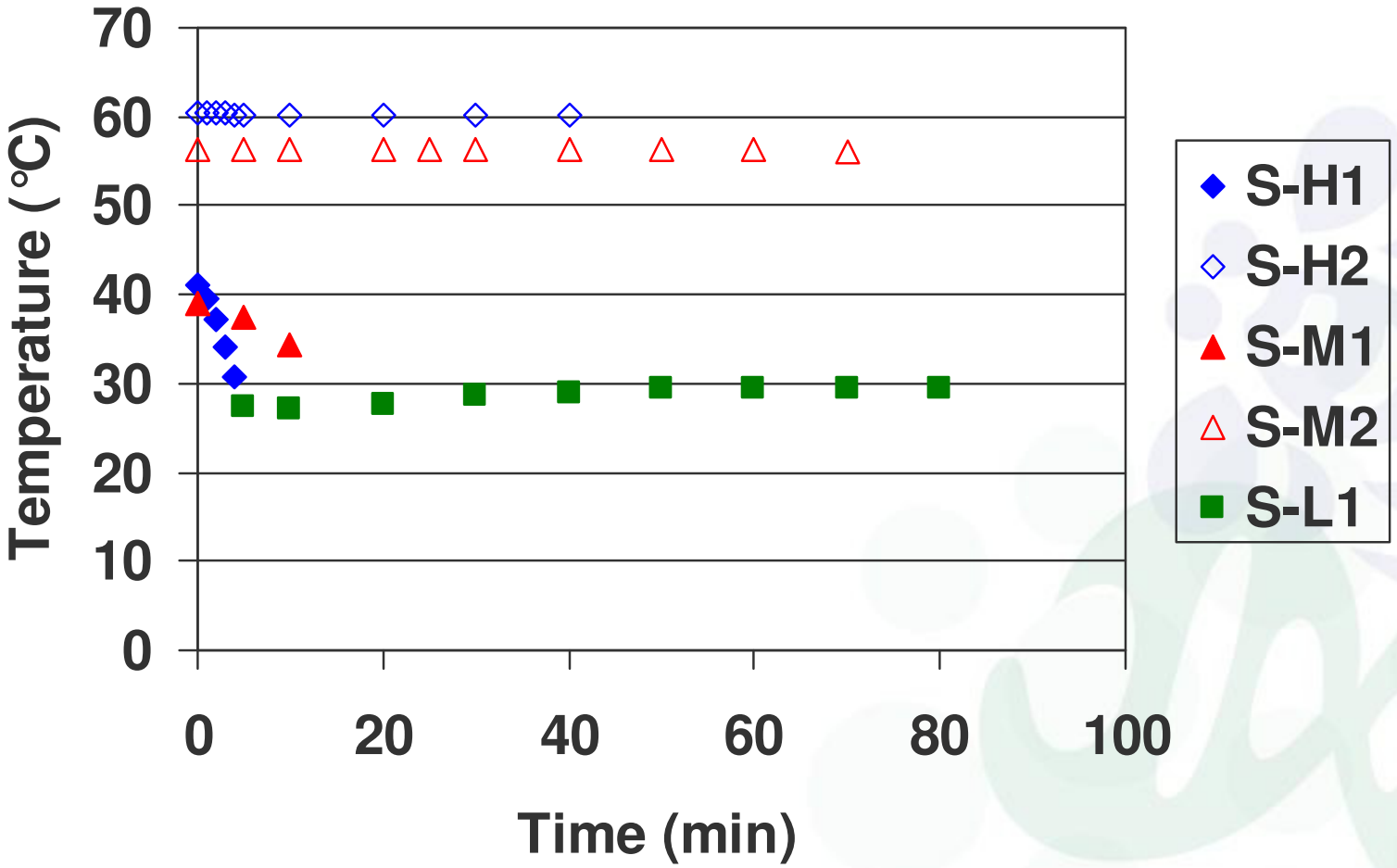
PPP/POP peak evolution at 20°C



StStSt/StOSt peak evolution at 15°C



StStSt/StOSt peak evolution at 20°C



Stop and Return DSC

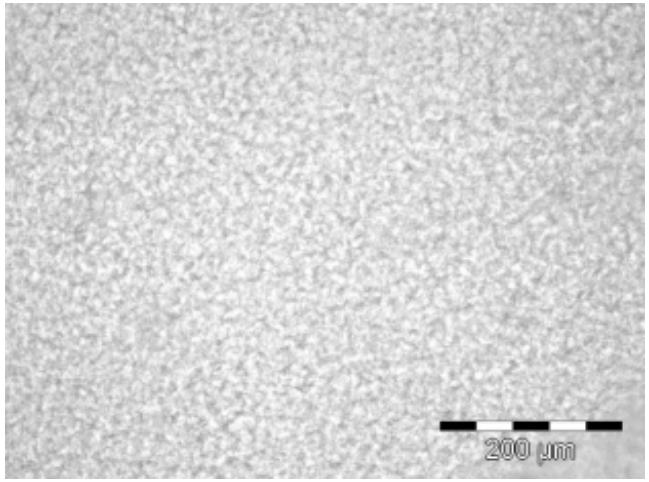
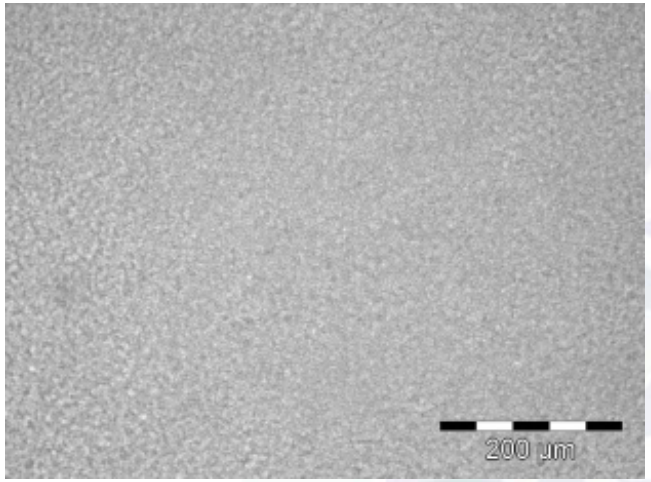
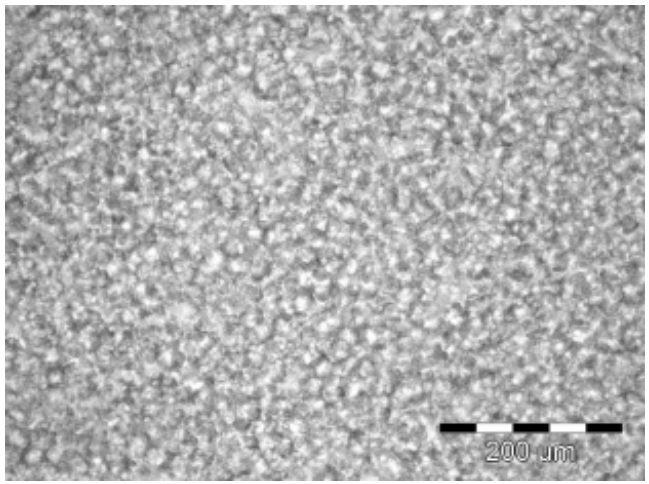
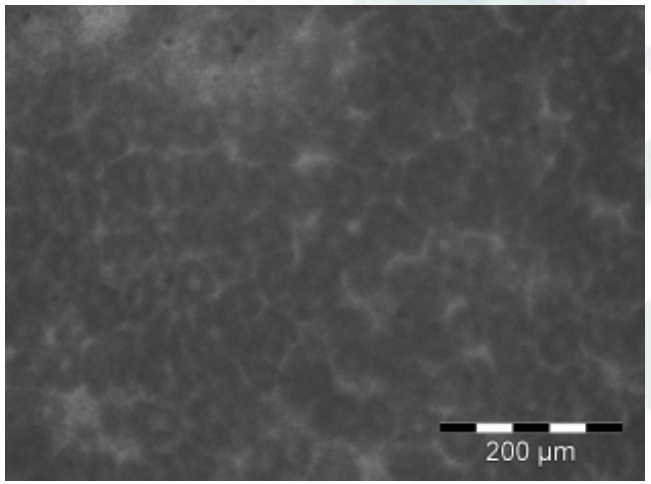
- Both P & St blends
  - Some crystallisation occurred during cooling
    - Except for lowest SSS
  - Likely to be polymorphic transformation during crystallisation
    - Disappearance of low melting peak – faster for P than St
    - Initial crystallisation in, e.g. α, which transforms to β'

- P blends
  - Similar to 'normal' DSC
  - High PPP gives faster crystallisation
  - One-step crystallisation
    - Suggests co-crystallisation of PPP & POP

- St blends
  - Lesser effect of StStSt on crystallisation at 15°C
    - Possibly due to larger degree of undercooling
  - Two step crystallisation evident
  - Slower crystallisation than P blends, except at low SSS
    - PPP better seed for POP than is StStSt for StOSt
  - Polymorphic transformation evident on re-heating

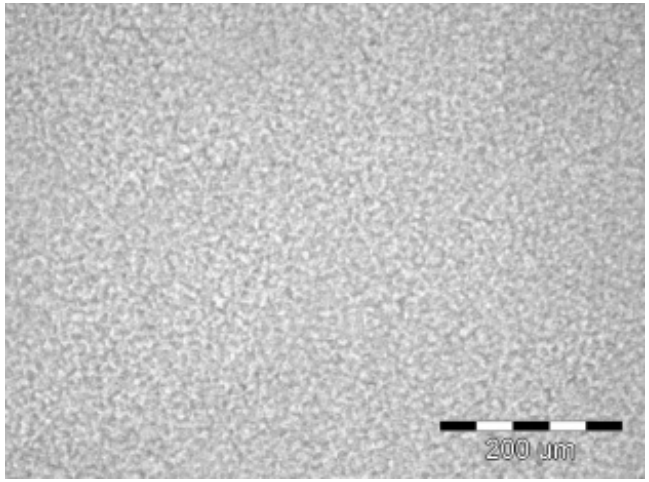
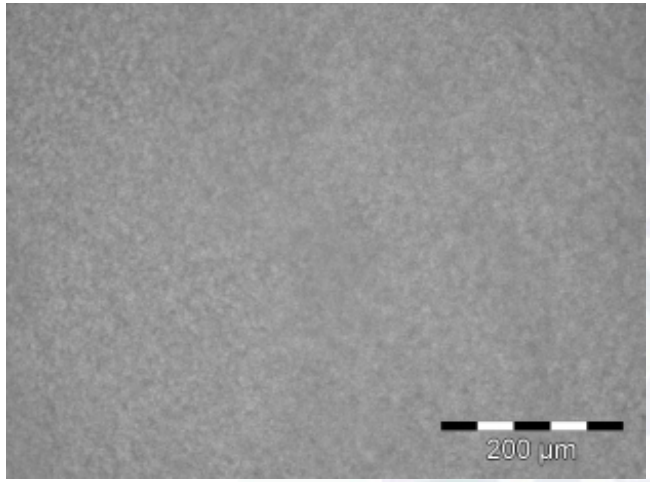
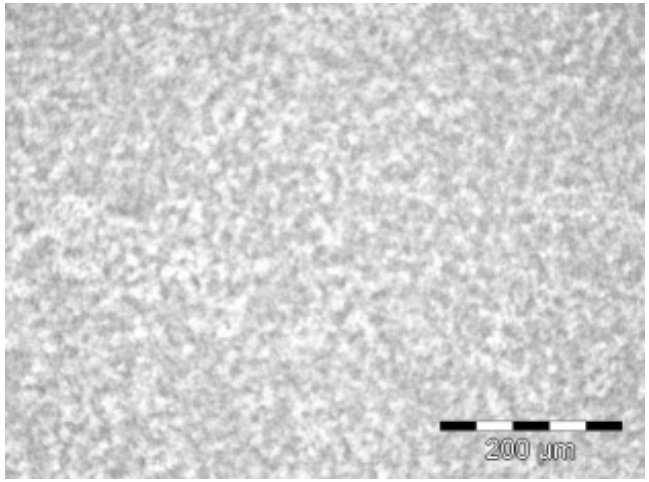
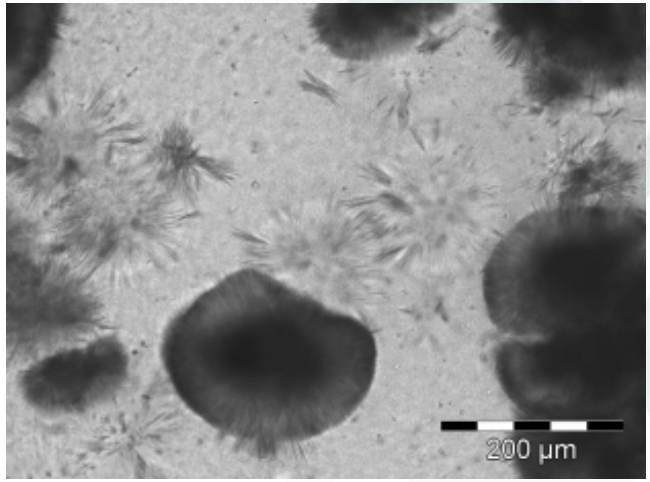
Microstructure, crystallised at 15°C

Storage time

	0	1 month
P-H		
P-L		

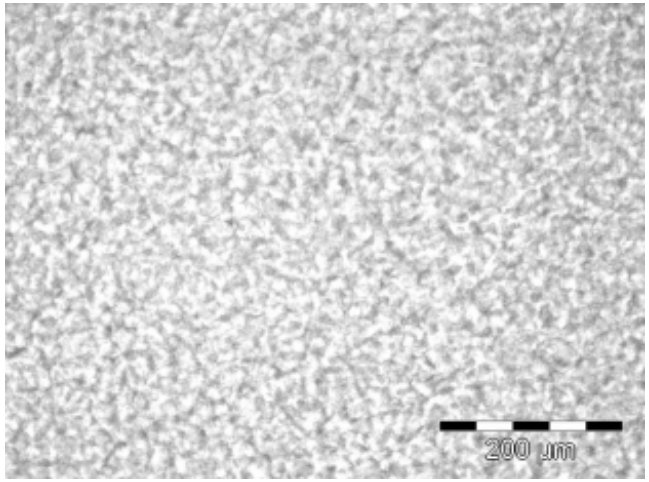
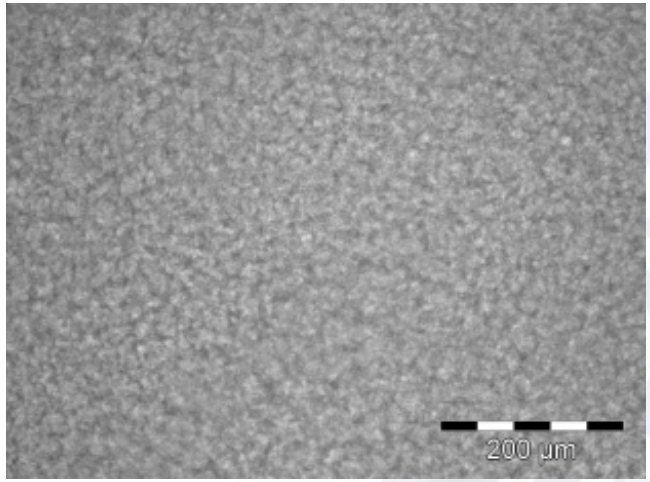
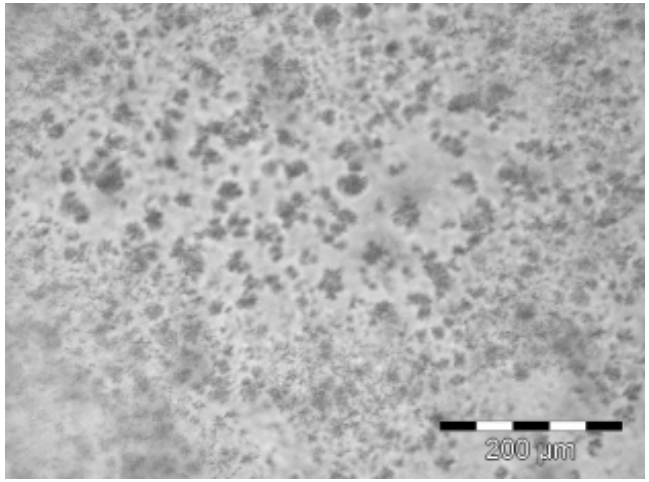
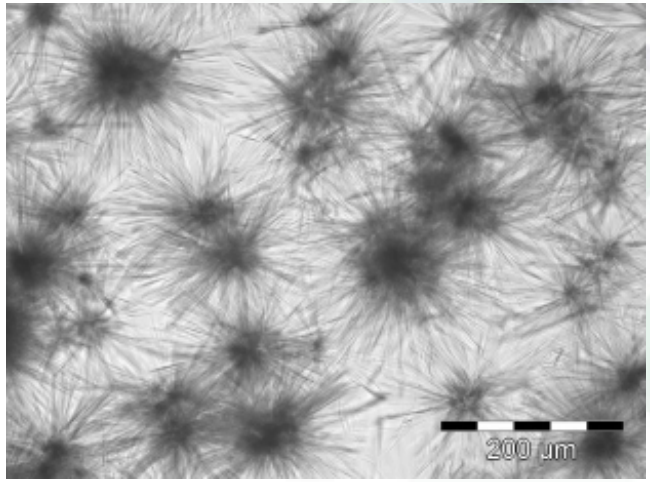
Microstructure, crystallised at 15°C

Storage time

	0	1 month
S-H		
S-L		

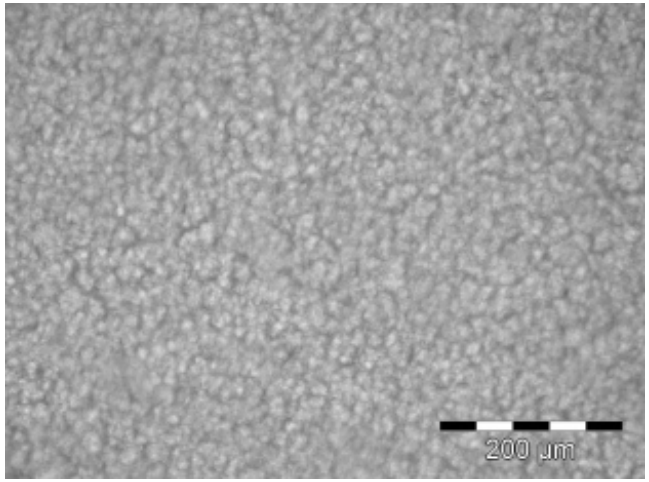
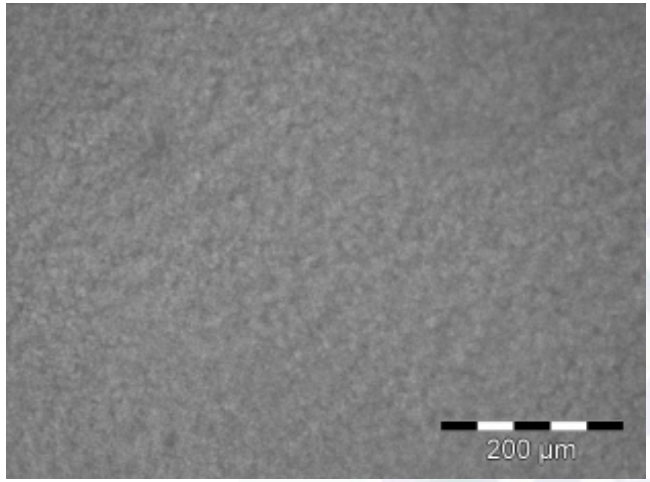
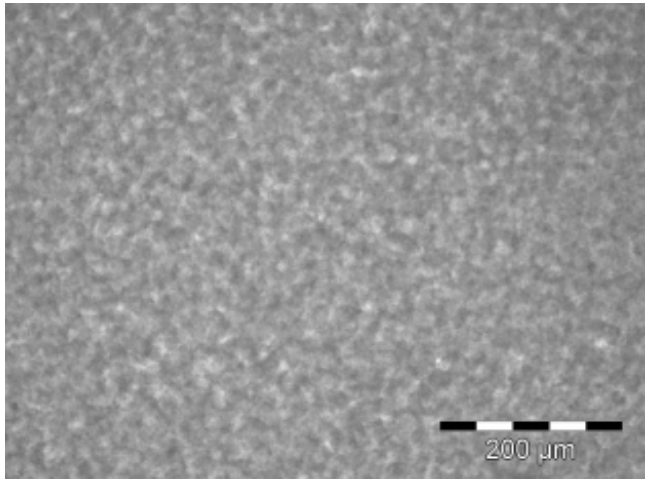
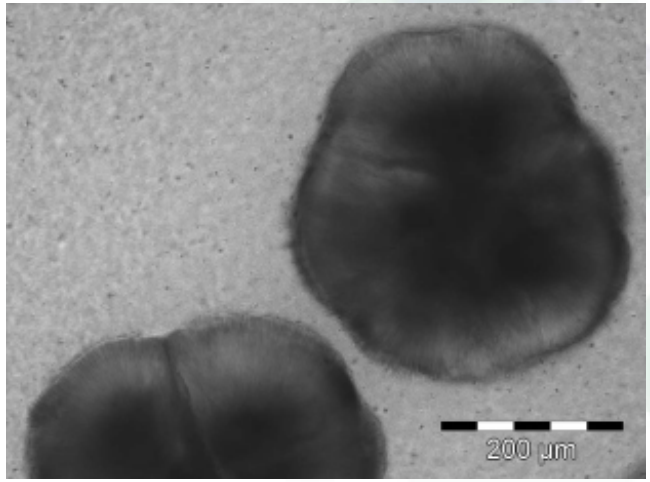
Microstructure, crystallised at 20 °C

Storage time

	0	1 month
P-H		
P-L		

Microstructure, crystallised at 20 °C

Storage time

	0	1 month
S-H		
S-L		

Microstructure

- Crystal size decreases as SSS increases
  - Much larger in blends without SSS
  - Seeding effect of SSS
- Crystal size very slightly larger at 20℃ compared to 15℃
  - Faster nucleation rate at 15℃
- All crystals increase in size during storage
  - Low SSS blends show much greater size increase
    - Possibly due to polymorphic transformation

Summary

- Higher SSS levels lead to:
  - Faster crystallisation
  - Higher melting
- PPP has a greater seeding effect on POP than does StStSt on StOSt
- Evidence for polymorphic transformation occurring during crystallisation
  - Occurs more rapidly for P than St blends
- Larger crystals form with low levels of SSS
  - Recrystallise on storage to even greater size
- Important to formulate a fat to have the right proportion of SSS and SOS, as well as P and St
  - Crystallisation behaviour
  - Structure
  - Storage stability

Acknowledgements

- Ria Dhian Anggreni

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