Research Center Jülich - Institute for Solid State Research

Structural Study of the Influence of Partially Crystalline Copolymers on Paraffin Crystallization in Dilute Solutions with Small Angle Neutron Scattering

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Paraffin Waxes - Properties

→ alkanes (paraffins) : straight chain molecules, single C - C bonds: C_nH_{2n+2} or simply C_n

→ gaseous: C_1 - C_4

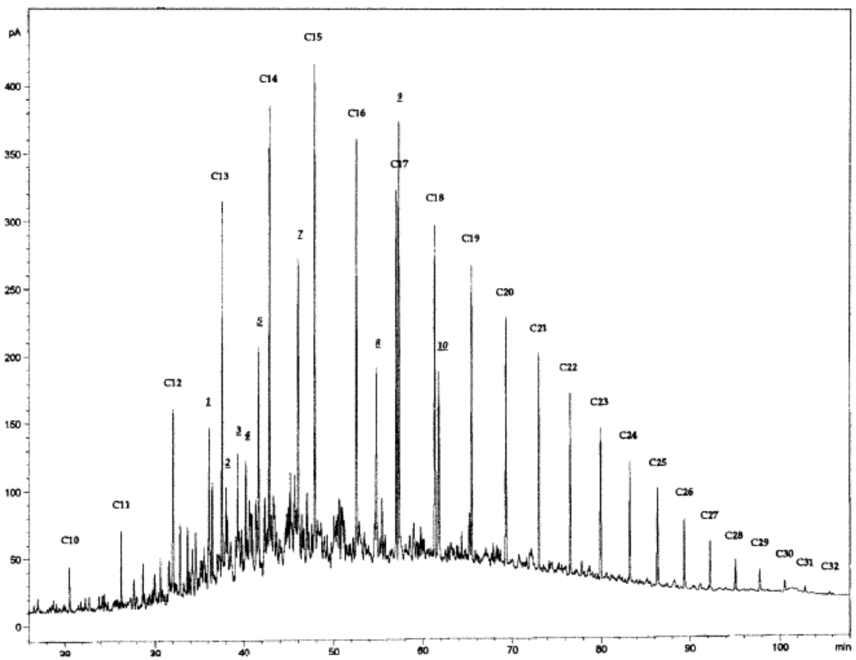
→ liquid: C_5 - C_{17}

→ solid: C_{18} ($T_m \cong 28.2°C$) and n larger → known as "waxes"

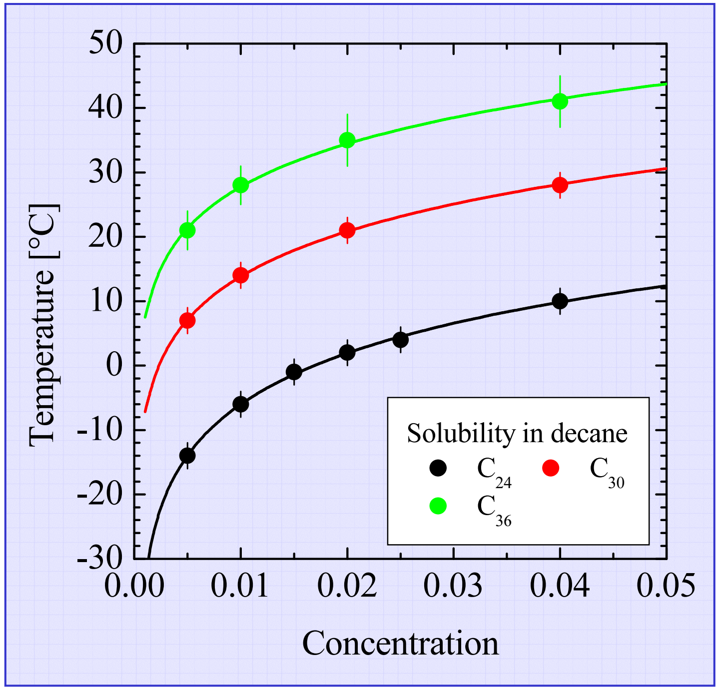
→ paraffin waxes: orthorhombic, hexagonal, monoclinic and triclinic structures

Composition of Diesel Fuel

Chromatography analysis
of Diesel fuel (C_{12} and larger)



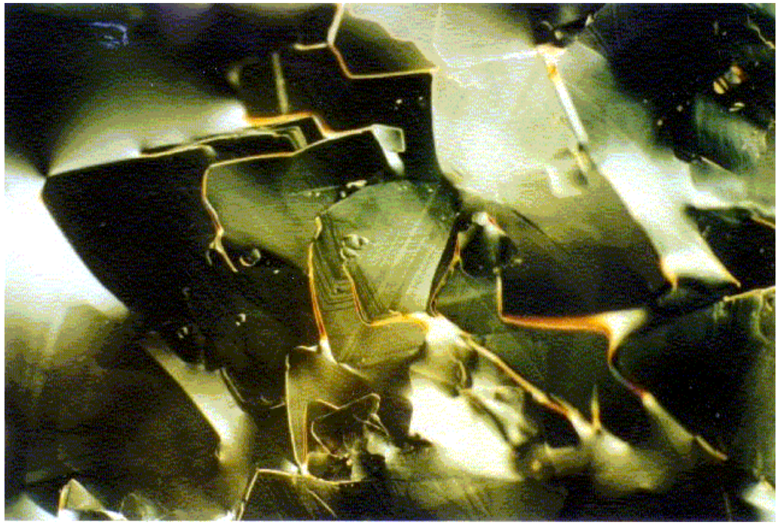
Wax solubility lines in decane
(C_{10} ; $T_m \cong -30°C$)

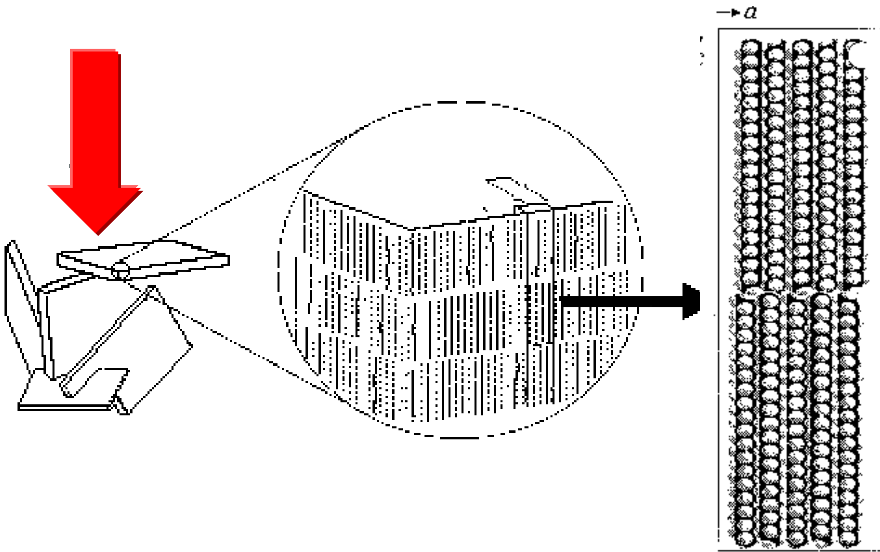


Paraffins: - important component of middle - distillate fuels (10-35%)

- major components of crude oils

Crystallization of Paraffin Waxes





- Wax crystals form gels and stop flow
- Gels inhibit crude oil recovery from deep sea reservoirs
- Wax crystals in Diesel oil plug filters

Cold Flow Properties of Middle-Distillate Fuels

→ the cloud point (**CP**) - temperature when wax crystals appear **(WAT)**

→ the pour point (**PP**) - temperature when fuel gels

→ the cold filter plugging point (**CFPP**) - temperature when a 45 mm filter is plugged in standard condition

→ typical diesel fuel without additives → **PP** ≅ 10°C

Polymeric Additives

→ **Crystal growth of wax**

- sensitive to impurities, e.g. *modify size and shape of wax crystals*
- when intentionally added ⇒ impurities become *additives*

→ **Promoters**

- crystallize prior to paraffins
- useful for the separation of waxes

→ **Inhibitors**

- wax dispersants/flow improvers (WDFI)
- crude oils and diesel fuels
  - remain fluid at low temperature and
  - pass through filters

Polymeric Additives

Choice largely by trial and error

→ polymers in general self assemble

→ interplay between polymer aggregate and wax crystallization important

Example: poly(ethylene-co-vinylacetate) - EVA

→ poorly characterized

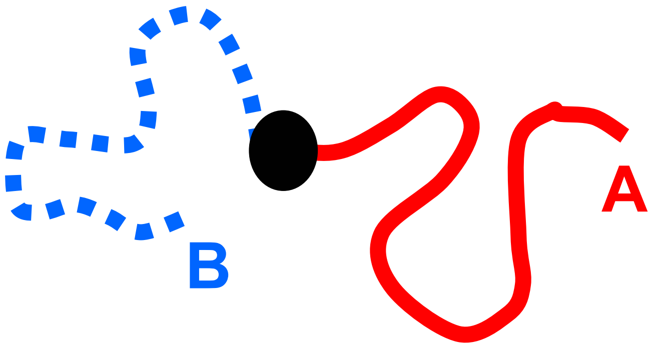
→ not very efficient in certain oils

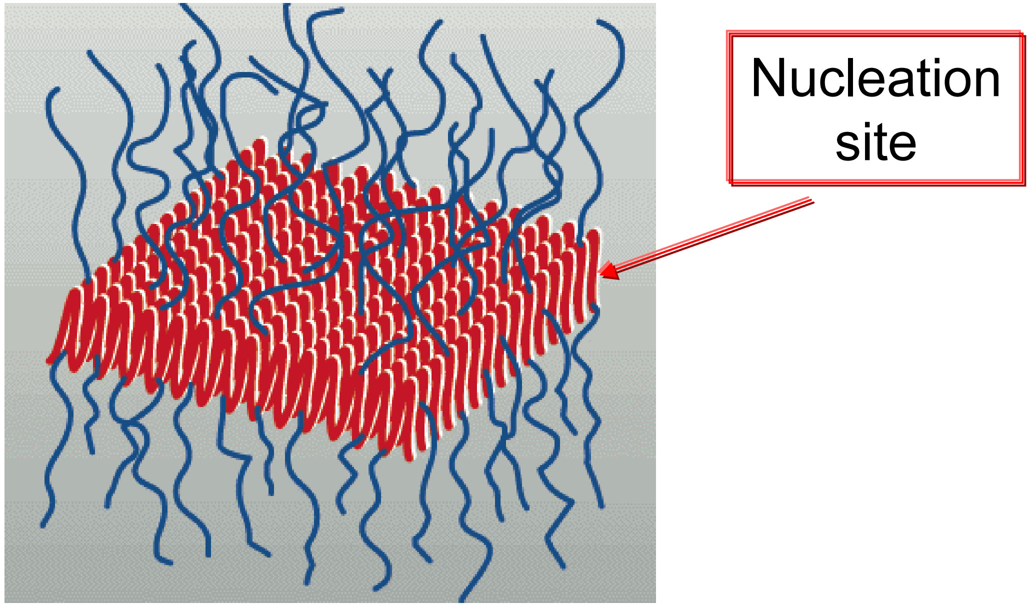
→ 50% precipitation already at high T

Polymeric Additives explored with SANS

1. **Diblock Copolymers**

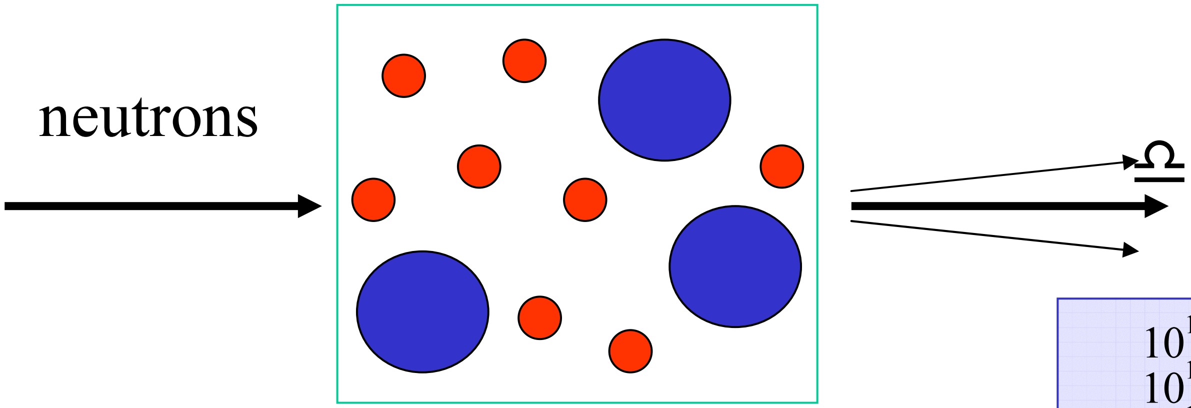
PE – PEP

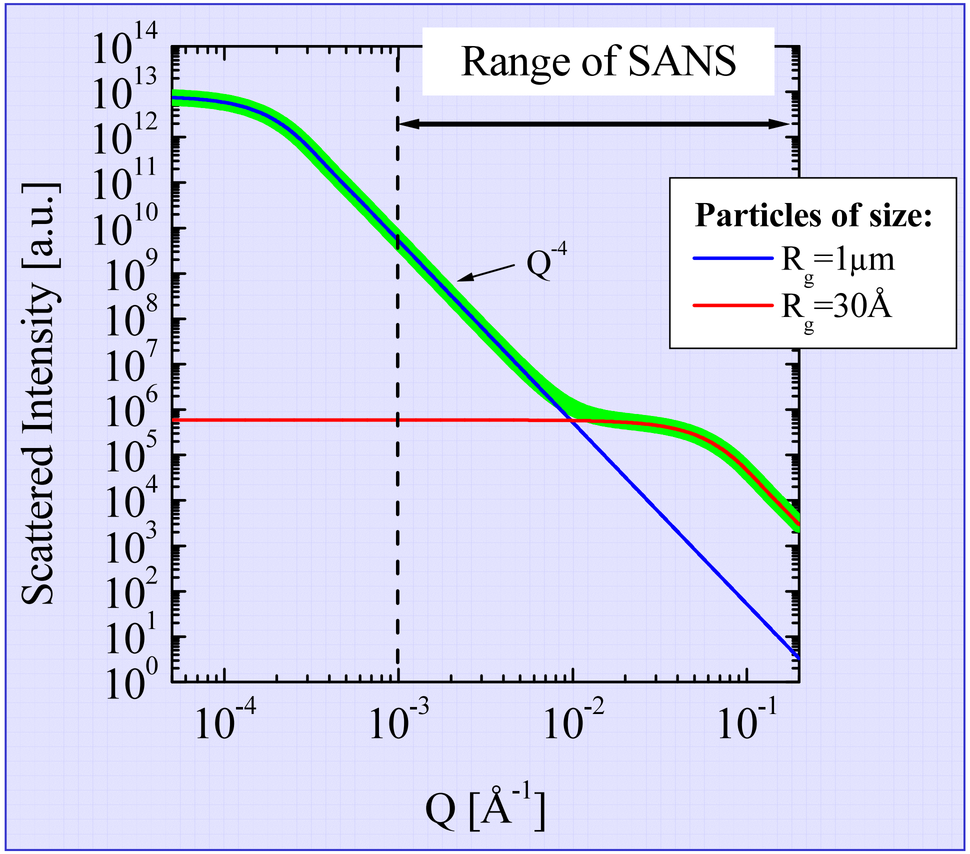




2. **Random Copolymers**
   PEB-n type (ethylene/butylene copolymers)

General Remarks on SANS experiments





Wave number:

Q=(4π/●)sin(♎/2)

Range SANS Instruments

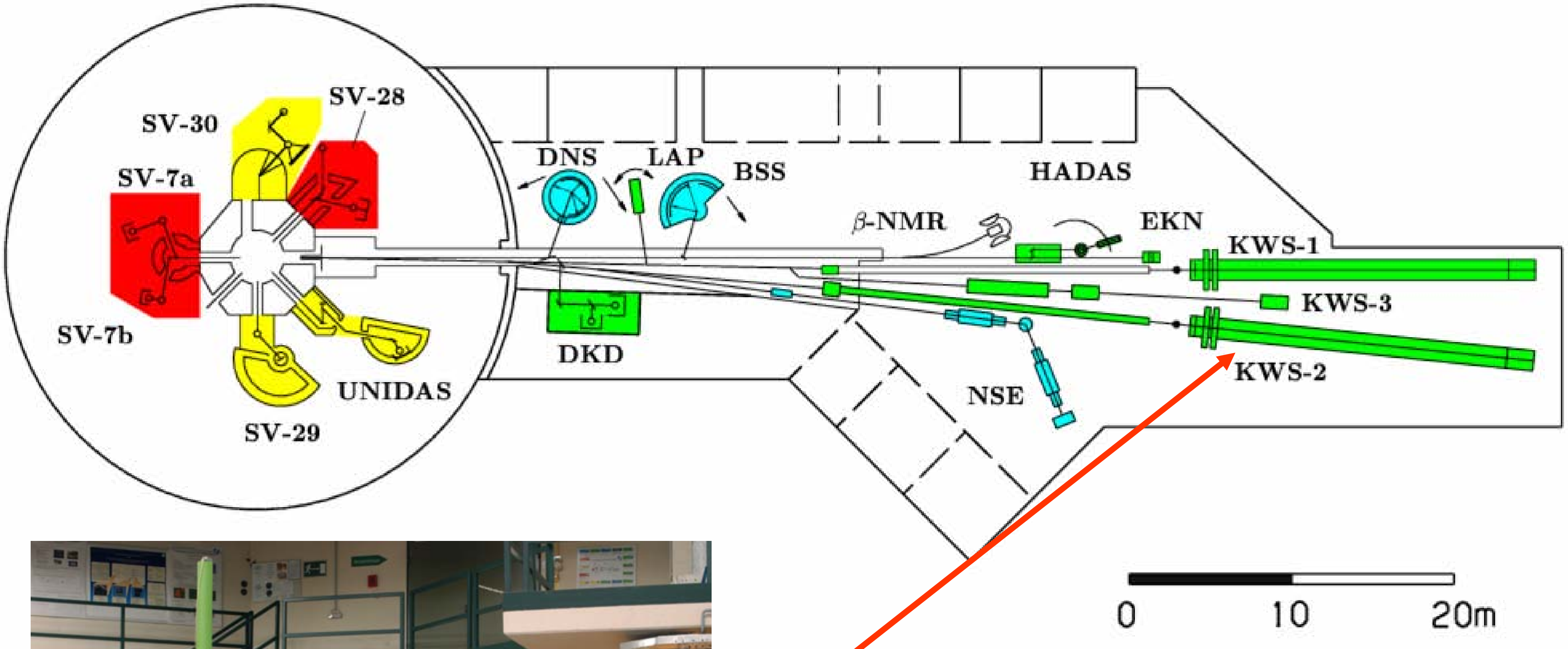
According to **D ✍ ●/♎** one can explore particles of size:

Light (● ✍ 6000 Å)	0.5 µm ⦿ D ⦿ 20 µm
Neutrons (● ✍ (2 – 15) Å)	10 Å ⦿ D ⦿ 20 µm

Three different SANS techniques allow to measure a particle size in a range of **four orders of magnitude (Q ✍ 2◘/D):**

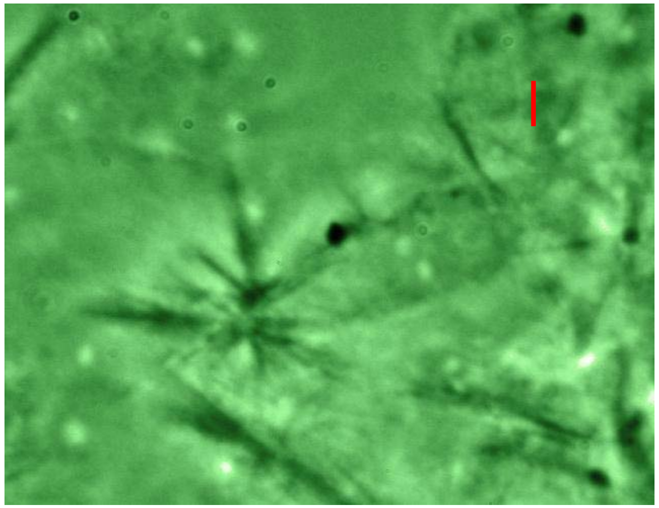
Pin - Hole SANS	**$0.2Å^{-1}$ ¤ Q ¤ 10^{-3} $Å^{-1}$**
Focusing SANS	$5 \cdot 10^{-3}$ $Å^{-1}$ ¤ Q ¤ 10^{-4} $Å^{-1}$
Double Crystal Diffractometer	10^{-3} $Å^{-1}$ ¤ Q ¤ $2 \cdot 10^{-5}$ $Å^{-1}$

Instrumentation at FRJ-2 in Jülich



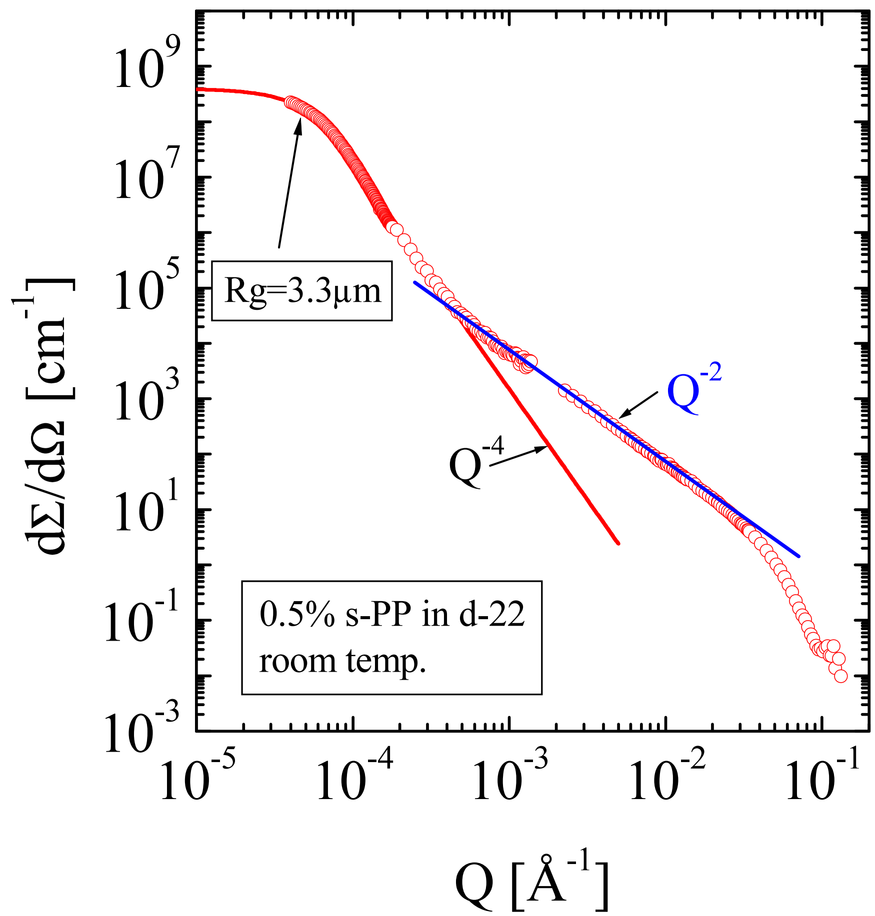
Crystallization of *syndio*-Polypropylene in d-22 solution - large scale view

Spherulitic morphology



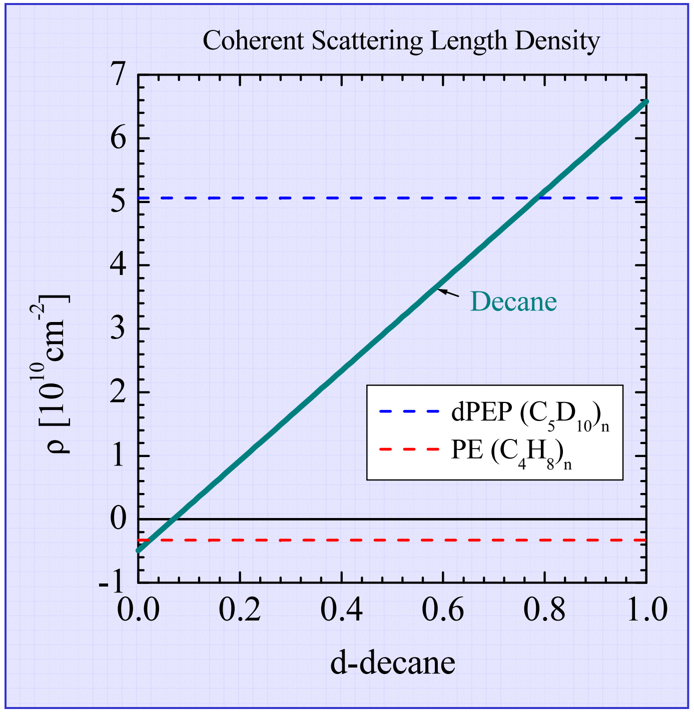
(Scale bar 2 µm)

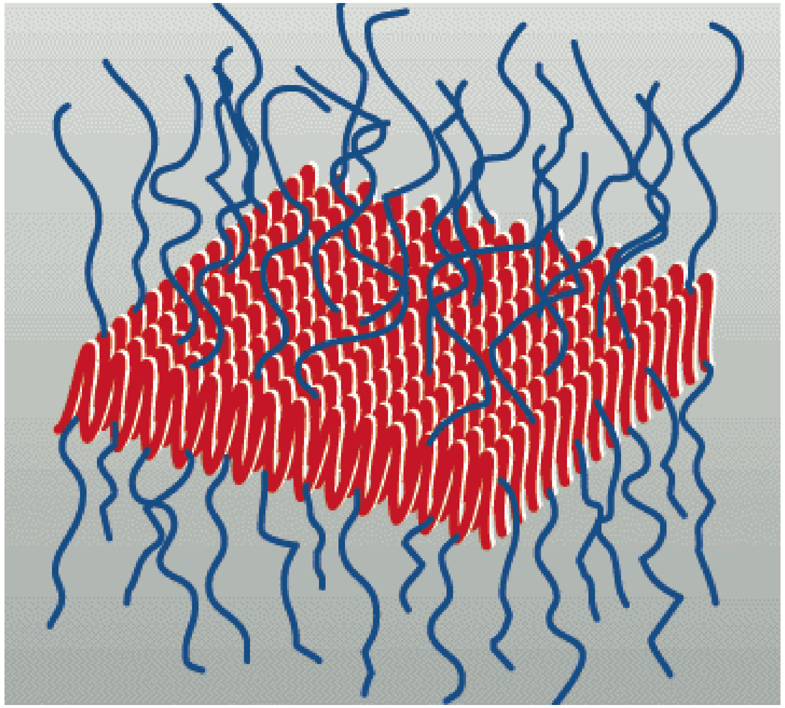
DKD, Focusing SANS, Pin - Hole SANS



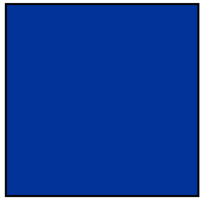
PE-PEP Diblock as Wax Crystal Modifiers

Contrast variation





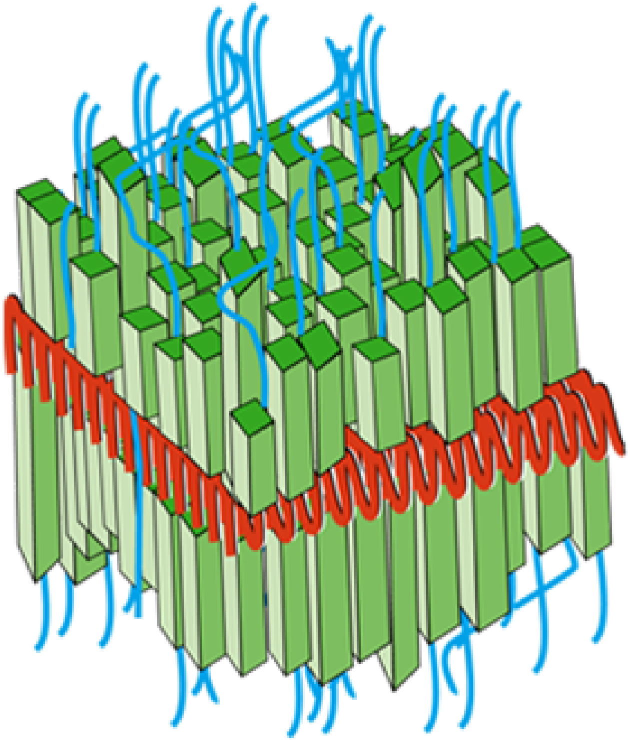
Core Contrast =



Brush Contrast =

PE-PEP Diblock as Antifreeze for Diesel

polymer aggregates work as nucleation agents



suppression of large crystals

4 years from discovery to commercialization

Random Copolymers of the PEB-n Type

$$-\overbrace{\left(CH_2 - CH = CH - CH_2\right)_x}^{1,4} - \overbrace{\left(CH_2 - \underset{\substack{|\\ \mathrm{CH = CH_2}}}{CH}\right)}^{1,2\ (vinyl)}{}_{(1-x)} -$$

PEB-n precursor

$$-CH_2 - CH_2 - CH_2 - CH_2 \,\ldots\ldots\ldots\, CH_2 - \underset{\substack{|\\ CH_2\\ |\\ CH_3}}{CH_2} -$$

$M_w \cong 6K$

PEB-n
n: number of ethyl branches/ 100 backbone carbons

Model system for studying co-crystallization of paraffin and polymer additives in fuel oil at low temperatures

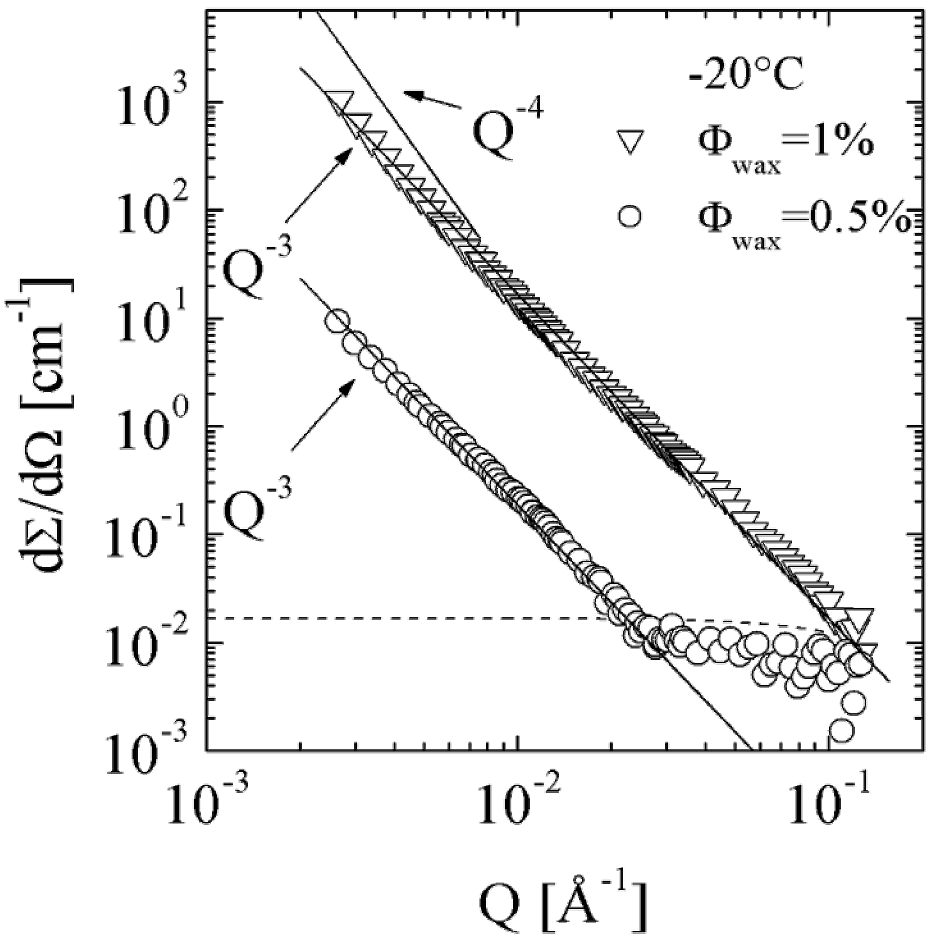
Scattering from Objects with characteristic Morphologies

$$d\Sigma / d\Omega(Q) \propto Q^{-\alpha}$$

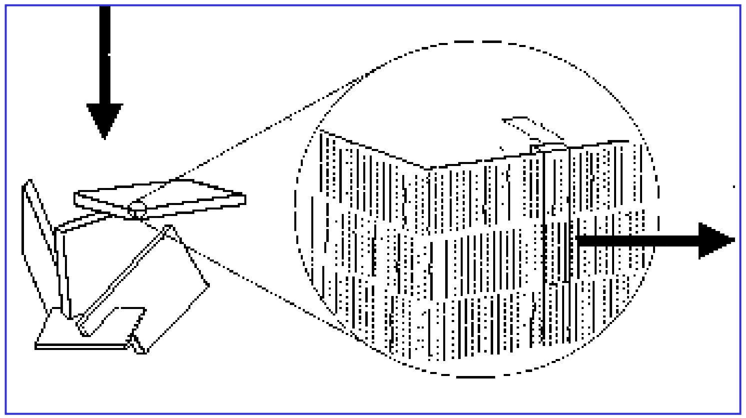
α	**characteristic morphology**
3/5 (Flory exponent)	swollen chain in good solvent
2	swollen chain in Θ-solvent
1	rods
2	plates
4	3-D objects (R>1/Q)
<3	mass fractals
$3 < \alpha < 4$	surface fractals
>4	diffuse interfaces

Crystallization of pure Wax

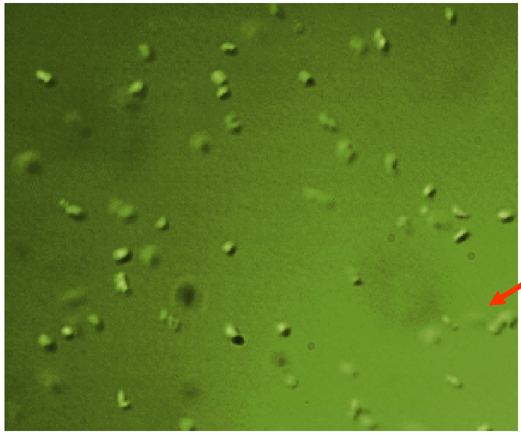
C_{24} in decane

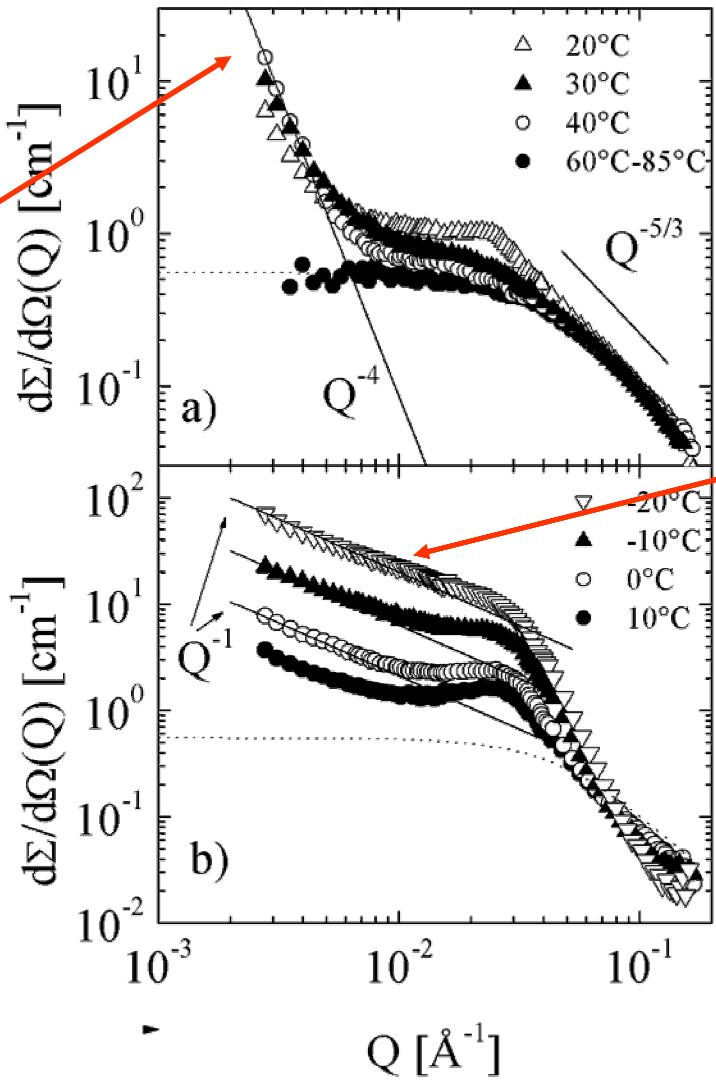


mass fractal: card house



Aggregation Behavior of PEB-7.5 (☞$_{pol}$=1%)





Rod like structures at lower temperatures

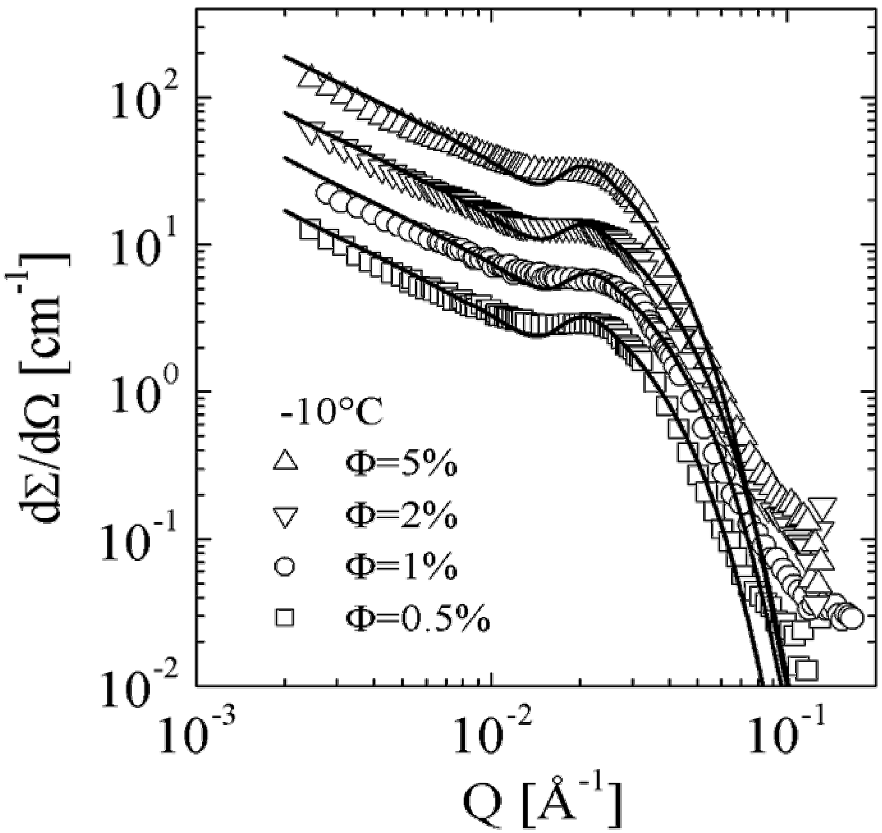
Correlation peak?

Large compact objects at by minority

From Porod constant and micrograph 0.7% polymer participation

Aggregation Behavior of PEB-7.5

concentration dependence

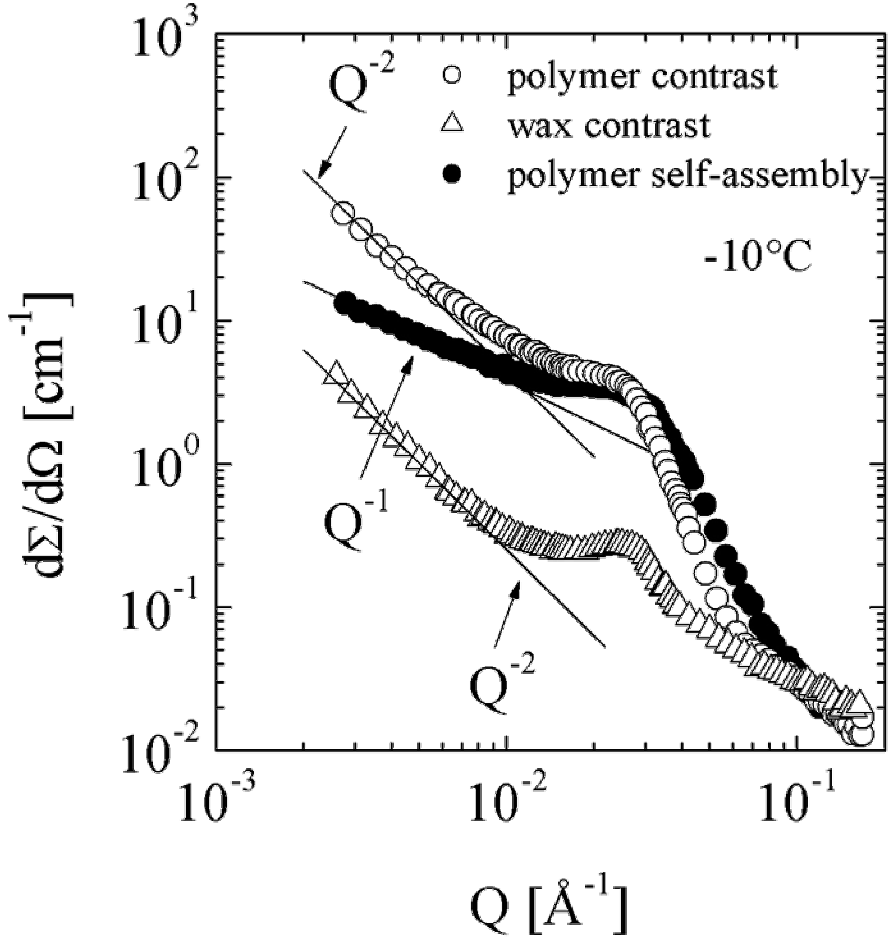


Rod like structure

Density modulation along the rod of ~ 350 Å length;

Polymer density within the rod: $4\% < \phi_{pol} < 30\%$

PEB-7.5 affects C_{24} Crystallization



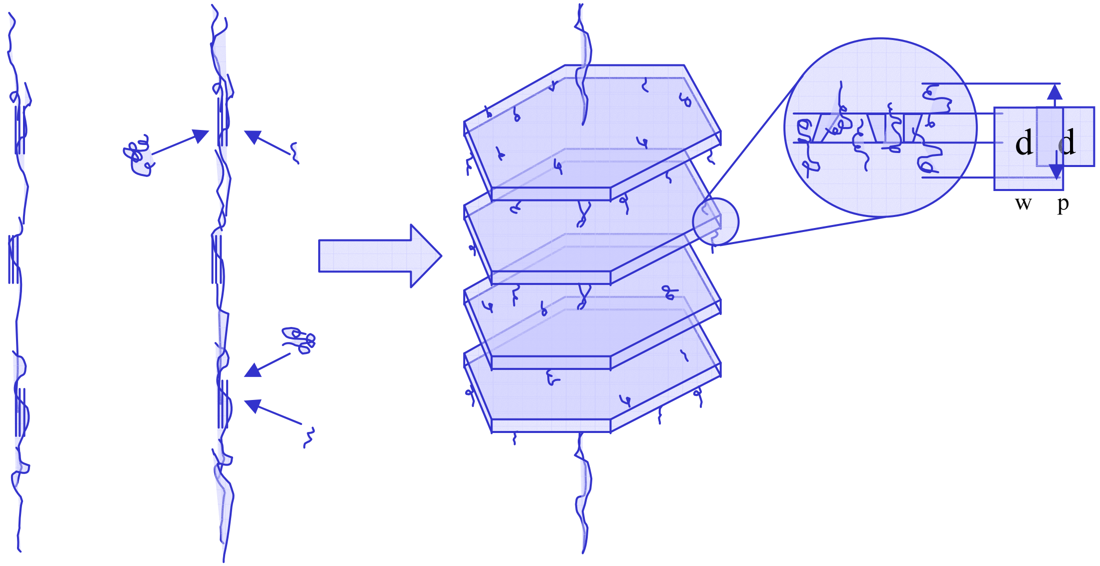
→ Aggregate morphology changes from 1D → 2D

→ Primordial modulation of the PEB 7.5 structure remains

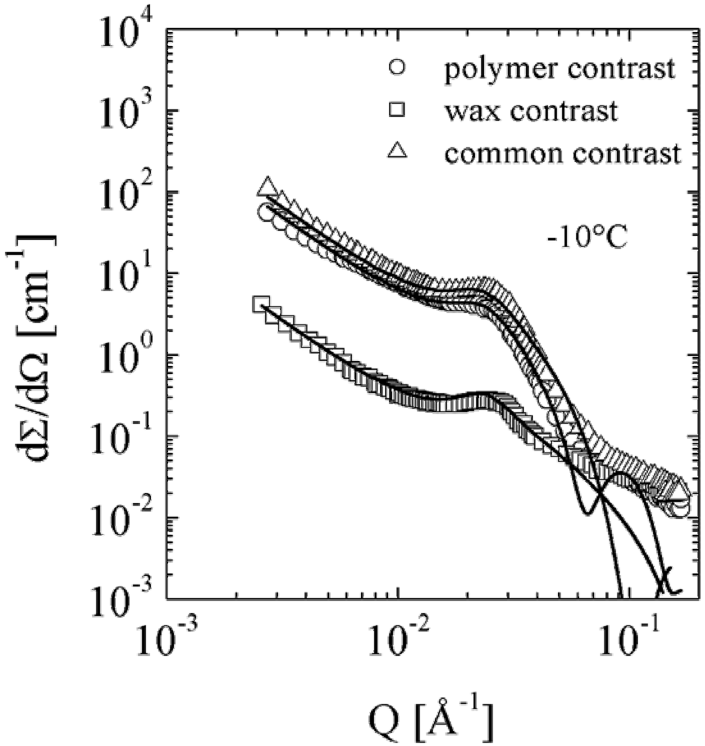
PEB 7.5 self-assembles first

PEB-7.5 and C_{24}: Co-crystallization in correlated Plates

linear morphology | **correlated plates** | **containing wax + polymer**

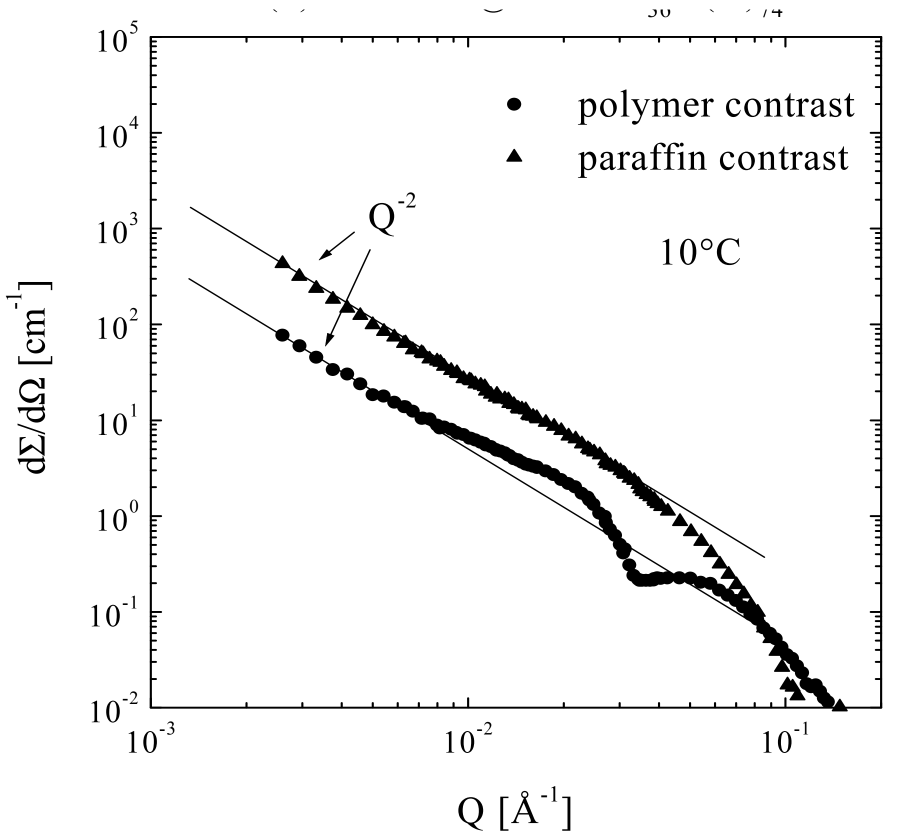


Model yields quantitative fits



Shish-kebab morphology: similar to PE crystallization under flow

PEB-7.5 und C_{36}



wax plates

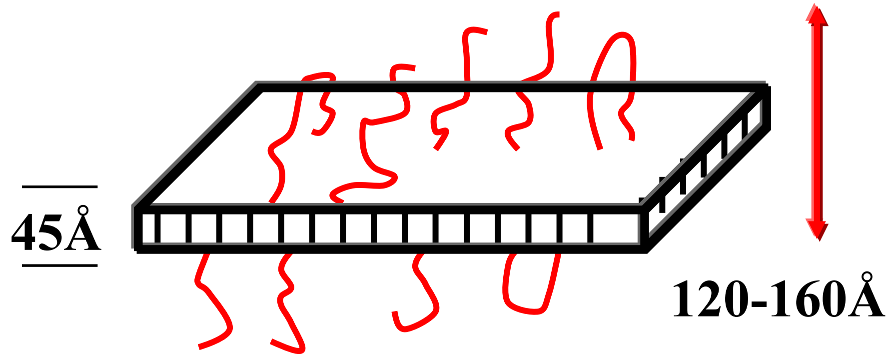
→ thickness d_{wax} < 45Å

→ single C_{36} plates

polymer plates

→ no correlation peak

→ brush like form factor



T=10°C below wax solubility line; wax co-crystallizes with polymer and suppresses the pure PEB-7.5 aggregation features

Wax Modification Efficiency

Results from evaluation of structures under different contrast

<u>Example:</u> wax and polymer content in platelets at 0°C, ☞$_{w}$ = 2%, and ☞$_{pol}$ = 0.6%

	☞$_{wax}$	☞$_{pol}$
C_{36}	91%	9%
C_{24}	36%	64%

PEB-7.5 optimized for C_{36}; PEB-11 would be the optimized polymer for C_{24}

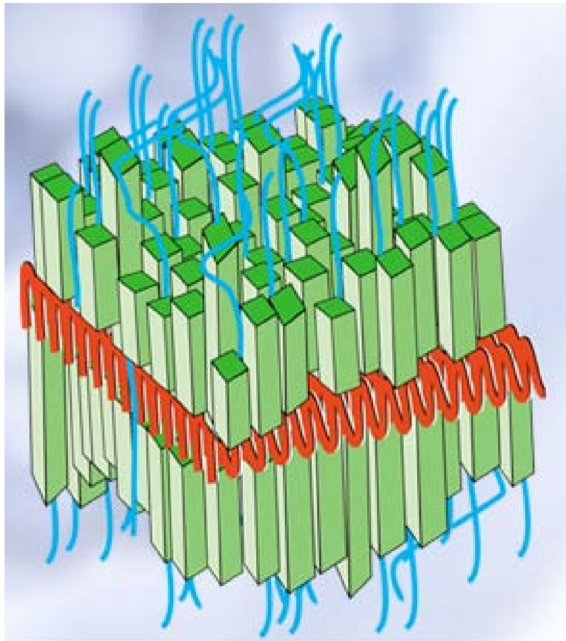
<u>Take home message:</u>

Efficiency highest if polymer and wax jointly crystallize

Conclusions

1. Crystalline – amorphous blockcopolymers

- polymers form templates



polymer templates nucleate wax crystals

PE-PEP is commercialized as

Paraflow™

Diesel fuel additive

Wax crystal modification by partially crystalline polymers

Conclusions

2. Random crystalline amorphous copolymers

A. Polymer aggregation commences at temperatures above wax solubility line

polymer form templates for crystallization

nucleation from the polymer structures

Limited efficiency

Conclusions

B. Wax solubility line in the order of polymer aggregation temperature

=> co-crystallization dominates wax

PEB-7 + C_{36}

- plates at high *T*, suppression of 3-d objects
- polymer incorporated in wax plates

nucleation is mediated by the joint polymer wax structure

High efficiency

Conclusions

3. Pour point reduction

- most efficiency if polymer and wax crystallization coincide
- tuning is possible by changing PEB-n microstructure