FACULTY OF
BIOSCIENCE ENGINEERING

DEPARTMENT OF GREEN CHEMISTRY AND TECHNOLOGY
LABORATORY FOR CIRCULAR PROCESS ENGINEERING

DISTRIBUTION OF ORGANIC ADDITIVES SUCH AS PLASTICISERS DURING DISSOLUTION-PRECIPITATION POLYMER RECYCLING

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CONTEXT

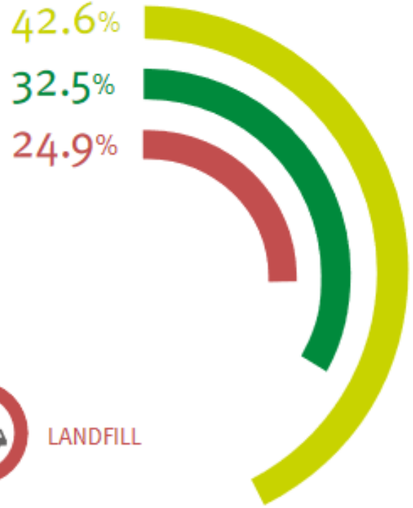
World

2018 **359** million tonnes → 2019 **368** million tonnes

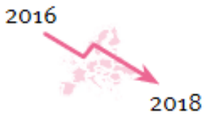
Europe (EU28+NO/CH)

2018 **61.8** million tonnes → 2019 **57.9** million tonnes

29.1 Mt Collected plastic post-consumer waste



-39% Plastic waste extra-EU exports



ENERGY RECOVERY

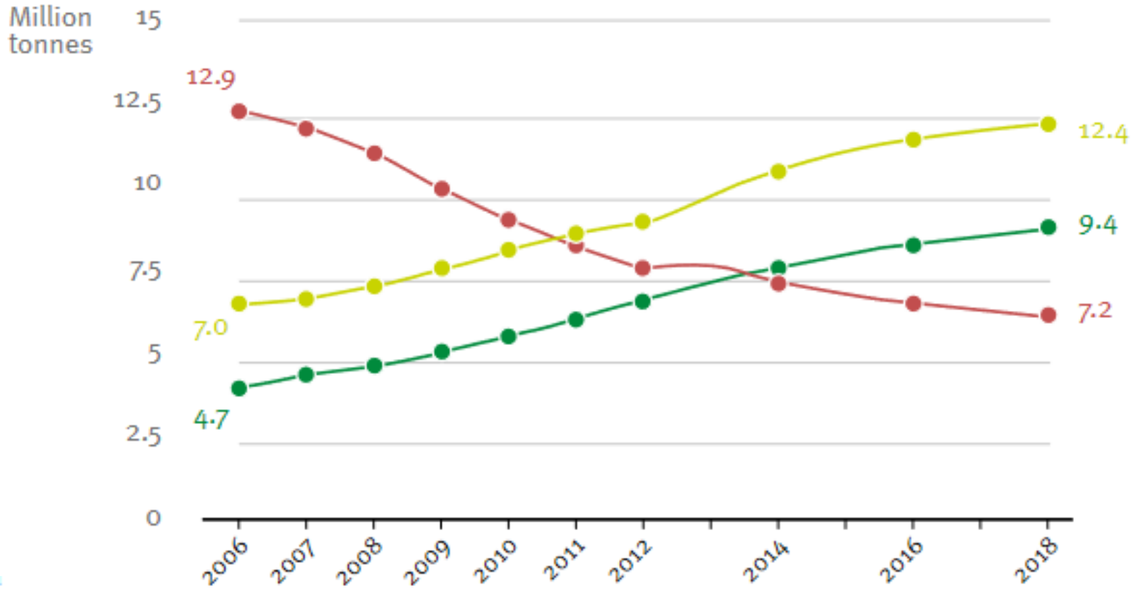
RECYCLING

LANDFILL

2006-2018 evolution of plastic post-consumer waste treatment

(EU28+NO/CH)

+100%	+77%	-44%	+19%
RECYCLING	ENERGY RECOVERY	LANDFILL	COLLECTED PLASTIC POST-CONSUMER WASTE 2006-2018



Source: (PlasticsEurope, 2020)

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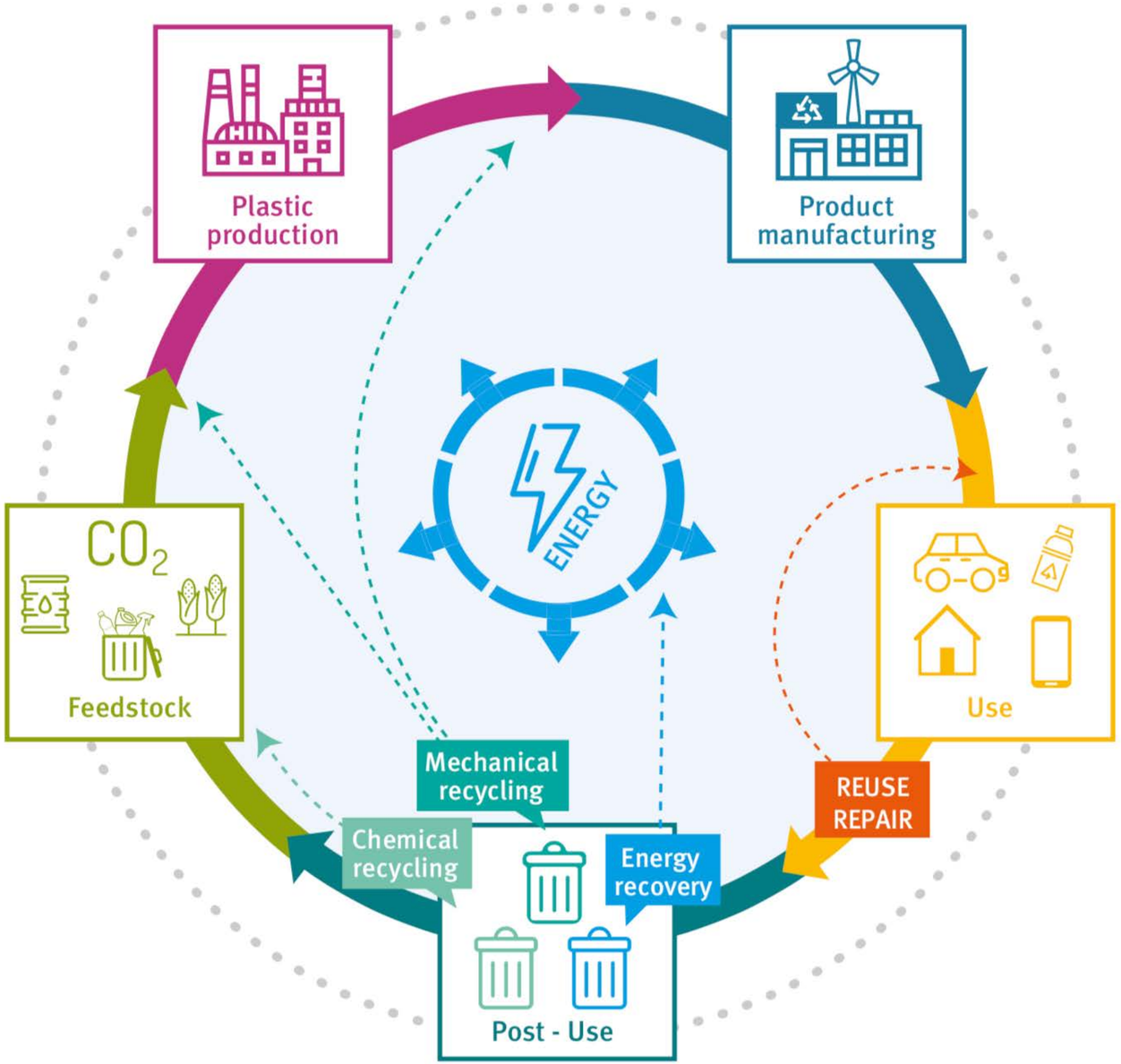
GOAL: CIRCULAR ECONOMY



Source: (PlasticsEurope, 2018)

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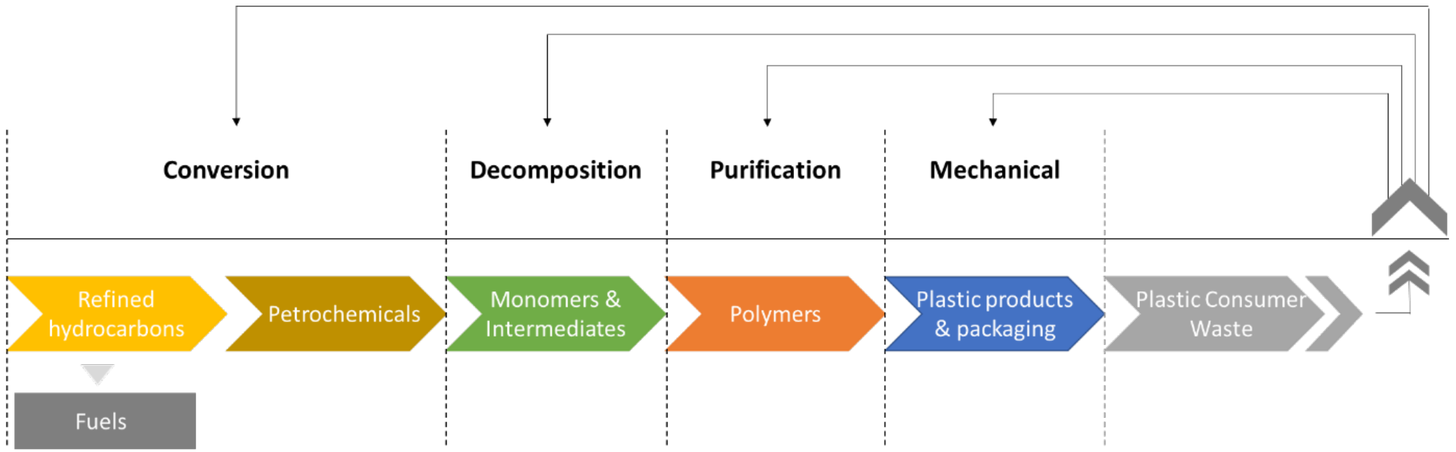
CHEMICAL RECYCLING

1. **Solvent-based purification**, the polymer does not change on a molecular level (*physicochemical process*)
2. **Decomposition**, breaking of molecular bonds to recover the monomers of the polymer (*solvolysis*)
3. **Conversion**, breaking of molecular bonds but the output often resembles petroleum products (*pyrolysis and gasification*)



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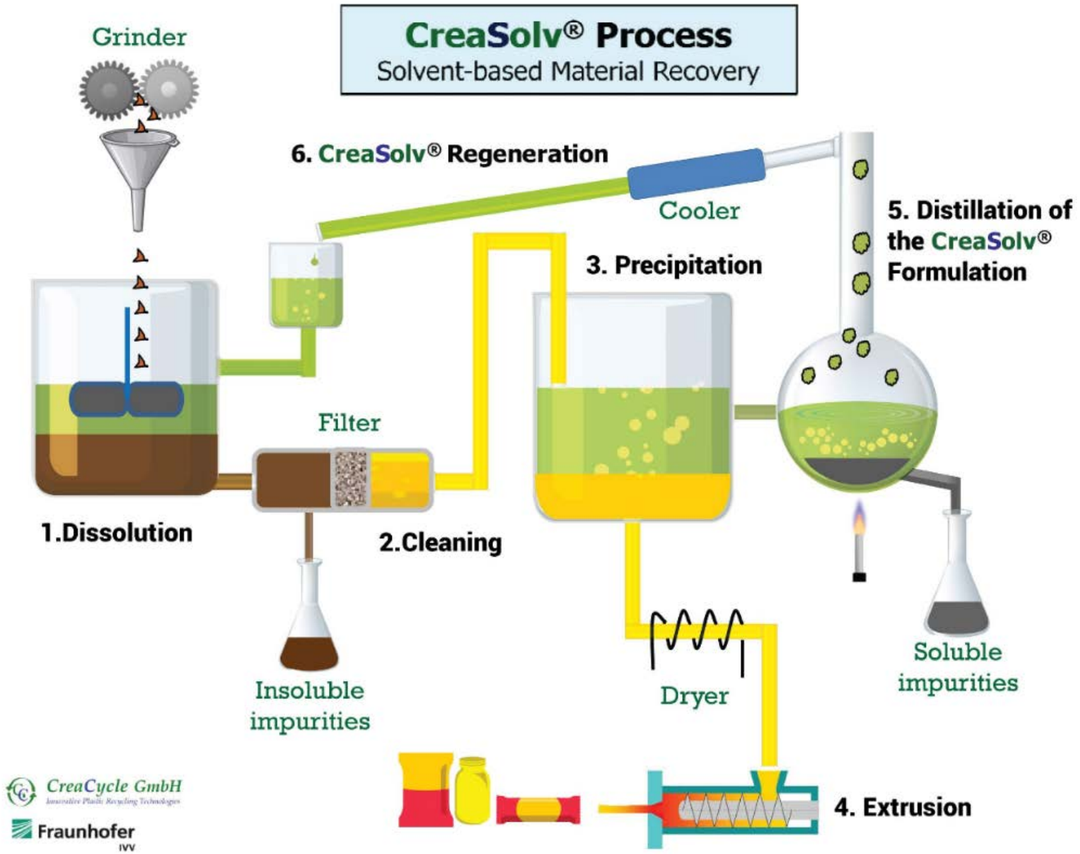
DISSOLUTION PRECIPITATION PROCESS



Source: (CreaCycle, 2018)

Benefits:

- Selective dissolution
- Removal of impurities
- No chain degradation

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HANSEN SOLUBILITY PARAMETERS

Total cohesive energy split into three parts:

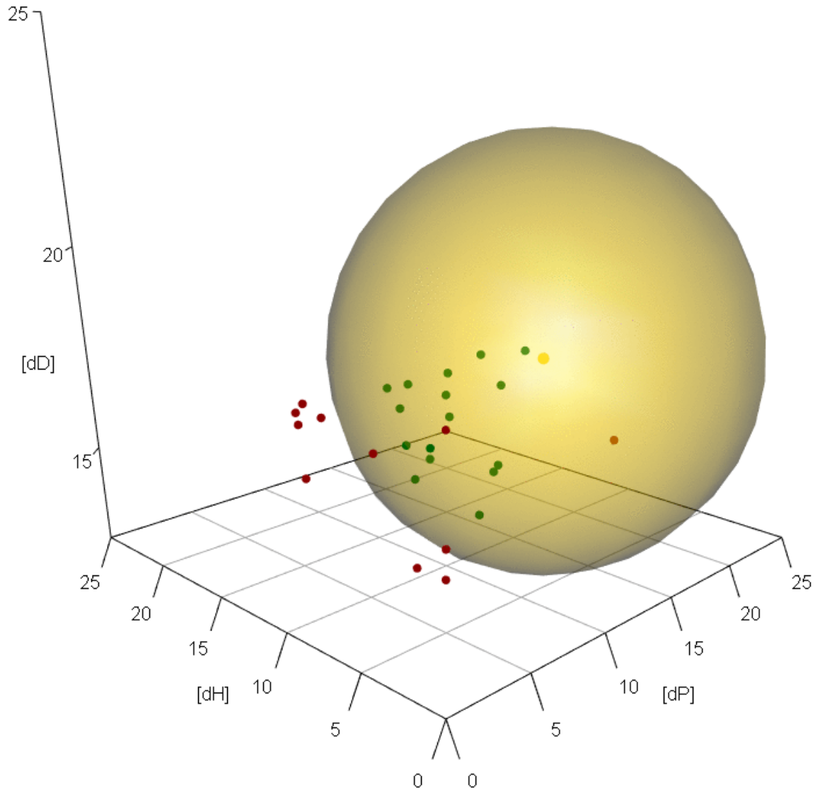
→ **δD**: dispersive forces

→ **δP**: permanent dipole interactions

→ **δH**: hydrogen bonds

A measure of “like”,

to determine good and bad solvents



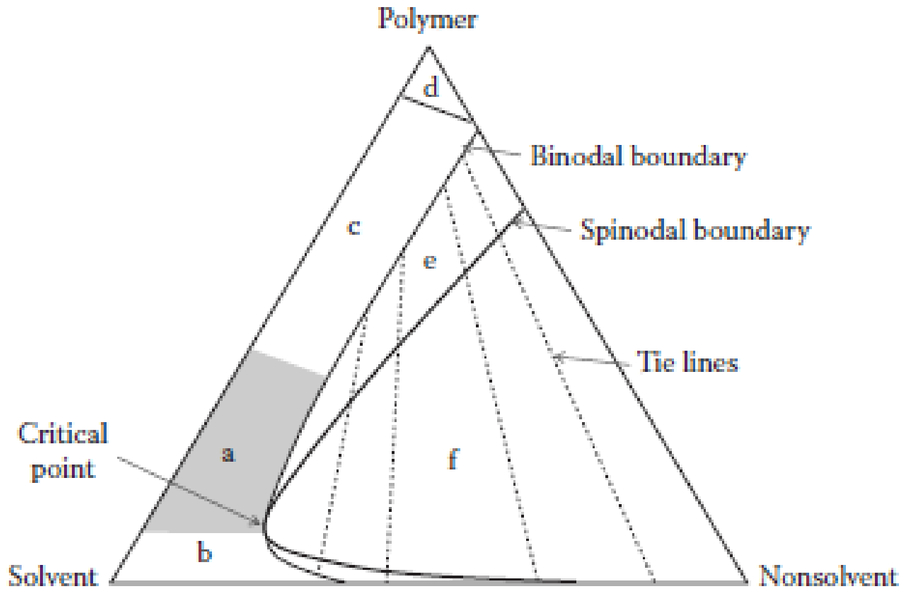
TERNARY DIAGRAM FOR POLYMERS

Commonly used to predict the membrane structure in membrane phase inversion processes.

Binodal curve: boundary between stable and metastable region

Spinodal curve: boundary between metastable and unstable region

→ Theoretical construction: combine **HSP** and **Flory-Huggins** theory



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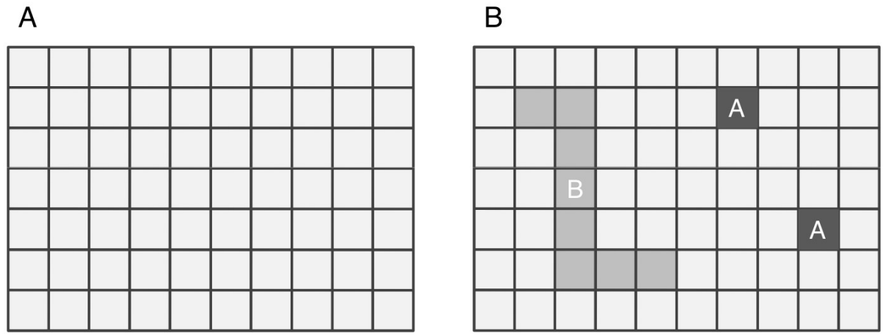
Source: N. Hilal, A. F. Ismail, and C. Wright, Membrane Fabrication. CRC Press, 2015.

THEORETICAL CONSTRUCTION

Theoretical construction in ternary diagram based on extended **Flory-Huggins** theory:

$$\frac{\Delta G_m}{RT} = n_1 ln\phi_1 + n_2 ln\phi_2 + n_3 ln\phi_3 + g_{12}(u_2) n_1 \phi_2 + \chi_{13} n_1 \phi_3 + \chi_{23} n_2 \phi_3$$

Binodal cu …etween two phases:



With: ΔG_m = Gibbs free energy of mixing

n_i = moles of component i

ϕ_i = volume fraction of component i

g_{ij} = binary interaction parameter

χ = Flory-Huggins interaction parameter

$u_2 = \frac{\phi_1}{\phi_1 + \phi_2}$

$_1$, $_2$ & $_3$ = nonsolvent, solvent & polymer, respectively

Spinodal curve, boundary between unstable and metastable region

$$\frac{\partial^2 \Delta G}{\partial \phi^2} = 0$$

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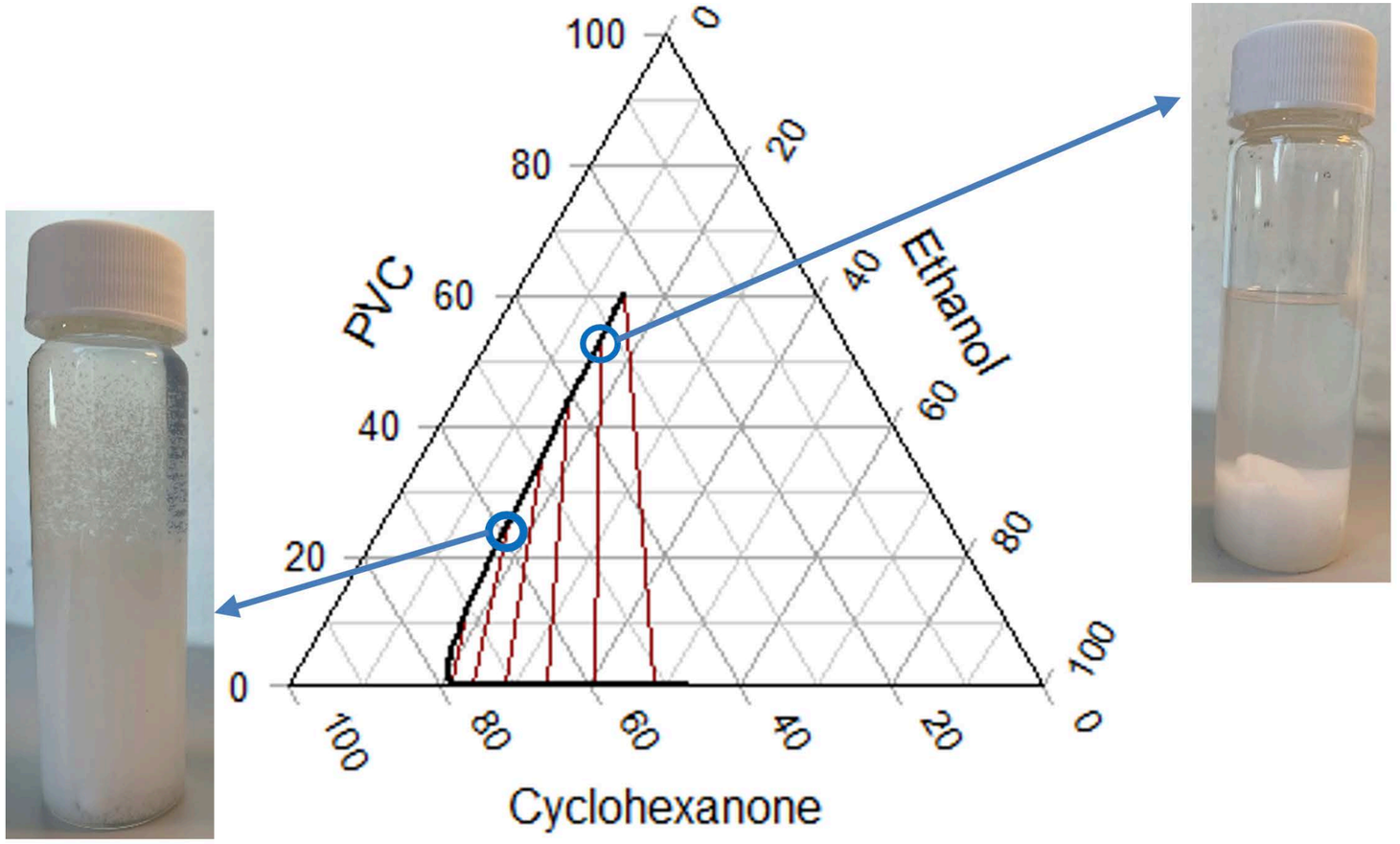
BUT WHAT DOES IT SAY?

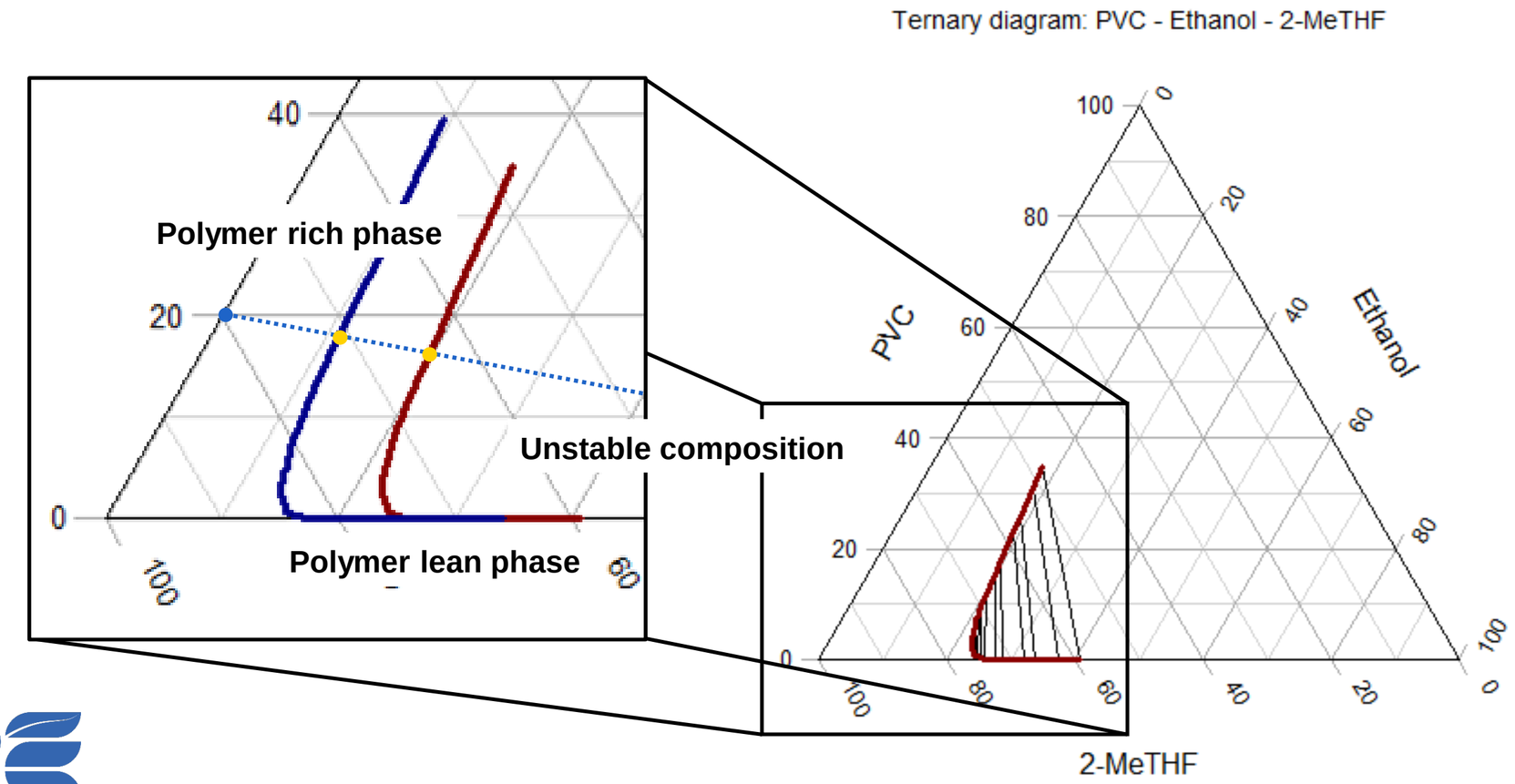
Precipitation form depends on:

- NS/S-ratio
- Temperature
- …



WHAT ELSE DOES IT SAY

- Mass balances
- Minimum nonsolvent addition



PHTHALATE ANALYSIS

Polymer sample

Vacuum drying

Cryo ball mill

Ultrasonic extraction

TGA

GC-MS

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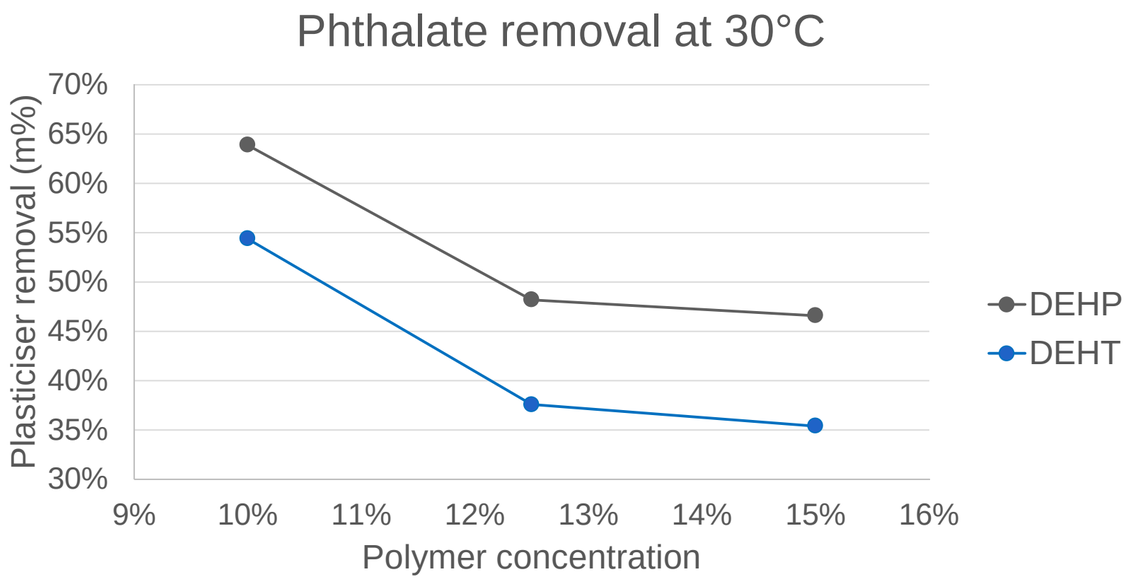
PHTHALATE REMOVAL (PRELIMINARY DATA)

Temperature (°C)	Polymer concentration in solution (m%)	DEHP removal (m%)	DEHT removal (m%)
20	10	59.3	48.9
20	12.5	46.7	35.4
30	10	63.9	54.4
30	12.5	48.2	37.6
30	15	46.6	33.6



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CONCLUSION

Prediction of:

- Nonsolvent requirements
- Polymer precipitation
- Phase compositions
- Mass balances

Plasticisers are removable, but:

- Further optimisation required
- Include more plasticisers

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