POLYOLEFIN DISSOLUTION KINETICS: EFFECTS OF PARTICLE SIZE, TEMPERATURE, AND SOLVENT

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BACKGROUND

- Polyolefins dominate plastics: **~200 Mt** produced annually
- PP ≈ **42%** of polyolefin production in 2023
- Only **~3%** of PP recycled → ~76 Mt/year waste

PP recycling is challenging:
- Widely used, poorly recycled
- Recycling limited by contamination, degradation, and additives

Mechanical recycling: Thermal processing degrades PP, limiting reuse quality.
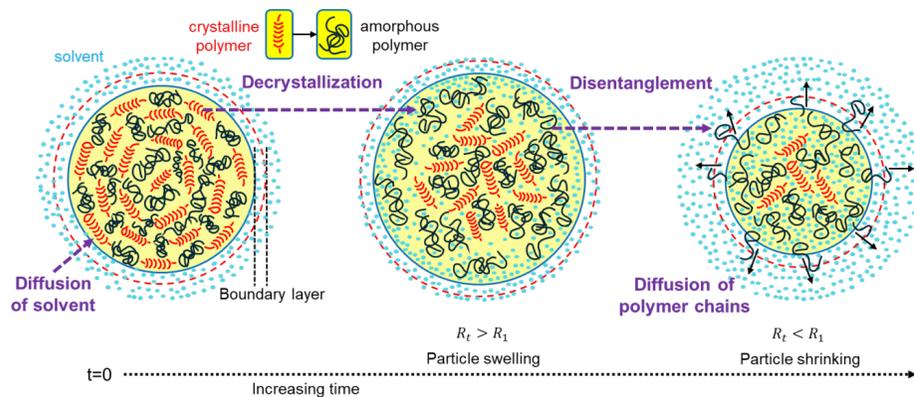**Chemical recycling:** Energy-intensive and greenhouse-gas emitting.

Dissolution/precipitation recycling

✓ Retains polymer molecular structure (true recycling)

Key advantages: ✓ Lower energy use and emissions than pyrolysis
✓ Removes additives and impurities effectively

Knowledge gap: Polyolefin dissolution mechanisms remain poorly understood

NOVELTY
- First mechanistic model for polyolefin dissolution kinetics
- Links microscopic mechanisms to macroscopic dissolution behavior
- Predictive power across particle sizes, temperatures, and solvents

SPHERICAL PP PELLET DISSOLUTION MODELING

solvent | crystalline polymer → amorphous polymer
Decrystallization | Disentanglement
Diffusion of solvent | Boundary layer | Diffusion of polymer chains
$R_t > R_1$ Particle swelling | $R_t < R_1$ Particle shrinking
t=0 ———— Increasing time ————→
(1) Initial semicrystalline particle | (2) Solvent diffusion, swelling and decrystallization | (3) Chain disentanglement and dissolution

Solvent diffusion
$$\frac{\partial \emptyset_s}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_s \frac{\partial \emptyset_s}{\partial r}\right)$$

Vrentas-Duda free volume theory
$$D_s = D_{1a}[(1 - 2\chi_a\emptyset_{1a})(1 - \emptyset_{1a})^2](1 - \emptyset_c)$$

- Solvent volume fraction ($\emptyset_s$)
- Crystalline domains ($\emptyset_c$)
- Temperature
- Type of solvent & polymer

Polyolefin decrystallization
$$\frac{\partial \emptyset_{p,c}}{\partial t} = -k_{dec}\emptyset_{p,c}\emptyset_s$$

Diffusion of polymer chains in boundary layer
$$\frac{\partial \emptyset_{p,a}}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_p \frac{\partial \emptyset_{p,a}}{\partial r}\right) - \frac{dR}{dt}\frac{\partial \emptyset_{p,a}}{\partial r}$$

Polyolefin chain disentanglement
$$D_p \frac{\partial \emptyset_{p,a}}{\partial r} = -r_{dis}$$

All parameters are known, except the two fitting parameters: **K_dec & r_dis**
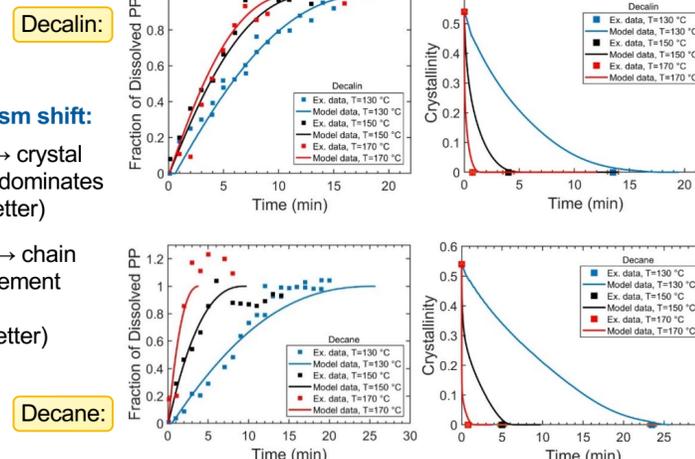
ABSTRACT:

Solvent resistance, or resistance to solvent swelling and dissolution, is a highly desirable property of semicrystalline polyolefins, which enables their applications in packaging, consumer goods, and industrial products. However, recalcitrance to dissolution can hinder the solvent processing of polyolefins. Thus, there is both a need for fundamental understanding of semicrystalline polymer dissolution, and an opportunity for the development of environmentally responsible solvents and processes capable of dissolving polymers that are not meant to dissolve.

To this end, using a joined experiment and modeling approach, we resolve the fundamentals and identify suitable solvents and conditions for the dissolution of semicrystalline polyolefins, the majority constituents of plastic waste, and a prime candidate for dissolution-precipitation recycling. A phenomenological model that captures the phenomena governing the dissolution of semicrystalline polymers, i.e., solvent diffusion, transformation from crystalline to amorphous domains, specimen swelling, and polymer chain untangling, is validated for the cases of high-density polyethylene (HDPE) and polypropylene (PP) dissolution. Parametric sensitivity analysis assesses the impact of various parameters on polymer dissolution: film thickness or particle radius, initial degree of crystallinity, temperature, solvent type.

This work offers insights on the interplay of decrystallization and polymer chain disentanglement during the time-course of HDPE and PP dissolution. Further, this work facilitates the design and optimization of dissolution-precipitation recycling process that can unlock value from the million tons of polyolefins annually that are currently being landfilled or incinerated following their use.

FITTING MODEL TO EXPERIMENTAL DATA

- Model accurately captures **dissolved PP fraction** and **crystallinity evolution**.
- Key parameters **K_dec** (decrystallization rate) and **r_dis** (disentanglement rate) were obtained via fitting the model to experimental data.
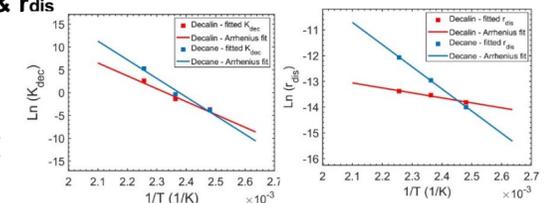
Decalin:

Mechanism shift:
- Low T → crystal disruption dominates (decalin better)
- High T → chain disentanglement dominates (decane better)

Decane:

## EFFECT OF TEMPERATURE ON K_dec & r_dis

Arrhenius behavior:
- Decalin: lower decrystallization E_a → faster crystal disruption
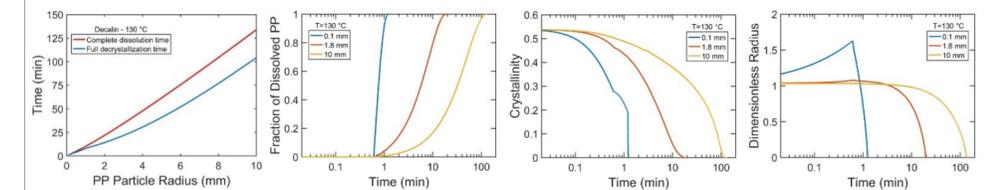- Decane: higher disentanglement E_a → faster chain disentanglement at high T

EFFECT OF SOLVENT TYPE ON K_dec & r_dis

Solvent impacts **K_dec & r_dis** via size & shape

Mechanism:
- Moderate T → size: decalin better (smaller, lower χ)
- High T → shape: decane faster (linear, PP-compatible)
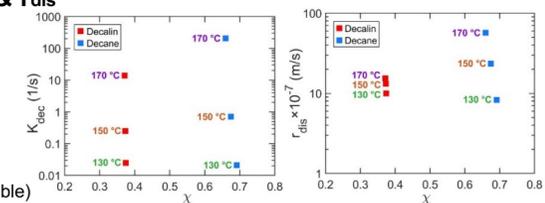
EFFECT OF PARTICLE SIZE ON K_dec & r_dis

- Rate-limiting step shifts from decrystallization (small) to disentanglement (large).
- Small particle → fast swelling & uniform dissolution
- Large particle → slow, crystalline core persists; chain disentanglement limits rate

CONCLUSIONS

- Model validated for HDPE and PP dissolution across solvents & temperatures.
- Arrhenius-type kinetics show temperature dominates over solvent effects.
- Solvent chemical structure & particle size shift the controlling mechanism:
  - Decalin disrupts crystals more effectively at low T; decane enhances disentanglement at high T
  - Particle size strongly affects kinetics via diffusion limitations
- The extracted kinetic parameters (K_dec, r_dis) enable predictive design of dissolution-precipitation recycling systems by optimizing solvent choice, operating temperature, and feedstock particle size.
- The framework is extendable to other semicrystalline polymers, supporting the scale-up of advanced recycling processes.

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