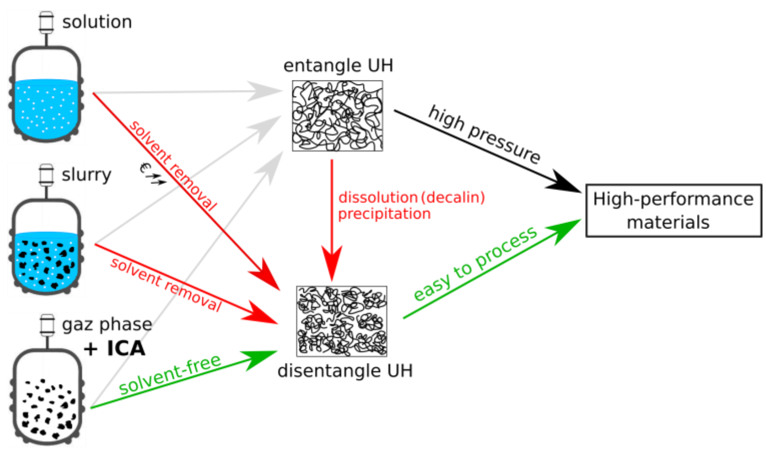
Crystallization and Entanglement of Ultra-High Molecular Weight Polyethylene

Laboratory : Catalysis, Polymerization, Processes and Materials (CP2M).
Funding : Ministère de l'Enseignement supérieur et de la Recherche
Contract : Doctoral contract (3 years)
Discipline : Catalysis / Polymer / Physical-chemistry
Deadline for application : April 1, 2024
Start date : September 1, 2024

Ultra-high molecular weight polyethylene (UH) is an exceptional material with a molecular weight exceeding one million g/mol, endowing it with remarkable physical properties. Due to its outstanding physical properties (high resistance to abrasion, impact and fatigue) UH is a high value-added polymer and is often considered to be an engineering plastic. [1] While extensive entanglement of these exceedingly long UH chains enhances the polymer's toughness it also presents a challenge, as it leads to elevated melt viscosity, making the processing of entangled UH a challenging task. Typically, reducing entanglement to produce fibers or molded components involves recrystallization, often under high pressure or from diluted solutions that require flammable and toxic solvents. An alternative approach is to synthesize disentangled UH directly, with separated catalytic centers. However, these methods, relying on solution or slurry polymerization, necessitate the use of solvents, presenting industrial challenges.



In a recently completed project sponsored by the Dutch Polymer Institute,[2] the CP2M showed that the presence of induced condensing agents (ICAs) in the gas phase polymerization of ethylene on supported ZN catalysts significantly increase the crystallinity and the molecular weight of the resulting polyethylene (Mw > 3x10 6 g/mol). Using vaporized n-pentane as ICA, disentangled UH with a draw ratio of 60-100 was obtained which puts them on a par with commercially interesting products (DR = 100).[3] This method offers a solvent-free route for manufacturing disentangled UH, however, more in-depth study is required to allow us explained the role of the ICA and the relationship between entanglement and crystallization and propose an optimal process. Recent molecular dynamics (MD) simulations have enhanced our understanding of the action mechanism of ICAs, suggesting innovative ways for improving this synthesis. Preliminary MD simulations reveal that the n-alkanes used as ICA adsorb onto the surface of polyethylene (PE) macromolecules leading to a reduction in the attractive interaction between PE macromolecules. This surfactant-like behavior of ICA may be attributed to the presence of CH3 groups, which exhibit slightly lower solubility in PE compared to CH2 groups. These simulations enable us to screen various compounds as ICA and thus to explore innovative ways of synthesizing disantangle UH using branched alkanes (e.g. tert-butyl) and mixture of alkanes. However, this mechanism is most notable in early polymerization stages while later stages usually involve additional factors like crystallization and reduced chain mobility, but studying them poses inherent challenges within the MD framework. Consequently, we will employ thermal and rheological analyses to investigate the interplay between crystallization and entanglements, as well as X -ray scattering to study the crystalline morphology.

The aim of this project is thus to : (i) Identify the composition of the reaction medium required to produce disentangled UH using a heterogeneous Ziegler-Natta catalyst in the presence of various ICA. (ii) Characterize the UH microstructure/morphology using SAXS/WAXS experiment. (iii) Analyze the melting/crystallization kinetics by DSC to develop new protocols to measure the degree of entanglement. (iv) Rheological measurements on polymers in a molten state and in solution to assess the re-entanglement kinetics. This PhD project aims to optimize the production of disentangled UHMWPE and explore the relationship between its microstructure, thermal properties, and rheological characteristics.

Skills and Experience of the future PhD student

Students with a master's degree or an engineer in materials science, chemistry, physical chemistry. Experience in chemical engineering and polymer chemistry is desired. Experience with catalysis and polymer chemistry will be a plus. Finally, the candidate must demonstrate great curiosity and an interest in process engineering.

Contact

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References

[1] Kurtz, The UHMWPE Handbook, 2004 (DOI :10.1016/B978-0-12-429851-4.X5000-1)
[2] Roberta Lopes do Roasario, PhD thesis UCBL
[3] Lopes do Rosario et al. J. Polym. Sci. 2022 (DOI :10.1002/pol.20230038)