Anionic polymerisation of styrene to polymeric organic semiconductors in a microreactor

Novel Process Windows in Chemical Engineering
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Motivation

Exploitation of microreaction technology for the synthesis of complex macromolecular block copolymers via living anionic polymerisation

Objectives

→ Novel access to organic semiconductors*
→ Process enhancement due to µRT
→ Availability of a fast preparation procedure for screening purposes
→ Support an advanced technique for energy generation

Benefits of µRT

- Reduced reaction time and experimental effort
- Precise temperature control of highly exothermic reactions
- Efficient mixing of monomer / initiator
- Precise molecular weight adjustment

→ Low polydispersity index

T. Iwasaki and J. Yoshida, Macromolecules, 2005, 38, 4, 1159
Our Approach

Model synthesis I:
Experimental investigation + CFD calculations of homo polymerisation of styrene
→ Choice of micromixer
→ Determination of process parameters

Model synthesis II:
Blocking of polystyrene with a dialdehyde for coil-rod-coil ABA triblock copolymer synthesis

Synthesis of organic semiconductors with ABA triblock structure containing pi-conjugated poly(phenylenevinylene) and polystyrene segments

Accompanying SLCA investigations for green process design
Experimental Plant
Testing of Micromixers via Homo Polymerisation of Styrene

IMM Interdigital Micromixer (SSIMM)

**Ag/Cu-LIGA**-mixing element
- Clogging

**Stainless steel**-mixing element
- Partly clogging, but
  - High mixing efficiency
  - PDI between 1.2 and 1.4
LTF Mixers
- Steady performance

Chicane mixer MSLT
- Insufficient mixing efficiency for anionic polymerisation in polar solvents
- PDI on an average of 1.8

Split and Recombine Mixer VST 3-1
- High mixing efficiency
- Homogeneous polymers (PDI: 1.1 – 1.3)
- 3. inlet for quenching or blocking
Determination of reaction engineering characteristics of different micromixers

Software tool: ANSYS CFX

**Determination of:**
- Mixing quality
- Mixing time
- Residence time distribution
- Analysis of fluid dynamics

**Mixer:**
- IMM Interdigital Micromixer (SSIMM)
- LTF Y-Mixer (reference mixer)
- LTF Chicane Mixer (LTF MSLT; MR-Lab Series)
- IMM Caterpillar Micromixer with different channel widths (CPMM-R300/12, CPMM-R600/12, CPMM-R1200/8)
Mixing time

→ Time for achieving a mixing degree of 95 %
IMM Caterpillar Mixer 300 μm

- No clogging
- Steady performance
- PDI: 1.1 – 1.2

Split-and-recombine micromixers favourable for anionic polymerisation
Comparison of Environmental Impacts

Cumulative Energy Demand - Scaled Impact

- Solvent disposal
- El. current, synthesis
- El. current, S recycling
- Ar (l)
- N2 (l)
- CO2 (s)
- n-BuLi in n-heptane
- Propanol
- n-BuLi in n-hexane
- Methanol
- Tetrahydrofuran
- Styrene

S comb = solvent combustion
S recyc = Solvent recycling
Sty 10w% = 10 w% Styrene

Synthesis of Block-Copolymers

**Organic semiconductors**
Integration of chromophores into the polymer backbone to control the optical, electronic and physical properties

**Bulk heterojunction photovoltaic devices**
Current power conversion efficiency (PCE): 5 %
→ PCE of more than 10% is foreseeable*

Rod-Coil Copolymers

**Coil:**
- Flexible
- Not conjugated
- No absorption in VIS spectrum
- Alkyl or oligo(ethyleneglycol), PS, PMMA

**Rod:**
- Rigid
- Conjugated
- Defined optoelectronic properties
- Oligo- or poly-phenylene, -phenylenevinylene, -phenyleneethinylene

Diblock- (A), Triblock- (B), Multiblock- (C) Rod-Coil Copolymer
IR spectroscopy: Absence of aldehyde group $\rightarrow$ double-sided conversion

GPC: narrow PDI $< 1.3$ $\rightarrow$ in both types of split-and-recombine micromixer

$\rightarrow$ Fast preparation of triblock copolymers available via $\mu$RT
Next steps...

- Synthesis of ABA triblock copolymers containing pi-conjugated poly(phenylenevinylene) and polystyrene segments
- Control of bandgap and redox potential of ABA triblock copolymers for optimised photovoltaic applications
Conclusion

- Selection of best suitable micromixer and reaction conditions by experimental testing + CFD calculations
  → Split-and-recombine micromixer
- Accompanying environmental assessment (SLCA):
  - Recyclability of solvents
  - $\mu$RT → environmental benefits compared to batch mode
  - Estimation of potential impacts of production scale processing leads to similar results
- Model syntheses I and II → Reproducible results and narrow PDIs
- Current target: implementation of previous results into the synthesis of chromophoric macromolecular block copolymers
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