Case Studies with Optimal Estimation of Reactivity Ratios in Terpolymerization Systems

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Introduction

- **Terpolymerization systems are of great importance** in both academia and industry, and there is always a need for understanding the underlying kinetics of such complex reaction systems.
- **Reactivity ratios** describe the tendency of incorporation of monomers with respect to each other.
- Based on an analogy between copolymerization and terpolymerization mechanisms, binary reactivity ratios have been **commonly, albeit misleadingly,** used in models dealing with terpolymerizations.

- ***Our objectives:***
  - ✓ **Illustrate the correct approach for estimating ternary reactivity ratios directly based on terpolymerization data**

Experimental Case Study

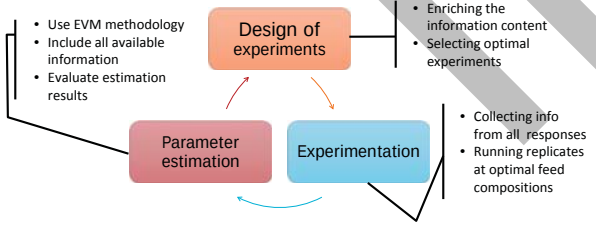
Terpolymerization
2-Acrylamido-2-methylpropane sulfonic acid (AMPS),
Acrylamide (AAm), Acrylic acid (AAc)

- A water-soluble polymer with several applications in enhanced-oil-recovery, drug delivery, wastewater treatment, …
- Reactivity ratios
  - *inform about kinetics of this system*
  - *improve the prediction performance of the model for further studies*
- A systematic study for determining reactivity ratios for this system:

Binary reactivity ratio estimates → **Preliminary terpolymerization experiments** → **Optimal terpolymerization experiments** → **Ternary reactivity ratio estimates**

EVM Framework

- A sequential process, within the Error-in-Variables-Model (EVM) context, that provides the most reliable reactivity ratio estimates

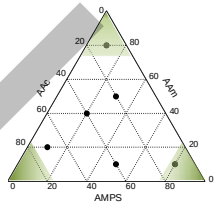


Literature Binary Reactivity Ratios

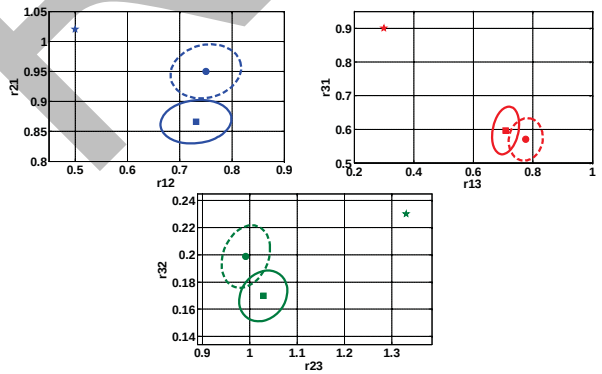
AMPS/AAm copolymerization	• AAm is more reactive than AMPS • Reactivity ratios at pH=7 : r_{AMPS}=0.5, r_{AAm}=1.02
AMPS/AAc copolymerization	• AAc is more reactive than AMPS. • Reactivity ratios at pH=7 : r_{AMPS}=0.3, r_{AAc}=0.9
AAm/AAc copolymerization	• AAm is much more reactive than AAc. • Reactivity ratios at pH=7 : r_{AAm}=1.33, r_{AAc}=0.23

Ternary Reactivity Ratio Estimation

- Experiments were performed at 40°C, pH=7, [M]=1
- Samples were collected at low conversion levels as well as at medium-high conversion levels
- The experiment with **80% AAm has the highest rate** of polymerization and the experiment with **70% AAc has the lowest rate** of polymerization.
- Green regions → **optimal feed compositions**



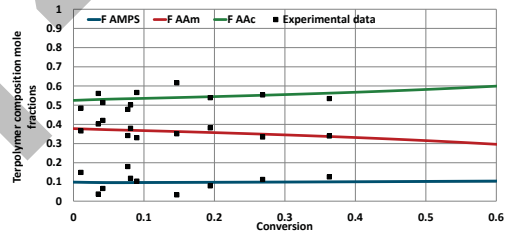
AMPS (M_1) – AAm (M_2) – AAc (M_3)
Reactivity ratio estimates, complete data set (—) , optimal data (- - -)



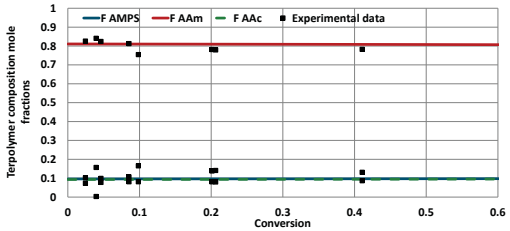
- Overall, the ternary reactivity ratio estimates **differ from binary values**.
- Reactivity ratio estimates from the complete data set and optimal data are in agreement, while the optimal reactivity ratios are estimated with only three experiments (**50% less experimentation)!**
- This system should have an **azeotrope at 0.155/0.840/0.005** feed composition.

Terpolymer Composition Predictions

Terpolymer composition mole fraction versus conversion for 0.1/0.2/0.7 experiments



Terpolymer composition mole fraction versus conversion for 0.1/0.8/0.1 experiments



- The optimal ternary reactivity ratios provide **very good predictions** for the experimental data.
- A '**pseudo-azeotropic' composition (0.1/0.8/0.1)** shows almost **no composition drift.**

Concluding Remarks

- The **correct approach for estimating ternary reactivity ratios** is illustrated for the AMPS/AAm/AAc terpolymerization system.
- Optimal ternary reactivity ratios are estimated based on **three experiments** only!
- Ternary reactivity ratios show **considerable differences compared to binary** reactivity ratios.
- The joint confidence regions and the prediction results confirm that the EVM framework provides **reliable** and **accurate** reactivity ratios for this terpolymerization system, and for terpolymerizations, in general.

Bibliography

- Kazemi, N., Duever, T. A., and Penlidis, A., *AIChE Journal* (2014), 60, 1752-1766.
- Kazemi, N., Duever, T. A., and Penlidis, *Computers & Chemical Engineering* (2013), 48, 200-208.
- Riahinezhad, M., Kazemi, N., McManus, N., & Penlidis, A., Journal of Polymer Science Part A: Polymer Chemistry, (2013), 51, 22, 4819-4827.
- Abdel-Azim, A.-A. A., Farahat, M. S., Atta, A. M. and Abdel-Fattah, A. A., Polymers for Advanced Technologies (1998), 9, 282–289