Optimal Design of Experiments Applied to Complex Polymerization Processes

A. Nabifar, N.T. McManus, and A. Penlidis, Institute for Polymer Research (IPR),
Department of Chemical Engineering, University of Waterloo

INTRODUCTION

A *systematic approach* to studying complex polymerization processes consists of two major phases:

- Using a mechanistic mathematical model to improve process understanding which will eventually lead to more effective process troubleshooting and optimization
- Extensive data collection and sample characterization through the full conversion range to maximize the information content of the process
  - However, without carefully planned experiments, there would be little information content to maximize!

It is extremely important to avoid performing many tedious experiments and analyses only to find that the data collected have virtually no information content.

Design of experiments using rigorous statistical techniques!

CLASSICAL STATISTICAL DESIGN

- Elegant and efficient
- Very useful for obtaining scientifically acceptable estimates of parameters of fundamental importance in science and engineering

However:

- Classical statistical theory designs large number of experiments
  - Provides fractional factorial experiments **but** often resources available do not match the number of trials
- Other problems such as
  - Missing observations
  - Impractical treatment combinations
  - Redefinition of factor levels
  - Dropping/ adding factors
  - Mixed number of levels

BUT more importantly:

- Only minimal amount of prior knowledge is used
  - Purpose of an experiment is often to **strengthen an opinion** which is already held

While some of the above problems have solutions which are known to experts in the design of experiments, it often happens that the practicing scientist or engineer cannot handle them and gives up on the use of statistical designs!

What is the solution?

Bayesian design of experiments

BAYESIAN DESIGN OF EXPERIMENTS

- Requires fewer trials
- No confounding of any of the effects
- Experimental flexibility; no restrictions in number of experiments, sequence of experimentation, factor levels, dropping/adding factors, etc.

BUT what is the "trade-off"? Is this really a "trade-off"? No! Actually, it is an additional advantage!

- Requires prior knowledge
  - Exercise of casting the prior knowledge about a process into a mathematical form forces the experimenter to brainstorm/hypothesize and perhaps come to a clearer understanding of the process or even anticipate/solve some of the problems that triggered the experiments even before starting the experiments
  - Prior information can be updated in a sequential manner, thus allowing, in parallel, the optimal update of key unknown parameters
  - Prior information involves contributions from both the prior experimental region and a (usually non-linear) mathematical model for the process, thus making use of both experimental information and mechanistic models (in a way similar to optimal filtering techniques)

PROCEDURE FOR BAYESIAN DESIGN OF EXPERIMENTS

How do we choose the next best experiment(s)?

The procedure is **optimal**, **sequential**, and **iterative**; it contains several steps that are omitted here for the sake of brevity.

IMPLEMENTATION OF BAYESIAN DESIGN

A) Nitroxide-Mediated Radical Polymerization (NMRP) of Styrene

- Direct extension of MASc degree work
- Through MASc research in NMRP of styrene we made the following three important observations:
  - Many groups were making (rather unfounded) mechanistic claims, based on only a few data points over a typical course of polymerization of about 50 hrs
  - Hardly any group employed rigorous principles from the statistical design of experiments
  - Hardly any group tried to combine the available information from both experimental observations and mathematical models in an experimental design scheme
- The project will involve both experimental and modeling stages, leading eventually to a protocol for optimal design of experiments/ parameter estimation based on complex non-linear mechanistic models

B) Emulsion Copolymerization of Acrylonitrile or Styrene with Butadiene (NBR/ SBR rubber)

- Revived interest from industry (automotive, construction, specialty products)
  - Large volume production for commodity polymers (CSTR train)
  - Specialty products (value-added)
  - New interest in "nanotechnology"
- Quality specs; customers are becoming more demanding (superior environmental resistance and strength properties)
  - Production of tailor-made polymeric materials to fit the performance requirements of each application
- Selective and minimum of experimentation extremely important to minimize waste, loss of production, and go to target properties as quickly as possible (optimal grade transition)

C) Multi-Component Polymerization Systems with Depropagation at Elevated Temperatures

- Is there a practical way to estimate reliable values of equilibrium constants?
- How can we narrow down the "experimental region" to the "optimal" one?

D) Polypropylene (PP) Degradation Using Conventional and Tetra-Functional Peroxides

- PP can be degraded to give narrow MWDs but difficult to impart branching
- Could a tetra-functional initiator do that and, if so, what would the benefits be?

CONCLUDING REMARKS

- The Bayesian approach (based on Bayes theorem) to the design of (fractional) factorial experiments represents a largely unstudied and improved approach
- It accommodates practical limitations usually encountered in real experiments
- It is optimal, sequential, iterative, and combines powerful non-linear mechanistic models with experimental information (essentially, an **optimal model-based design of experiments**)
- The Bayesian approach has the distinct advantage of incorporating prior knowledge into the design
  - Limits on time and material resources make the Bayesian design of experiments particularly attractive from an industrial perspective