A course in . . .

POLYMERIZATION REACTOR ENGINEERING

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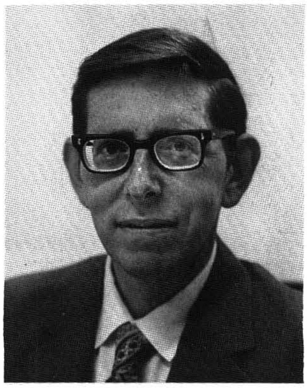
MICHIGAN TECHNOLOGICAL University, together with the Michigan Molecular Institute (MMI) and Central Michigan University, has formed the Michigan Polymer Consortium to provide graduate degree programs and collaborative research in polymer science and technology. Michigan Tech brings to the consortium the particular strengths of a combined Department of Chemistry and Chemical Engineering, conducive to interdisciplinary research, and an extensive research program in polymer composite materials.

In support of the polymer research program the department of chemistry and chemical engineering at Michigan Tech has structured a series of elective courses, open to graduate students and qualified seniors, grouped in four blocks (see Table 1). Although the blocks stand by themselves and can be taken in any order, students are advised to traverse the sequence in the direction shown.



J. M. Skaates received his BSc (1957) at Case Institute of Technology and his MS (1958) and PhD (1961) at Ohio State University. He worked at California Research Corporation for three years before joining the faculty at Michigan Tech. His teaching duties have included undergraduate and graduate courses in thermodynamics and kinetics, an undergraduate course in process control, and graduate courses in catalysis and in process optimization. He has been involved in research in catalysis, biomass pyrolysis, and wet oxidation.

TABLE 1
Sequence of Polymer Courses

Polymer Chemistry →	*Polymerization Reactor Design* →	*Polymer Forming Operations* →	*Composite Materials*
Polymer synthesis Polymer properties	Design and operation of polymerization reactors	Rheology Extrusion Molding etc.	Compounding and mechanical properties of composites
(five courses)	CM490	(three courses)	(courses in materials science and solid mechanics)

The polymerization reactor engineering course (CM 490) has as its focus the design and operation of industrial polymerization reactors to achieve a desired degree of polymerization and molcular weight distribution. Topics covered in the ten-week course are shown in Table 2. For the benefit of students who have not taken the polymer chemistry courses, the mechanisms and kinetics of polymerization reactions

TABLE 2
Topics Covered in CM490

- Kinetics of condensation polymerization
- Design of condensation polymerization reactors
- Design of agitated thin-film evaporators
- Kinetics of addition polymerization
- Mechanism of free-radical addition polymerization
- Autoacceleration
- Predicting molecular weight distribution in addition polymerization
    - Generating function method
    - Moment generating function
    - Z transform methods
    - The continuous variable technique
- Gel permeation chromatography
- Copolymerization kinetics
- Types of polymerization reactors
- Control and stability of addition polymerization reactors
- Optimization of polymerization reactors
- Flowsheets for the production of polystyrene
- Flowsheets for the production of polyethylene

are treated first. From the many available textbooks emphasizing different aspects of polymer science, the text by Rudin [1) was chosen because of its outstanding treatment of polymerization kinetics.

Polymerization reactor design and operation are taught with the aid of a series of literature articles (Table 3). These were selected to illustrate the development of experimental technique and sophistication of modeling during the past two decades. These papers are assigned, in the order shown, at the rate of two or three per week. Students must answer a series of written questions on each paper and these homework assignments constitute 20% of the course grade. Discussion of the papers, led by student volunteers, is carried out at the weekly recitation session.

TABLE 3
Assigned Outside Readings

1. Duerksen, J. H., A. F. Hamielec, and J. W. Hodgins, "Polymer Reactors and Molecular Weight Distribution: Part I. Free Radical Polymerization in a Continuous Stirred Tank Reactor," *AIChE J 13*, 1081 (1967)
2. Hamielec, A. F., J. W. Hodgins, and K. Tebbens, "Polymer Reactors and Molecular Weight Distribution: Part II. Free Radical Polymerization in a Batch Reactor," *AIChE J 13*, 1087 (1967)
3. Albright, L., and C. G. Bild, "Designing Reaction Vessels for Polymerization," *Chem. Eng.*, Sept. 15, 1975, 121-128
4. Gerrens, Heinz, "How to Select Polymerization Reactors," Part 1: *CHEMTECH*, June, 1982, 380-383, Part 2: *CHEMTECH*, July, 1982, 434-443
5. King, P. E., and J. M. Skaates, "Two-Position Control of a Batch Prepolymerization Reactor," *I&EC Process Des. and Dev. 8*, 114 (1969)
6. Wallis, J. P. A., R. A. Ritter, and H. Andre, "Continuous Production of Polystyrene in a Tubular Reactor," Part I: *AIChE J 21*, 686-691 (1975), Part II: *AIChE J 21*, 691-698 (1975)
7. Chen, C. H., J. G. Vermeychuk, J. A. Howell, and P. Ehrlich, "Computer Model for Tubular High-Pressure Polyethylene Reactors," *AIChE J 22*, 463 (1976)
8. Marini, L., and C. Georgakis, "Low-Density Polyethylene Vessel Reactors: Part I: Steady-State and Dynamic Modeling, Part II: A Novel Controller *AIChE J 30*, 401-415 (1984)
9. Henderson, L. S., "Stability Analysis of Polymerization in Continuous Stirred Tank Reactors," *Chem. Eng. Prog.*, March, 1987, 42-50
10. Mutsakis, M., F. A. Streiff, and E. Schneider, "Advances in Static Mixing Technology," *Chem. Eng. Prog.*, July, 1986, 42-48
11. Choi, K-Y, and W. Harmon Ray, "The Dynamic Behavior of Fluidized Bed Reactors for Solid Catalyzed Gas Phase Olefin Polymerization," *Chem. Eng. Sci. 40*, 2261-2279 (1985)

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The study of reactor modeling centers largely around the work of the two leading research groups in the field—those of W. Harmon Ray at the University of Wisconsin-Madison, and of A. Hamielec at McMaster University.

Two weeks of the course are devoted to the difficult problem of predicting the molecular weight distribution in a free-radical addition polymerization. The topic begins with a discussion of the possibility of direct solution of all the rate equations, as exemplified by the monumental paper of Liu and Amundson [2]. Attention is then directed to mathematical techniques for compressing these equations using generating functions or the z transform. It is emphasized that limiting assumptions are often required to make these techniques computationally feasible. Finally, the continuous variable technique, pioneered by Zeman and Amundson [3], is presented as the logical successor to the other methods. A twenty-page handout tracing the important mathematical ideas in Zeman's thesis is given to the students. It is shown that Zeman's idea of replacing the discrete variables by continuous variables has been successfully applied to other fields (size reduction, crystallization, aerosol physics) where detailed population balances are required to understand observed rate behavior.

Industrial practice in polymerization reactor design is introduced with the excellent review articles of Albright and Bild, and Gerrens. These are supplemented by a series of overhead transparencies showing polymerization reactors in industrial installations. Auxiliary equipment (agitated thin film evaporators, motionless mixers, vented extruders) used to complete the polymerization and remove unreacted monomer, is also described. The course closes with the study of flowsheets for two important families of polymers (polystyrene, polyethylene), starting with monomer synthesis and purification, and going to the various grades of finished polymer.

REFERENCES

1. Rudin, Alfred, *The Elements of Polymer Science and Engineering*, Academic Press, 1982.
2. Liu, S.-L., and N. R. Amundson, *Rubber Chem. and Technology* 34, 995 (1961).
3. Zeman, Ronald J., "Continuous Polymerization Models," Thesis, U. of Minnesota, 1964. □