A Course on

POLYMERIZATION REACTION ENGINEERING

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IN RECENT YEARS POLYMER science and engineering has become an integral part of almost every chemical engineering curriculum. The transition of polymer education from chemistry to chemical engineering and the significant interest in polymer research within ChE Departments have been explained in recent reports as a natural trend of the interdisciplinary approach of chemical engineering. A 1977 *Chemical and Engineering News* report [1] points out that at least 30% of the graduating chemical engineers will be employed by industries involved in polymers. The annual guide of the Plastics Institute of America [2] reveals that chemical engineering is the center of polymer activities in 65% of the universities with active polymer programs. Even more surprising are the results of a recent survey of undergraduate and graduate polymer education conducted among chemical engineering departments [3]. Out of 88 ChE departments that replied to this survey, 63 offer at least one polymer course, while thirteen departments offer at least five different polymer courses.

Most chemical engineering programs offering one course in polymers concentrate on a survey of polymer science and engineering, usually emphasizing the basics of polymer characterization, polymerization kinetics and polymer processing. For programs offering more than one polymer course, the natural trend is toward teaching of separate courses on rheology and processing, physical chemistry and mechanical behavior of polymers [4]. However, polymerization reaction engineering is less frequently taught as a separate course. Turning again to the preliminary data of the AIChE survey [3], it is noted that out of 188 surveyed courses, only fourteen are courses specializing in polymerization reaction engineering. This area is usually treated as a graduate subject, and ten of the courses offered are addressed to graduate students. Individual questionnaires attribute this trend partially to the apparent lack of an appropriate textbook in this area and to the many complexities of polymerization reactions which require advanced knowledge in related areas.

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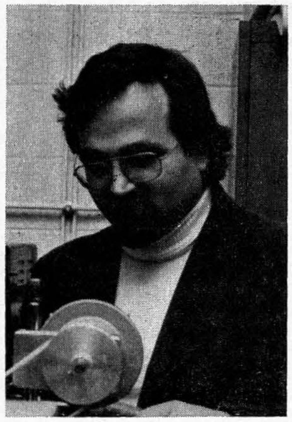
The rather unfortunate lack of emphasis on the engineering aspects of polymerization reactions is of some concern, especially since reaction engineering is a "natural" for chemical engineers. Certain educators claim that a combination of an undergraduate or graduate reaction engineering course with basic knowledge of polymerization kinetics obtained in a general polymer course adequately cover the needs in polymerization reaction engineering. Our disagreement stems from the fact that the study of polymerization reactions differs significantly from the study of more conventional chemical reactions.

Reactions of macromolecules evince a range of phenomena which are distinctly different to the ones observed in most of the reactions of small molecules. Kinetically the steps of initiation, propagation and termination may comprise a series of reactions (characterized by distinct kinetic constants) which contribute towards the formation and growth of a specific chain. The type of initiation is of importance in most polymerization rates. In addition, the termination step controls important polymer properties. In some types of polymerization reactions the termination step is non-existent leading to non-terminated macromolecular chains constituting living polymers. Premature termination of growing chains can be observed when chain transfer reactions to the monomer, initiator or solvent prevail. Finally, important differences in the kinetic mechanism (e.g. step versus chain polymerization) may lead to considerable differences in reactor design.

It must be emphasized that understanding of the reaction parameters is most important in controlling polymerization rate, molecular weight and molecular weight distribution, polymer



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particle size and its distribution, and structural modification such as crosslinking and branching.

With very few exceptions polymerization reactions lead to macromolecular systems with a wide distribution of molecular weights. The mobility of growing macromolecular chains and/or the lack thereof, is responsible for impediment of termination, autoacceleration (Trommsdorff) effects, diffusion-controlled effects etc. Side reactions in the presence of functional groups and small quantities of crosslinking agents can lead to highly branched and crosslinked polymers. Thus, a phenomenon, which in "conventional" chemical reactions could be considered highly undesirable, is effectively used to provide polymers with important structural characteristics and desirable properties. Finally, phenomena related to continuous increase of the viscosity of the reacting medium affect mass and heat transfer, in turn creating a series of challenging engineering problems related to modelling, design and operation of polymerization reactors.

Although incomplete in many aspects, this partial list of special phenomena observed in polymerization reactions shows that conventional chemical reaction engineering cannot provide the answers to all the challenging questions of this area. In fact, polymer reaction engineering requires background knowledge extracted from such diverse fields as probability theory, organic and physical chemistry, transport phenomena, control theory etc.

Here we present a new polymer course which was recently developed and favorably received by both graduate students and qualified seniors in chemical engineering. ChE 543, *Polymerization Reaction Engineering* is a three credit-hour course offered usually in the fall semester of the academic year. At Purdue University a semester consists of fifteen weeks and one week of final examinations. Therefore, a maximum of forty five lecture hours are available, with at least three hours reserved for quizzes and examinations.

ChE 543 can be taken independently of other polymer courses and no previous knowledge of polymers is required. Prerequisites include organic chemistry and an undergraduate course in reaction engineering. The course emphasizes the fundamentals of polymerization kinetics, methods, and reaction engineering and it includes topics on industrial operation. Kinetics and polymerization methods are covered thoroughly in approximately eight weeks in a rather fast pace. The reaction engineering aspects are discussed in the last six

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weeks of the course. Table 1 gives a detailed outline of the course subjects pointing out the special emphasis on reaction engineering topics.

Selection of an appropriate textbook for ChE 543 or similar courses is a rather difficult task. The textbook by G. Odian, *Principles of Polymerization*, McGraw-Hill, 1971 is highly recommended as the basic reference for the kinetics portion of the course. Topics covered in Odian's book (excluding Chapters 7 and 9) are extensively discussed in the first eight weeks. Notes and review articles (see Table 2) are presented where we feel that additional emphasis is required. Typically five to seven articles of this list will be used in a semester as additional reading material. For example, subjects covered in depth include molecular weight distributions, Markov chains and stochastic processes, gelation theory, Z-transforms, fundamentals of copolymerization reactions, and the kinetics of emulsion polymerizations. Additional reference books on reserve for this course are listed below, with reference to the chapters covered in ChE 543.

- A. E. Hamielec, Polymerization Reaction Engineering, four volumes, McMaster University, 1977; Chapters covered include 1, 2, 3, 4, and 6.
- H. Sawada, Thermodynamics of Polymerization, Dekker, 1976; selected topics.
- G. G. Lowry, Markov Chains and Monte Carlo Calculations in Polymer Science, Dekker, 1970; selected topics.

Coverage of the reaction engineering aspects of polymerization is achieved mainly through notes. No book presents a thorough analysis of these subjects, although Hamielec's book (mostly in the form of chapters written by various academic and industrial authors) covers some of the basic needs for this portion of the course. J. Throne's textbook on *Plastics Process Engineering*, Dekker, 1979, appeared late in 1979 and his chapters 2 and 3 have not been tried yet in ChE 543. It is worth noting that the lack of an appropriate textbook on reaction engineering aspects of polymerization has also been noted by other educators. Out of the fourteen courses surveyed recently [3], eight use personal notes throughout the course; the only textbook with more than one user is Odian's (four courses), although the engineering aspects are again covered by notes and review articles. Preliminary notes on this subject from three different authors are used on a limited basis, and it is now known that two of these sets of notes will be published as books during 1981.

After an introductory review of chemical and physical structure of polymeric materials, a thorough analysis of molecular weights and molecular weight distributions is presented with emphasis on theoretical and empirical distributions such as the Flory, Schulz, Wesslau and other distributions. In the analysis of polycondensation kinetics, we emphasize the use of Markov chains to statistically describe polycondensation reactions. The degree of polycondensation is treated as the fundamental random variable. The probability distributions and first and second moments of the

TABLE 1: Course Outline

I. Introduction to polymer science (3 lectures)
- 1. Chemical Structure, physical behavior
- 2. Molecular weights, molecular weight distributions

II. Polymerization kinetics (20 lectures)
- 1. Polycondensation reactions
  - 1a. Kinetics, molecular weight distributions
  - 1b. Markov chains and stochastic processes
- 2. Multichain polymerization
  - 2a. Gelation theory
  - 2b. Crosslinking reactions, kinetics
  - 2c. Real networks
- 3. Radical polymerizations
  - 3a. Kinetics, initiation effects, chain transfer
  - 3b. Inhibition and retardation
  - 3c. Autoacceleration
  - 3d. Moment distribution functions (Z-transforms)
  - 3e. Thermodynamics, ceiling temperature, depolymerization
  - 3f. Pressure effects
- 4. Ionic polymerizations
  - 4a. Cationic polymerizations
  - 4b. Anionic polymerizations
  - 4c. Reactions without termination, monodispersity
  - 4d. Solvent polarity effects
- 5. Copolymerizations
  - 5a. Kinetics, chain transfer, depolymerization, penultimate effects
  - 5b. Multicomponent copolymerization
  - 5c. Q-e schemes
  - 5d. Statistical methods of determination of reactivity ratios
- 6. Stereospecific polymerizations
  - 6a. Ziegler-Natta catalysts
  - 6b. Heterogeneous catalytic reactions
  - 6c. Other reactions

III. Polymerization methods (5 lectures)
- 1. Bulk polymerization
- 2. Solution polymerization
- 3. Suspension polymerization
  - 3a. Particle size distribution and its control
- 4. Emulsion polymerization
- 5. Gaseous and plasma polymerizations

IV. Polymerization reaction engineering (12 lectures)
- 1. Modelling of polymerization reaction systems
  - 1a. Batch and semibatch operation
  - 1b. Tubular reactors
  - 1c. Continuous stirred tank reactors
  - 1d. Uniqueness and multiplicity of steady states, stability analysis
  - 1e. Copolymerization reactor design
  - 1f. Heterogeneous catalytic polymerization reaction engineering
- 2. Modelling of emulsion polymerization reactions
  - 2a. Modelling characteristics
  - 2b. Control of molecular weight distribution
  - 2c. Control of particle size distribution

V. Problems of industrial operation (5 lectures)
- 1. Industrial problems with reactor design
  - 1a. Heat and viscosity effects, hot-spots and thermal runaways, heat transfer
  - 1b. Polymer build-up, agitation
- 2. Product purification
  - 2a. Separation and drying equipment
  - 2b. Size reduction, pelletizers
- 3. Computer control of polymerization reactors
- 4. On-line testing of polymer properties

distribution are determined. This analysis is applied to difunctional monomers. Multichain polymerizations, branching and crosslinking reactions are analyzed using probability theory; the Stockmayer gelation theory is also presented and analyzed.

The lectures on radical polymerizations are straightforward, although emphasis is placed on the thermodynamics of polymerization reactions and the importance of ceiling temperatures. The kinetics of the Trommsdorff effect are analyzed in view of recent experimental results and their importance in reactor design is stressed.

Discrete moment generation functions (Z-transforms) are introduced at this point and their importance in determining the moments of a discrete distribution with applications to addition polymerization is analyzed. Other topics where special emphasis is placed include the effect of solvent polarity on ionic polymerization kinetics (cage effect) and the kinetic analysis of copolymerizations where penultimate groups effects are important. Stereospecific polymerizations are covered to considerable extent and their rather complicated kinetics are discussed.

After an analysis of the various polymerization methods (Table 1) where the student is exposed to the special characteristics of each technique and to the major difference in kinetics of each polymerization, the basics of the modelling of polymerization reactions systems are introduced. Topics of special interest include the mathematical analysis of semibatch operations, tubular reactors and copolymerization reactors. Techniques for the prediction and control of molecular weight and particle size distribution are analyzed.

The final part of this course concentrates on the analysis of heat and mass transfer related problems and computer control of polymerization reactors. Basic information on product purification is also presented to some extent.

ChE 543 presents an integral view of polymerization reactions with strong emphasis on the transition from the kinetic expressions to the design of the proper reactor. This course constitutes one of three main courses in our graduate polymer program and it is recommended in addition to ChE 544, *Structure and Physical Behavior of Polymer Systems,* (a course on statistical mechanics, physical chemistry, elasticity, viscoelasticity and diffusion in polymers) and ChE 697B, *Rheology of Macromolecular and Other Non-Newtonian Fluids.* Topics on reactive processing of polymers (e.g. reaction injection molding) are not covered in ChE 543, but rather in ChE 597N, *Processing of Polymer Solids and Fluids.* A limited number of laboratory experiments, mostly on polymerization kinetics are included in a *Polymer Laboratory* course, ChE 597 0, which will be offered this academic year. □

TABLE 2
Review Articles for ChE 543

R. Shinnar and S. Katz, Polymerization Kinetics and Reactor Design, in K. B. Bischoff, ed., "Chemical Reaction Engineering," 56-74, Advances in Chemistry Series, **Vol. 109, ACS, Washington, 1972.**

D. C. Pepper, Analogies and Discrepancies between Cationic and Anionic Polymerizations, J. Polym. Sci., Symp., **50, 51-69, (1975).**

A. T. Bell, Fundamentals of Plasma Polymerization, J. Macromol. Sci., Macromol. Chem., **A10, 369-381, (1976).**

J. Ugelstad and F. K. Hansen, Kinetics and Mechanisms of Emulsion Polymerization, Rubb. Chem. Techn., 49, **536-**609, (1976).

W. H. Ray, On the Mathematical Modelling of Polymerization, J. Macrom. Sci., Revs. Macromol. Chem., C8, **1-56, (1972).**

R. J. Zeman and N. R. Amundson, Continuous Polymerization Models. Part I, II, Chem. Eng. Sci., 20, **331-361, 637-664, (1965).**

J. A. Biesenberger, R. Capinpin and D. Sebastian, Thermal Ignition Phenomena in Chain Addition **Polymerizations,** Appl. Polym. Symp., 26, **211-236, (1975).**

R. P. Goldstein and N. R. Amundson, An Analysis of Chemical Reactor Stability and Control. Parts Xa, Xb, XI, XII, Chem. Eng. Sci., 20, **195-236, 449-476, 477-479, 501-527, (1965).**

K. W. Min and W. H. Ray, On the Mathematical Modelling of Emulsion Polymerization Reactors, J. Macrom. Sci., Revs. Macromol. Chem., **C11, 177-255, (1974).**

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1. R. L. Rawls, "Polymer Education Edges Away from Chemistry," *Chem. Eng. News, 55* (21), 19, (1977).
2. "Polymer Science and Engineering Programs," Plastics Institute of America, Hoboken, NJ 1978.
3. N. A. Peppas, "Teaching of Polymer Science and Engineering Courses in Chemical Engineering Departments," a report prepared under the auspices of the AIChE Chemical Engineering Educational Projects Committee, to be presented at the 73rd Annual Meeting, Chicago, November 1980.
4. R. G. Griskey, "A New Polymer Department—An Option Within an Existing Department of an Interdisciplinary Program: Which Route for Polymer Education?" *S.P.E. Techn. Papers, 26,* 663, (1980).