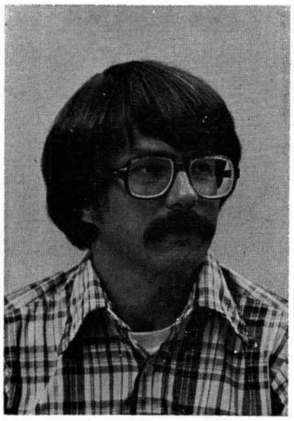
Two Courses in

POLYMER SCIENCE

CURTIS W. FRANK
Stanford University
Stanford, CA 94305

IN THE LAST THREE decades the growth of polymers as engineering materials has been phenomenal. As production levels have climbed, so has employment of chemical engineers. Currently, it is estimated that at least 30% of all Ch.E. graduates will work in some polymer related activity even though they often enter the field with no prior coursework in polymers. Certainly it is a tribute to the broad educational background of most chemical engineers that this has not impaired success. However, as demands on material performance and processing requirements become more stringent, specific education in polymer science is essential. Generally, coursework in polymers is not to be found in the traditional chemistry departments, in spite of the extensive employment of chemists in the polymer industry. [1] This task has been taken over largely by materials science and chemical engineering departments and by specialized polymer institutes or interdisciplinary groups in "macromolecular science."



Curtis W. Frank is an Associate Professor in the ChE Department at Stanford University. He did his undergraduate work at the U. of Minnesota, receiving his B.Ch.E. in 1967. His graduate training was at the U. of Illinois from which he received his M.S. in 1969 and Ph.D. in 1972. Before leaving Illinois he co-authored with Professor H. G. Drickamer the monograph **Electronic Transitions and the High Pressure Chemistry and Physics of Solids** (1972). He began his professional career at Sandia Laboratories in Albuquerque, New Mexico where he worked in the Polymer Science and Engineering Division until joining the Stanford faculty in July 1976. His research interests include the application of fluorescence methods to the study of polymer blend compatibility, solid state relaxation phenomena, and segmental diffusion in dilute solution at high pressure as well as synthesis and characterization of polyvinylidene fluoride, a piezoelectric polymer.

The polymer science research and teaching program in the Department of Chemical Engineering at Stanford consists of four faculty members: C. W. Frank (fluorescence studies of amorphous solid state blends and dilute polymer solutions, piezoelectric behavior of polymers), G. Fuller (dynamic light scattering of flowing polymer solutions and colloidal suspensions), A. S. Michaels (macromolecular transport through ultrafiltration membranes, recombinant DNA bioengineering, gas permeation of semicrystalline polymers) and C. R. Robertson (renal transport phenomena, biomaterial compatibility, recombinant DNA bioengineering). A series of four courses in polymer science are offered or are currently in preparation by three of these faculty members. This series includes Ch.E. 170 (solid state properties), Ch.E. 212 (thermodynamics and statistics), Ch.E. 217 (polymer synthesis) and Ch.E. 209 (hydrodynamics and scattering theory). The first two have been taught by the author for the past three years and will be considered in this paper in some detail. The third course, given by Professor Alan Michaels, has been presented before at the University of California–Berkeley and will be offered for the first time at Stanford during the 1979-80 academic year. The fourth course will be taught by Dr. Gerry Fuller after he joins the faculty in September 1980. The latter two courses will be outlined briefly at the end of the paper. This series should provide a sound background in most of the important areas of polymer science, with the exception of polymer processing.

The selection of these courses is a result of numerous compromises involving faculty interest and the overall course structure. The philosophy of the Stanford Ch.E. department is that a broad background in chemical engineering fundamentals is preferable to concentration in any given area. An attempt has been made to balance this view with the multifaceted nature of polymer science by offering two of the graduate courses (Ch.E. 217

and 209) as special topics on an alternate year basis. In the future, Ch.E. 212 also may be given in a similar manner. Thus, it will be possible to put together a coherent polymer program while at the same time leaving sufficient scheduling flexibility for the remainder of the curriculum.

No separate polymer laboratory course is offered at this time. However, several polymer experiments (dilatometric measurement of the glass transition, temperature, viscoelastic creep of an amorphous polymer and measurement of crystallization kinetics by differential scanning calorimetry) are included in the two quarter senior level chemical engineering laboratory.

Stanford is on ten week quarters with many department courses, including Ch.E. 170 and Ch.E. 212, being taught twice weekly for 75 minute periods. Since a single midterm is given in each, the courses are divided into nineteen lectures. Although a number of different texts have been used in each course, the lectures are organized closely around extensive class handouts. Since the pace of both Ch.E. 170 and Ch.E. 212 is rather fast, there is always the danger that the student could lose sight of the overall objectives while immersed in the details of a particular topic. Thus, much of the more tedious algebra or matrix manipulation is written out in full and supplied to the student before class. In addition, copies of figures presented via viewgraphs are provided as are detailed outlines of the lecture topics. Students are encouraged to use space provided on the handouts for notes on additional points of discussion or for analyses not written out. Ideally, the handouts should allow more time for thought on a particular topic without the burden of note taking while at the same time requiring enough effort to maintain attention. Although the class notes are still evolving, student response has been quite favorable.

Ch.E. 170, offered fall quarter, is a required senior level undergraduate course which has been taken also by most graduate students in the terminal Master's program and a number of those in the Ph.D. program who are working in one of the polymer oriented research groups. The course outline is given in Table 1 with the number of lectures for a particular topic listed in parenthesis. The first three lectures serve as an introduction both to the structure of high polymers and to selected topics of dilute solution behavior. The remainder of the course emphasizes the solid state with consideration of morphology, linear viscoelasticity and rubber elasticity. Rheology is given only brief mention since aspects of it are included in the senior level fluid mechanics course. A much deeper treatment of hydrodynamics will be included in Ch.E. 209.

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The required text for Ch.E. 170 is *Mechanical Properties of Solid Polymers*, I.M. Ward, Wiley-Interscience, 1971. Recommended texts in which additional reading is assigned include:

- R. G. C. Arridge, **Mechanics of Polymers**, Clarendon Press, 1975.
- J. J. Aklonis, W. J. Macknight and M. Shen, **Introduction to Polymer Viscoelasticity**, Wiley-Interscience, 1972.
- F. W. Billmeyer, **Textbook of Polymer Science**, Wiley-Interscience, 1971.
- J. D. Ferry, **Viscoelastic Properties of Polymers**, Wiley, 1970.
- H. S. Kaufman and J. J. Falcetta, **Introduction to Polymer Science and Technology**, Wiley-Interscience, 1977.
- F. Rodriguez, **Principles of Polymer Systems**, McGraw-Hill, 1970.
- J. Schultz, **Polymer Materials Science**, Prentice-Hall, 1974.
- L. R. G. Treloar, **The Physics of Rubber Elasticity**, Claredon Press, 1975.

Ch.E. 212, offered winter quarter, is the first of two graduate courses which cover polymer behavior in solution. The course outline is given in Table 2. It emphasizes the molecular and statistical approaches much more than the phenomenological and continuum treatments of Ch.E. 170. Ideally, students should take Ch.E. 212 only after an introductory polymer course, such as Ch.E. 170. However, this generally is not possible due to competition from graduate level courses taken by first year graduate students during fall quarter. Thus, in order to ensure a basic familiarity with polymers for all students, regardless of background, the first four lectures provided a rapid overview of selected topics from Ch.E. 170. In addition, all students are asked to read the paperback by S. L. Rosen, *Fundamental Principles of Polymeric Materials For Practicing Engineers*, Cahners Books, 1971, during the first two weeks of class. This introductory text provides a broad survey of polymer science and permits the course to be placed in perspective.

The emphasis throughout the remainder of the course follows Professor P. J. Flory's application of statistical mechanics to the thermodynamics and configurational properties of high polymers. Although most of our first year graduate students have had undergraduate courses in statistical mechanics and linear algebra, brief reviews of important concepts and methods are given at appropriate points. The course has been offered previously with the order of topics as in Table 2 and with the configurational statistics preceding the thermodynamics. The former approach works much better, perhaps because student familiarity with classical thermodynamics allows a more gradual transition into thinking about macromolecules. Extensive reference to the original and current literature is made throughout the course.

There is no required text for Ch.E. 212. However, the two books by P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953 and *Statistical Mechanics of Chain Molecules*, Wiley, 1969 are highly recommended. Additional texts in which reading assignments are made include:

- H.-G. Elias, **Macromolecules, Vol. 1, Structure and Properties**, Plenum, 1977.
- H. Morawetz, **Macromolecules in Solution**, Wiley-Interscience 1975.
- C. Tanford, **Physical Chemistry of Macromolecules**, Wiley, 1961.
- H. Yamakawa, **Modern Theory of Polymer Solutions**, Harper and Row, 1971.

Ch.E. 217 is a review of the principal methods of polymer synthesis with emphasis on molecular polymerization mechanisms and reaction kinetics and their roles in influencing polymer composition, structure and ultimate properties. Topics include: condensation, radical and ion initiated chain polymerizations; heterogeneous and stereoregulated polymerizations; copolymerization; bulk, solution emulsion and suspension polymerization; and application of the principles of syn-

TABLE 1

Course Outline—ChE 170

- I. Polymer constitution and solution properties
  - A. Introduction (1)
    - 1. Commercial significance
    - 2. Repeat unit and structural classification
  - B. Molecular weight (1)
    - 1. Averaging procedures
    - 2. Determination of M_n by osmotic pressure
    - 3. Determination of M_w by light scattering
    - 4. Determination of M_υ by viscosity
  - C. Polymer solution thermodynamics (1)
    - 1. Solubility parameter
    - 2. Prediction of polymer blend compatibility
- II. Morphology
  - A. Semicrystalline polymers (2)
    - 1. Molecular requirements for crystallization
    - 2. Single crystal formation
    - 3. Spherulite formation
    - 4. Molecular models for chain folding
    - 5. Macroscopic crystallization kinetics
  - B. Amorphous polymers (2)
    - 1. Phenomenological observations of the glass transition
    - 2. Theoretical approaches to the glass transition
    - 3. Structure-property relationships for transition temperatures
- III. Rheology (1)
    - 1. Introduction to non-Newtonian and time dependent flow
    - 2. Power law constitutive relation
    - 3. Effect of temperature on zero shear viscosity
    - 4. Effect of molecular weight on zero shear viscosity
- IV. Linear viscoelasticity
  - A. Phenomenological treatment using mechanical models (2)
    - 1. Stress relaxation and the Maxwell model
    - 2. Creep and the Voigt Model
  - B. Dynamic response (2)
    - 1. Frequency response of the standard linear solid
    - 2. Complex variable notation for modulus and compliance
    - 3. Time-temperature equivalence
  - C. Extension to multiple relaxation and retardation times (1)
    - 1. Maxwell-Reichert relaxation time model
    - 2. Voigt-Kelvin retardation time model
  - D. Boltzmann superposition principle (1)
- V. Rubber elasticity
  - A. Generalized definition of strain (2)
    - 1. Displacement coordinate scheme
    - 2. Principle axes and the strain ellipsoid
    - 3. Components of infinitesimal and finite strain
    - 4. Strain invariants
  - B. Stress-strain relationships (1)
    - 1. Stress tensor
    - 2. Material parameters—Young's modulus, shear modulus, Poisson's ratio, Lame's constant, bulk modulus
    - 3. Strain energy functions
  - C. Statistics of molecular networks (1)
    - 1. Model polymer chains
    - 2. Gaussian distribution function
    - 3. Entropy of deformation
  - D. Thermodynamic analysis of network elasticity (1)
    - 1. Force-extension relations for a Gaussian network
    - 2. Stress-temperature relations
    - 3. Internal energy and volume changes

TABLE 2
Course Outline—ChE 212

- I. Introduction to polymeric materials
  - A. Molecular architecture (1)
    - 1. Repeat unit and structural classification
    - 2. Tacticity
    - 3. Experimental determination of average molecular weights
  - B. Morphology (1)
    - 1. Single crystal formation
    - 2. Spherulite formation
    - 3. Structure property relationships for the glass transition temperature
  - C. Mechanical properties (2)
    - 1. Stress relaxation and the Maxwell model
    - 2. Creep and the Voigt model
    - 3. Dynamic mechanical testing
    - 4. Time-temperature superposition
- II. Thermodynamics of concentrated polymer solutions
  - A. Flory-Huggins lattice theory (1)
    - 1. Introduction to statistical mechanics and combinatorial probability
    - 2. Configurational entropy
    - 3. Enthalpy of mixing
    - 4. Free energy of mixing
  - B. Phase equilibria (1)
    - 1. Necessary and sufficient conditions for phase stability
    - 2. Binodal and spinodal curves
    - 3. Critical conditions for phase separation
  - C. Applications of Flory-Huggins theory (1)
    - 1. Regular solution theory and the solubility parameter
    - 2. Polymer/solvent compatibility
    - 3. Polymer (1)/Polymer (2) compatibility
  - D. Corresponding states theory (1)
    - 1. Configurational partition function
    - 2. Equation of state
    - 3. Derivation of equation of state parameters
  - E. Application of corresponding states theory to mixtures (1)
    - 1. Combining rules
    - 2. Configurational partition function
    - 3. Intermolecular energy
    - 4. Chemical potential
- III. Random coil statistics
  - A. The freely jointed model chain (1)
    - 1. Bond vector representation for end-to-end distance and radius of gyration
    - 2. Gaussian distribution function
    - 3. The equivalent chain
  - B. Excluded volume (1)
    - 1. Mean field model
    - 2. Probability of binary encounters
    - 3. Probability of alteration of chain configuration
  - C. Experimental characterization of random coil dimensions in dilute solution (1)
    - 1. Intrinsic viscosity
    - 2. Light scattering
    - 3. Determination of theta point from osmotic pressure measurements
- IV. Configurational statistics of real chains
  - A. Rotational isomerism in small molecules (1)
    - 1. Independent rotational potentials
    - 2. Interdependent rotational potentials
    - 3. Rotational isomeric state approximation
  - B. Statistical weight matrix (1)
    - 1. Conformational energy maps
    - 2. First order interactions
    - 3. Second order interactions
    - 4. Statistical weight matrix for symmetric chains
  - C. Configurational partition function (1)
    - 1. Fundamental concepts of statistical mechanics
    - 2. Generation of configurational partition functions by matrix multiplication
    - 3. Evaluation of rotational state probabilities
  - D. Evaluation of configuration dependent properties for a given chain configuration (1)
    - 1. Bond vector coordinate system
    - 2. Transformation matrix
    - 3. Generator matrix for chain displacement vector
  - E. Evaluation of configuration dependent properties averaged overall chain configurations (1)
    - 1. Statistical mechanical averaging of the chain displacement vector
    - 2. Generator matrix for the squared end-to-end distance
- V. Experimental methods of polymer physics (2)
  - A. Dynamic light scattering
  - B. Neutron scattering
  - C. Fourier transform infrared spectroscopy
  - D. ^{13}C nuclear magnetic resonance
  - E. Fluorescence spectroscopy

thetic polymer chemistry to the design of large scale industrial polymer manufacturing processes.

Ch.E. 209 is a detailed treatment of macromolecular hydrodynamics in dilute and concentrated solutions along with analysis of various scattering methods for monitoring flow properties. Topics include: statistical mechanics and stochastic analysis (Gaussian statistics, excluded volume); application of scaling laws to polymer physics (excluded volume, concentrated polymer systems, renormalization theory); radiation scattering (light scattering, neutron scattering, total intensity measurements, quasi-elastic scattering, flow birefringence, electric birefringence); and transport properties (Yamakawa-Kirkwood theories, nonlinear modeling of macromolecules in flowing solution, viscoelasticity, introduction to network models).

REFERENCES

1. R. L. Rawls, Chemical and Engineering News, May 23, 1977, p. 19.