

THE SCIENCE OF SYNTHETIC AND BIOLOGICAL POLYMERS

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THE SCIENCE OF SYNTHETIC and Biological Polymers is a one semester (15 weeks) introductory graduate polymer course offered at Washington University that consists of three hours of lecture per week and carries three hours of credit. The material presented is designed to be of value to a range of engineering students including those in the materials science and biomedical engineering programs. For many students, this is the only polymer course they take. Accordingly, I try to cover a reasonably broad spectrum of material. The depth of presentation is designed to be sufficient for the students to appreciate the theoretical principles of polymer science, but it is not sufficient for them to be polymer specialists.

Because the scope of contemporary polymer science has become so broad, a one semester course can never cover more than a small fraction of the knowledge available. Thus, I am highly selective about what is presented. The choice of subject matter is prejudiced by my industrial research experience. Regardless of where today's students ultimately work, I am convinced that they will encounter many of the same types of problems that I encountered. These include problems associated with selection of polymers for a specific application, deterioration or change in polymer properties with use, pushing a polymer product to the limits of its capabilities, and assuming lot-to-lot reliability of polymer-containing products. All of these problems constantly plague polymer users. Accordingly, I slant the course material toward polymer characterization, selection, properties and weaknesses. Being a physical chemist, I take a physico-chemical approach to all material presented. The fundamental principles discussed are kept as simple and logical as I can make them. I try frequently to introduce practical

examples into the lecture material thereby illustrating the various topics discussed. My entire goal is to maximize long-term retention of useful knowledge of polymers by the students.

COURSE CONTENT

TABLE 1 CONTAINS an outline of the course material. I start with polymer nomenclature and follow this with a discussion of the chemistry involved in preparing various polymers. I then cover polymer characterization and polymer structure/property relationships. Polyelectrolytes and proteins are treated after polymer solution properties. In addition, I deliberately try to include illustrative examples of biological or water-soluble polymers throughout the course. This is done primarily for the benefit of the biomedical students, but the other students benefit too, since industrial uses of water-soluble polymers are steadily increasing. As noted previously, all topics are approached from a polymer user viewpoint. Basic principles are stressed constantly, but the course has a definite practical orientation. In order to visualize the subject matter given, it is appropriate to discuss in more detail the sequence of topics listed in Table I.

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The first topic is nomenclature. At times, one tends to look upon this as a trivial topic. However, consistent with my efforts to stress fundamentals, I spend several lectures on nomenclature. These introductory lectures also enable me to introduce the basic concepts of polymer structure.

Table I
COURSE OUTLINE

- I. Nomenclature
- II. Polymer Chemistry
 - A. Kinetics of polycondensation reactions
 - B. Kinetics of free radical polymerization
 - C. Copolymerization kinetics
 - D. Ionic polymerization reactions
 - E. Epoxy and urethane curing reactions
- III. Polymer Characterization
 - A. Solution Properties
 - 1. Solubility Behavior
 - 2. Fractionation
 - 3. Molecular Weight Determination
 - B. Polyelectrolytes and Proteins
 - C. Bulk Properties of Polymers
 - 1. The Glass Transition and Crystalline Melting Point
 - 2. Viscoelasticity
 - 3. Rubber Elasticity
- IV. Polymer Structure/Property Relationships
 - A. Factors That Affect the Glass Transition
 - B. Factors that Affect Crystallinity
 - C. Structural Analysis of Widely Used Plastics

The students are exposed to the difference between linear, branched, and crosslinked polymers, the meaning of stereoregularity, etc. I do my best to cover a broad spectrum of polymer terms in common use. The beauty and complexity of biological polymers from a structural viewpoint is introduced too. I also expect the students to learn the chemical structures of a number of widely used commercial polymers (e. g., polyethylene, poly(vinyl chloride), etc.). To me, knowing the chemical structures of a number of polymers provides a mental picture of how various polymers differ structurally and lays the groundwork for more meaningful discussion of polymer properties later in the course.

PREPARING POLYMERS

FOLLOWING NOMENCLATURE, I spend considerable time going over the chemistry involved in preparing various types of polymers. This takes about 25% of the total semester lecture time. I feel that spending so much time on polymer chemistry is easily justified, because polymers are constantly used under conditions where they depolymerize, oxidize, and/or crosslink. All of these reactions cause profound changes in polymer properties and occur when polymers deteriorate with use. By stressing to the students how polymer molecules are assembled, it is logical to point out simultaneously how various polymerization reactions can either be reversed



Curt Thies has been an Associate Professor of Chemical Engineering at Washington University since January 1973. He is a native of Michigan. He received a B.S. in Chemistry from Western Michigan University (1956); M.S. from the Institute of Paper Chemistry (1958); and Ph.D. in the Physical Chemistry of Polymers with a minor in Chemical Engineering from Michigan State University (1962). Prior to joining Washington University he had an industrial career culminating with the position of Head of the Polymer/Microencapsulation Research Section of NCR. His research and teaching interests are in the areas of colloid and surface behavior of polymers, microencapsulation, and polymer mixtures.

to cause depolymerization or altered to cause crosslinking.

Much of the chemistry discussed relates to condensation, free radical, and ionic polymerization processes. However, I also discuss the various mechanisms by which epoxy and urethane resins are cured. I spend time on these latter two families of polymers because: 1. they are widely used in situations engineers are likely to encounter (e. g., adhesives, foams, and composite materials); 2. it gives me an opportunity to go over the concept of crosslinking and thermoset resins in some detail. The level of organic chemistry presented is always relatively elementary, but I feel that it suffices to indicate to the students how the major types of polymerization reactions differ. I stress polymerization kinetics. From the kinetic approach, the students learn to appreciate that polymer chain length, rate of chain growth, etc., differ for the various polymerization process. I try to note how these important parameters can be controlled to thereby give the polymer producer a great degree of control over tailoring polymer molecules for specific end uses.

The kinetic expressions developed for free radical copolymerization reactions are also discussed. Many copolymers are of significant commercial importance and the students should have a grasp of the fundamental principles that poly-

mer producers use to minimize or avoid formation of compositionally heterogeneous copolymers. The discussion of copolymer kinetics also helps the students to appreciate the sequence in which monomers are added to a growing polymer chain and how differences in the sequence of monomer addition lead to gross changes in polymer structure with concomitant changes in properties.

POLYMER CHARACTERIZATION

FOLLOWING THE PRESENTATION of polymerization reactions, I devote a number of lectures to polymer characterization. The techniques discussed fall into two broad categories: those that utilize polymer solution properties and those that are based on polymer bulk properties. I begin with the former. One of the first points I try to make is that few commercial polymers are pure. Polymer manufacturers inevitably add to their products a range of additives like light stabilizers, anti-oxidants, processing aids, etc. Toxicity of these additives is of critical importance to those interested in biomedical applications because they can be leached from the polymer matrix during use. Thus, I stress that the first step to take in characterizing a polymer sample is to find out what is present, including the additives. Infrared spectroscopy is a convenient means of doing this. In the case of complex mixtures, the various components are separated by differences in solubility. This then leads into a general discussion of polymer solubility behavior. I stress that solubility in a range of solvents and over a range of temperatures not only enables one to separate complex mixtures and fractionate polymers into different molecular weight fractions, but also provides insight into the molecular structure of a polymer (e. g., crystalline polymers are more insoluble than noncrystalline polymers, crosslinked polymers are insoluble in all solvents, etc.).

After discussing polymer solubility, I swing into the theory underlying the commonly used methods of determining polymer molecular weight and the meaning of the various molecular weight averages. Included in the presentation is an introduction to gel filtration and gel permeation chromatography. I spend only about three to four lectures on these topics, because I am simply trying to get the students to appreciate how polymer molecular weights differ from those of non-polymeric species. I also am constantly warning them always to specify what molecular weight

average they mean when they quote the molecular weight of a polymer.

At this point, I begin to discuss what addition of ionic groups to a polymer chain does to the polymer and thereby develop the concept of polyelectrolytes. The discussion of polyelectrolytes, in turn, serves as a lead into a discussion of proteins. I spend several lectures presenting proteins and glycoproteins from a polymer chemist's viewpoint. The reactions that proteins undergo are not considered. I focus exclusively upon their primary, secondary, tertiary, and quaternary structure and the influence that intra-or inter-molecular bonding has upon each of these structures.

After proteins, I treat bulk polymer properties. The concept of glass transition (T_g) and melting point (T_m) is stressed and attention is focused upon how these events affect polymer properties. This involves showing how a polymer's modulus changes as one passes through T_m and/or T_g . The influence of crosslinking, crosslink density,

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and degree of crystallization on the modulus/temperature curves is used to illustrate how structural and/or morphological changes in a polymer influence its properties. At this point, the structural requirements for a polymer to develop crystallinity and the concept of folded-chain polymer crystals are also treated. This is followed by a discussion of the viscoelastic properties of polymers which involves going through the Voigt, Kelvin, and four-parameter models of viscoelasticity. The thermodynamics of rubber elasticity is also covered. Particular emphasis is placed upon the key structural features of polymers needed for elastic behavior.

The final portion of the course is devoted to a discussion of polymer structure/property relationships. Structural factors that favor increased T_g or T_m of a polymer are considered. The effect of copolymerization upon T_g or T_m of a polymer are considered. The effect of copolymerization upon T_g and the degree of crystallinity

exhibited by a polymer is also discussed. I try to show how polymer structure plays a key role in determining what properties a polymer has. This then determines the applications for which a polymer is suited. In order to drive this point home, I like to list the T_g and T_m values for a number of widely used polymers. I then go over the structural features of each polymer and indicate how these have affected its applications.

SOURCE MATERIAL

The required text for the course is Billmeyer's *Textbook of Polymer Science* (Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1971). I also have developed a set of lecture notes for parts of the course and pass these out to the students. The sequence of lecture material presentation that I favor differs significantly from that used by Billmeyer. Since a wide spectrum of subjects is covered, I also find that I like to supplement Billmeyer's text with additional material taken from the reference texts listed in Table II. Thus, I either formulate by own problems, turn to the example problems in Rosen's text, or give the homework problems in Rodriguez's book. My supply of problems is steadily increasing, but I never have enough. I favor assigning a range of problems that require relatively little time to solve rather than giving a limited number of problems that require considerable time to solve. This exposes the student to a broader range of problem situations.

CLASSROOM APPROACH

INSO FAR AS THE LECTURES are concerned, I try to provoke class participation by routinely asking lots of questions during the lectures. These are addressed to the class in general (i. e., anyone can volunteer an answer) and tend to be practical in nature. The questions are designed to establish dialogue between the students and myself during class. In this manner, I become more aware of what concepts they are not grasping well and can then spend more time on these. I also try to constantly relate my own experiences with polymers to them and warn them of some of the polymer problems that they are likely to encounter.

This past year, I was assisted in the course by Dr. Lawrence Nielsen, a Senior Scientist in the Corporate Research Department of the Monsanto Company and Affiliate Professor in the Chemical Engineering Department at Washington University. He is an experienced polymer physicist specializing in the mechanical properties of polymers and handled the lectures that dealt with this aspect of polymer science. During his lectures, the students were exposed to a concise

Table II

TEXTS FROM WHICH SUPPLEMENTAL COURSE MATERIAL IS DRAWN

Text	Supplemental Material Used
Flory, P. J., "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953.	Kinetics of polycondensation plus rubber elasticity.
Saunders, K. J., "Organic Polymer Chemistry," Chapman and Hall, London, England, 1973.	Organic polymer chemistry, including ionic polymerization processes and cure of epoxy and urethane resins.
Rosen, S. L., "Fundamental Principles of Polymeric Materials for Practicing Engineers," Barnes and Noble, Inc., New York, N. Y. 1971.	Primarily viscoelasticity. I also make extensive use of the example problems given throughout the text.
Tobolsky, A. V., "Properties and Structure of Polymers," John Wiley & Sons, Inc. New York, N. Y., 1960.	Factors affecting the glass transition, viscoelasticity.
Neurath, H., "The Proteins," Second Edition, Academic Press, New York, N. Y., 1965.	Structure of Proteins.
Rodriguez, F., "Principles of Polymer Systems," McGraw-Hill Book Co., New York, N. Y., 1970.	Homework problems.
Miller, M. L., "The Structure of Polymers," Reinhold Publishing Corp., New York, N. Y., 1966.	Polyelectrolytes and free radical polymerizations.

survey of the mechanical property behavior of polymers. The choice of relevant material presented was something only a seasoned expert could do and greatly strengthened the overall content of the course.

CONCLUSION

Before concluding, I wish to note that the content and arrangement of a course like this one is subject to constant modification. I am trying to increase the learning efficiency of the students without forcing too much knowledge on them too quickly. One means of doing this involves improving my style of delivery, especially for those topics which the students seem to consistently have greatest difficulty. My approach is to simplify the presentation as much as feasible. Furthermore, I am increasing the number of notes to be handed out before a lecture is given. In this manner, I hope to devote more of the lecture to class discussion. Only time will tell how successful these efforts are. □