Polymers Across the Curriculum: Macromolecules as a Unifying Theme Across the Foundational Courses in Chemistry

Context

Macromolecular chemistry is a highly interdisciplinary field that cuts across all five of the foundation areas of chemistry. Many chemistry programs provide an in-depth elective in polymer chemistry. However, given the important role of macromolecules in modern chemistry, it is desirable to introduce macromolecular concepts into foundation and in-depth courses across the curriculum. By doing so, student interest can be enhanced by their understanding of real-world applications of chemistry. This supplement suggests ways to introduce macromolecular concepts throughout the chemistry curriculum.

Conceptual Topics

- Basic reactions and reaction mechanisms that lead to polymerization or modification of polymers, and the impacts of reaction mechanisms on molecular weight and MW distributions.
- Impacts of length – evolution of properties as molecules grow larger – physical properties, impacts of entanglements, phase changes (glass transition vs. melting of crystalline regions).
- Properties of mixtures – polymer/polymer phase separation, solution formation and rheology.
- Properties of materials based on molecular structure and stereochemistry.
- Similarity of macromolecules generated by synthesis to those available in nature.

Practical Topics

Macromolecules can be used to illustrate a myriad of principles throughout the chemistry curriculum. In addition to an enrichment of lecture courses, there are numerous opportunities to include polymer experiments or demonstrations in all areas of chemistry. The brief listing below provides examples appropriate for each sub-discipline.

Organic Chemistry

- Functional group transformations as they relate to polymers: alkene addition, esterification, amide formation, Michael addition, enolate reactivity, isocyanate addition.
- Conformation analysis: propane → polypropylene → DNA.
- Utilization of chromatographic and spectroscopic methods in structure and size determination: monomer structure, molecular weight by size exclusion chromatography, end-group analysis using NMR.
- Absorbable sutures: glycolic acid/lactic acid polyesters.
- Green chemistry, sustainability, materials from renewable biosources.

Analytical Chemistry

- Size exclusion chromatography – determination of polymer molecular weight.
- Polymer stability using thermogravimetric analysis (TGA).
- Polymer molecular weight by end-group titration.
- Determination of copolymer composition by pyrolysis gas chromatography.
- Determination of additive levels using ultraviolet or infrared spectroscopy.

Physical Chemistry

- Dilute solution viscometry – determination of polymer molecular weight, hydrodynamic radius, chain branching, solvent interactions/ideal solutions.
- Non-Newtonian properties of polymer melts and solutions.
- Thermodynamics of polymer/polymer solutions and phase separation – comparison to small molecule analogs.
- DSC – observation of phase changes, determination of percent crystallinity.
- Dynamic mechanical analysis (DMA) – determination of viscoelastic properties of elastomers.
- Polymerization kinetics by several methods.
- Determination of monomer reactivity ratios using GC (monomer depletion) or NMR.

Inorganic Chemistry

- Coordination – catalyst formation, enzyme structure.
- Ziegler-Natta, metallocene catalysts – impact on societal development.
- Crystalline vs. amorphous structure – SiO2 → window glass; glass transition.
- Utilization of X-ray and calorimetry to determine percent crystallinity.
- Polymers with inorganic elements in the main chain; comparison and contrast impacts of inorganic backbone polymers to the properties of polymeric forms of carbon.
- Mineralogical and pre-ceramic polymers.
- Polymer/inorganic natural systems such as chitin/calcium carbonate composites.

Biochemistry

- Comparison of commercial and natural polyamides – intermolecular interactions, protein structure, folding.
- Polyacetals – starch vs. cellulose; membrane materials, impact of bonding and structure on biological activity.
- Polyesters – carboxylic and phosphoric acid polymers; comparison of the PET and DNA mainchains.
- Determination of molecular weight and structure for natural polyamides.
- Natural polymers modified with poly(ethylene glycol) [PEG] – enhancement of biological properties, drug delivery.

Illustrative Modes of Coverage

Organic Chemistry

The inclusion of polymeric materials into organic chemistry can serve to enhance students' awareness of their surroundings while illustrating the principles of organic chemistry. Examples of opportunities for course enrichment:

- **Alkenes**. The most important societal/ commercial reaction of alkenes is radical-initiated polymerization, which illustrates important concepts of reactivity, structural influence on the stability of reactive intermediates and the elements of a radical chain process and its influence on final molecular weight. Historical narrative about polymers influence on WW II, including the use of polyethylene as electrical insulation which made radar installations possible, poly(methyl methacrylate) to replace glass in canopies of fighter aircraft, and styrene-based rubbers developed to replace scarce supplies of natural rubber engage student's interest in chemistry.
- **Carboxylic acid derivatives**. Polyamides and polyesters can be used to introduce condensation polymerization and compare the differences in molecular weight and distribution between radical and condensation polymerizations. Comparison of the hydrolytic reactivity of polyanhydrides (used for controlled release of drugs), polyesters (used for dissolvable sutures), and polyamides (hydrolytically stable) reinforce the reactivity of carboxylic acid derivatives. Historically – the development of nylon 6,6 to replace silk (a natural, but expensive polyamide) allowed the Normandy invasion - there wasn't enough silk in the world for the Allies' parachutes.

- **Michael addition**. The electrophilic addition of water to cyanoacrylates (Superglue®) and the relation of Michael addition to anionic polymerization are practical applications of this concept.

Analytical Chemistry

Most of the analytical techniques useful in other areas of chemistry are applicable in the polymer area. In addition to the variety of experiments discussed above (Practical Topics), the importance of polymers may be emphasized in lecture in the following ways:

- **Determination of polymer stability** by thermogravimetry; quantification of fragment formation.
- **Metal content** of organometallic polymers by thermogravimetry.
- **Copolymer composition** by nuclear magnetic resonance spectroscopy.
- **Determination of the degree of branching** using size exclusion chromatography with multiple detection.
- **Determination of blend miscibility** using differential scanning calorimetry.
- **Determination of percent crystallinity** using differential scanning calorimetry.
- **Identification of and determination** of level of loading of plasticizer using infrared spectroscopy.
- **Determination of molecular weight** and molecular weight distribution of oligomers using matrix assisted laser desorption mass spectrometry.

Physical Chemistry

Synthetic polymers are often ideal for the illustration of the principles of physical chemistry. A few possibilities include:

- **Kinetics and thermodynamics**. The kinetics of step-growth polymerization can be extended to estimate the molecular mass as a function of the extent of reaction. Radical polymerization schemes provide a more complicated mechanism complete with a thermally activated step and the opportunity to make a steady-state approximation. The effect of temperature on chain length and reaction rate introduces a practical implication of thermodynamics.
- **Solubility**. Polymers provide a good illustration of “like dissolves like” and the importance of entropy of dissolution (much less positive for a polymer than for small molecules). Macro-molecular miscible and immiscible blends illustrate solubility and importance of entropy to mixing.
- **Basic statistics**. Distributions of molecular mass in polymers can be used to introduce statistics, distribution functions, and averages. The concepts of number and weight average molecular masses can be related to means, standard deviations, expansions, and summations.
- **Non-ideality**. Connectedness, due to permanent bonds linking monomers, introduces non-ideal and non-Newtonian viscoelastic behavior.
- **Physical and mechanical properties.** The concept of modulus may be introduced with a general discussion of thermodynamic functions. The change in physical behavior from methane to octane to polyethylene is enlightening. A comparison can be made between the expansion of gases (endothermic) and elastomers (exothermic), introducing the role of structure in thermodynamics and physical properties.

Inorganic Chemistry

Inclusion of polymer chemistry examples help students connect this topic to the real world.

- **Structure/bonding/property relationships**. The flexibility of polysiloxanes and polyphosphazenes and the conducting properties of polysilanes can be discussed.
- **Metal-based catalysts and initiators in polymerization**. Transition-metal polymerization catalysts can illustrate the 18-electron rule, *cis-trans* and octahedral geometries, oxidative addition, and reductive elimination. Organolithium and Grignard reagents for anionic polymerization and transition-metal carbenes for ROMP are but a few of the myriad initiators that can be discussed.
- **Polymeric conductors and semi-conductors** may be used as examples when discussing molecular orbital and band theory.

Biochemistry

Much of biochemistry, of course, is polymer chemistry. This can be emphasized in a biochemistry course.

- **The natural polyamides [polypeptides, proteins] and polyesters [RNA, DNA]** may be compared with commercial counterparts and unique features of the natural materials noted.
- **Intermolecular interactions and chain folding** for proteins and the importance of amine pendent groups on the nucleic acid polyester main chain are obvious points for discussion. Lipid self-assembly is a good example of supramolecular polymer synthesis and very important in biological systems.
- **Polymer catalysis is crucial to life.** Each student is subject to a wide range of organic reactions (metabolism)—all occurring in water of 37 °C—only possible because of enzyme catalysis.
- **A variety of medically related polymer topics**: heart valve repair using polydimethylsiloxane; polyvinylpyrrolidone or fluorocarbon emulsions as blood substitutes; cyanoacrylate polymers for wound closure or artificial skin; polyglycolic acid or glycolic/lactic acid copolymers for biodegradable sutures; polymeric substrates for the controlled release of drugs (therapeutic agents, insulin, birth control substances, vitamins, growth factors, etc.); polymethylmethacrylate (PMMA) for dental restoration; hydrogels for contact lenses; and many others.
- **Poly(ethylene glycol) [PEG]** is a water-soluble polyether, compatible with biological systems and of immense importance in biochemistry, most notably in protein solubilization and drug delivery.

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