Spring 2012
Polymer Science II
Chemistry 412/512
SYLLABUS

I. Introduction and Overview
- A) Terms
- B) MW Dependence of Properties
- C) Temperature Dependence of Properties
- D) History of Polymers
- E) Nomenclature

References:

Cowie	Chapter 1
Sperling	Chapter 1
Allcock	Chapter 1
Flory	Chapters 1 and 2

II. Chain Structure and Configuration
- A) MW Averages and MW Distribution
- B) Conformation of Chains
  - 1) long range
  - 2) short range
- C) Configurations
  - 1) sequential (polymer and copolymer)
  - 2) NMR analysis of runs
  - 3) optical
  - 4) geometric
  - 5) substitutional
  - 6) tacticity (NMR analysis)
  - 7) other types: stars, rings, interpenetrating networks, semi-interpenetrating networks

References:

Cowie	Chapter 6
Sperling	Chapter 2

III. Kinetics of Polymerization
- A) Condensation
  - 1) statistics
  - 2) non stiochiometric mixtures
  - 3) gels and branching, α_c, P_c
- B) Radical Chain Addition Polymerization
  - 4) inhibition and retardation
  - 5) statistics - Trommsdorff effect, autocatalytic, kinetic run number
- C) Entropy and Enthalpy of Polymerization
- D) Ionic Polymerization
- E) Living polymers
- F) Coordination Polymerization

References:

Cowie	Chapters 2, 3, 4, 5
Sperling	Chapter 1
Allcock	Chapters 11 and 12

IV. Statistics of Linear Macromolecules

A) Freely jointed chain

$r^2 = Nb^2$ $W_{(x,yz)}\, d_x d_y d_z$

$Rg^2 = 1/6\ r^2$ $W(r)4\pi r^2 dr$

B) Shape of Random Coil Chain, Moments of Inertia

C) Time Dependent Correlation-Memory Functions

$< \ell(o) \cdot \ell(t) > / < \ell^2 > /$ Vector

$$\frac{< \ell^2\,(o) \cdot \ell^2\,(t) > - < \ell^2 >2}{< \ell^4 > - < > \ell^2 > 2}$$ *Scalar*

$\ell \equiv r$ end-to-end length

D) Time scale of measurement versus time scale of memory functions

B) Conformational Analysis

1) Rotational isomer states
2) Matrix method
3) Average conformational properties
4) Exact calculation of end-to-end length

References: Cowie Chapter 10
Sperling Chapters 3 and 5
Flory Chapters 8 and 10

V. Polymer Solutions, Experimental

A) Colligative Properties

1) Boiling point and freezing point
2) Osmotic Pressure - M_n
   a) 2^{nd} viral coefficient
   b) Instrumentation

B) Electromagnetic Wave Scattering

1) Theory gases to solutions
   polarized to unpolarized
   single particle to many particles
2) M_w
   2^{nd} viral coefficient
   mean radius fo gyration
3) Turbidity
4) Zimm Plot
5) P(6) Scattering Function
6) Dissymmetry ratio
7) Instrumentation

C) Viscosity
definitions η, η_{rel}, η_{sp}, $[\eta]$
measurement
Mark Houwink
Volume - Rg

D) Gel permeation chromatography
theory
measurement equipment
$[\eta_x] M_x = [\eta_y] My$
calculation of MW distribution from standards

References: Cowie Chapter 9
Allcock Chapters 13 and 14
Sperling Chapter 3

VI. Polymer Solutions ΔH, Theory

A) General ΔG, ΔS, ΔH
B) ΔH and solubility parameters
C) Mixing ΔS for simple molecules from Raoult's Law
D) Mixing ΔS
1. statistical mechanics, $S = k \ln \Omega$ simple molecules
2. polymer lattice theory
3. polymer mixture
4. disordered polymer

E) Enthalpy of Mixing Lattice Theory
Application of $\Delta G = \Delta H - T\Delta S$
μ-μ,^{o} = osmotic pressure
2nd viral coefficient

F) θ Temperature
Phase Equilibria Polymer - Solvent Critical Temperature T*

G) Polymer - Polymer Miscibility
1. Blends
2. Phase Separation
nucleation and growth vs.
spinodal decomposition

References: Cowie Chapter 8
Flory Chapter 12
Sperling Chapters 3 and 4

VII. Crystalline State
A) Requirements for Crystallinity and Factors Affecting Tm
B) Crystallization from Bulk
C) Crystallization from Solution
D) Kinetics and Crystallization
1. Temperature dependence
2. Avrami Equation time dependence

References: Cowie Chapter 11
Sperling Chapter 6

VII. Glasses
VIII. Glasses
A) Thermodynamics of phase transition
First order, second order
Crystal, amorphous state-structure, short and long range order
B) Transition, free volume, mobility
C) Differential scanning calorimetry
D) Factors affecting Tg
Flexibility, polar groups, large groups, excess free volume
References: Cowie Chapter 12
Sperling Chapter 8

IX. Glass Rubber Transition
A) Thermal mechanical behavior
Tensile Modulus, Shear modulus, Bulk modulus, Poison's ratio
B) Rubber concepts
1. Basic equation
2. Observables
3. Thermodynamics of rubber elasticity
4. Statistical mechanics of rubber elasticity
C) Viscoelasticity
1. Models Maxwell, Voigt
2. Creep, compliance, J, time dependence
3. Fixed elongation, Shear modulus G, time dependence
4. Harmonic motion
G', G'', tan δ

$$\eta' = \frac{G''}{\omega} \quad \eta' = \sqrt{(G')^2 + (G'')^2}$$

5. WLF equation
Time vs. frequency effects
Time/frequency – temperature superposition

References: Cowie Chapters 13 and 14
Sperling Chapters 9, 10 and 11

X. Chemical Reaction: Time – Temperature Transformation Diagram

Changes in physical state for polymerizing system as a function of degree of cure.

References: Cowie Page 298

Approximately one unit will be covered each week.

Polymer Science II
Project on a Fore Front Area of Research for Graduate Students only

Select one of the following current forefront characterizations polymer topics. Let me know which one you have chosen in class or by email. Preferences will be based on date of request.

Prepare a 15 minute presentation for the class, a copy of your presentation notes for distribution to the class with three or more non-textbook references and 2 possible questions for the final with your answers.

Project is due April 17th

Project Topics
TEM
Atomic Force Microscopy and recent modifications
Reactive Processing of High Temperature Thermoplastics blended with Thermosets
Dynamic FT modulated DSC
Solid State NMR
Dendrimers
Dynamic Light Scattering
Mechanical Dynamic Analyzer, MDA, RDA
Fatigue
ESCA
ATR IR (FT)

Grading

Problem Sets	10%
Hour Exam I	25%
Hour Exam II	25%
Final	25%