ENAS 606 : Polymer Physics

Professor	Chinedum Osuji 302 Mason Lab, 432-4357, chinedum.osuji@yale.edu
Description	This course covers the static and dynamic properties of polymers in solution, melt and surface adsorbed states and their relevance in industrial polymer processing, nanotechnology, materials science and biophysics. Starting from basic considerations of polymerization mechanisms, control of chain architecture and a survey of polymer morphology, the course also addresses experimental methods for the study of structure and dynamics via various scattering (light, x-ray, neutron) and spectroscopic (rheology, photon correlation spectrscopy) methods as an integral component of polymer physics.
Course Topics	Polymerization basics Polymer morphology Static properties - Chain statistics and structure Solution and melt thermodynamics Scattering and rheology as tools in polymer physics Lab characterization of structure, thermodynamics and dynamics Gelation and network formation Polymer dynamics
TA	TBD, *if required*
Prerequisite	Undergraduate courses in physical chemistry, thermodynamics and basic physics, or the permission of the instructor
Class	Tuesdays and Thursdays, 11:35a-12:50p, 104 ML
Office Hours	As required

Textbook(s) "Polymer Physics" by M. Rubinstein and R. H. Colby

Additional reading

"Scaling Concepts in Polymer Physics" by P. G. de Gennes

"Principles of Polymer Chemistry" by P. J. Flory

"The Theory of Polymer Dynamics" by M. Doi and S. F. Edwards

"Introduction to Polymers" by R. J. Young and P. A. Lovell

"The Structure and Rheology of Complex Fluids" by R. G. Larson

"Principles of Polymerization" by G. Odian

"Methods of X-ray and Neutron Scattering in Polymer Science" by R-J. Roe

Exams There will be 3 exams, incremental in nature, based on material covered during lectures and on problem sets.

Homework There will be periodic homework assignments throughout the semester (≈ 5) which should be submitted at the start of class on their due date. Students are permitted to work cooperatively on assignments, but each person must submit his or her own individually prepared results.

Lab assignment There will be three topics for laboratory investigation. Students will be assigned in groups to one topic each and will submit a lab report of their work.

In class discussion In addition to general in-class participation, each student will give one 20 minute presentation of a seminal paper or recent publication of interest during the course of the semester.

Grading - a rough guide

Exam I	20 points
Exam II	20 points
Exam III	20 points
Graded Homework	20 points
Lab assignment	10 points
In class discussion	10 points
Total	100 points

Lecture Schedule (subject to change!)

Lecture #	Date	Lecture Topic	Chapter(s)
1	T Jan 13	Polymerization basics	–
2	R Jan 15	Polymerization basics; Polymer Morphology	–
Structure			
3	T Jan 20	Ideal, Gaussian conformations	2
4	R Jan 22	Models for coil structure	2
5	T Jan 27	Entropic free energy	2
6	R Jan 29	Non-ideal chains I	3
7	T Feb 03	Non-ideal chains II	3
8	R Feb 05	Adsorption and confinement effects	3
9	T Feb 10	Intro to Scattering Methods	–
	R Feb 12	*Literature discussion I*	–
	T Feb 17	**Exam I**	
Thermodynamics+			
10	R Feb 19	Lattice models, Flory-Huggins theory	4
11	T Feb 24	Stability and Demixing	4
12	R Feb 26	Microphase separation in block copolymers	–
13	T Mar 03	Osmotic Pressure; Solvency	4,5
14	R Mar 05	Polymer Brush Theory	–
	F Mar 06	*New England Complex Fluids Workshop@Yale*	
	T Mar 10	Spring recess	
	R Mar 12	Spring recess	
	T Mar 17	Spring recess	
	R Mar 19	Spring recess	
	T Mar 24	*Literature discussion II*	–
15	R Mar 26	Gelation and Network Formation	6
16	T Apr 1	Rubber Elasticity and Linear Viscoelasticity	7
17	R Apr 3	Intro to Rheological Methods	–
	T Apr 8	**Exam II**	
Dynamics			
18	R Apr 10	Unentangled Dynamics I	8
19	T Apr 15	Unentanged Dynamics II	8
20	R Apr 17	Glassy Dynamics; T_g	–
21	T Apr 22	Entangled Dynamics I	9
22	R Apr 24	Entangled Dynamics II	9
23	T Apr 29	*Literature discussion III*	–
24	R May 1	TBD	–
	∼ May 10	**Exam III**	

Course Topics - Detail

1. **Principles of Polymerization [1-2 lectures]**
   (a) Step growth and chain growth mechanisms
   (b) Anionic, radical and modern living chain polymerizations
   (c) Molecular weight distributions; characterization by osmotic pressure, light scattering, intrinsic viscosity

2. **Polymer Morphology [1-2 lectures]**
   (a) Crystalline and semi-crystalline polymers; Liquid crystalline polymers
   (b) Self-assembly by microphase separation of block copolymers
   (c) Morphology of polymer thin films vs. bulk - surface influence

3. **Static Properties of Polymers [4-5 lectures]**
   (a) Conformations of Ideal Chains
      i. Freely rotating, worm-like, hindered rotation and rotational isomeric state chain models
      ii. Random walk statistics, radius of gyration, end-to-end distance distributions
      iii. Free energy of an ideal chain
      iv. Measurement of single chain structure by scattering
   (b) Conformations of Real Chains
      i. Excluded volume and self-avoiding random walks
      ii. Flory theory of polymers in good solvents
      iii. Deformation of real chains by tension and compression
      iv. Adsorption of single chains
      v. Temperature effects on real chains
         A. Temperature dependence of coil size
         B. Flory theory of polymers in poor solvents
         C. Second virial coefficient
      vi. Dilute solution scattering

4. **Thermodynamics of Blends and Solutions [2-3 lectures]**
   (a) Flory interaction parameter; Flory-Huggins/lattice models for polymer mixing
   (b) Experimental investigations of binary mixtures; determination of interaction parameters
   (c) Osmotic pressure and osmotic compressibility
   (d) Spinodal and binodal decomposition; critical phenomena
   (e) Dilute and semi-dilute regimes
   (f) Measuring chain conformations in semi-dilute regime
   (g) Polymer brushes and multi-chain adsoprtion

5. **Gelation and Network Formation [3 lectures]**
   (a) Percolation models of gelation

(b) Mean-field and scaling models for gelation
(c) Rubber elasticity - entangled and unentangled systems
    i. Edwards and Mooney-Rivlin models
(d) Linear viscoelasticity
    i. Maxwell and Voigt models
    ii. Stress relaxation; Creep and creep recovery
    iii. Boltzmann superposition
    iv. Oscillatory shear and steady shear deformation

6. **Introduction to Scattering and Rheological Methods [2-3 lectures]**
   (a) Structure and Dynamics via Scattering
       i. Elastic and inelastic scattering
       ii. Rayleigh ratios and mass determination; Zimm plots
       iii. Structure factors and form factors; Debye function
       iv. Guinier and Porod/fractal regimes
       v. Time-correlation spectroscopies
   (b) Dynamics via Rheology
       i. Linear and non-linear regimes
       ii. Zero-shear viscosity; Einstein viscosity for hard spheres in solution
       iii. Frequency dependent viscoelasticity

7. **Unentangled Polymer Dynamics [4 lectures]**
   (a) Rouse and Zimm models
   (b) Intrinsic viscosity
   (c) Relaxation modes
   (d) Semi-flexible chain modes
       i. Bending energy and dynamics
       ii. Tensile modulus and stress relaxation
   (e) Temperature dependence of dynamics
       i. Time-temperature superposition
       ii. Glassy dynamics
   (f) Dynamic scattering

8. **Entangled Polymer Dynamics [4 lectures]**
   (a) Entanglements and reptation in polymer melts
       i. Relaxation times and diffusion
       ii. Stress relaxation and viscosity
   (b) Reptation in semi-dilute solutions
   (c) Dynamics of a single entangled chain
   (d) Many chain effects - constraint release
   (e) Entanglement in worm-like micelles