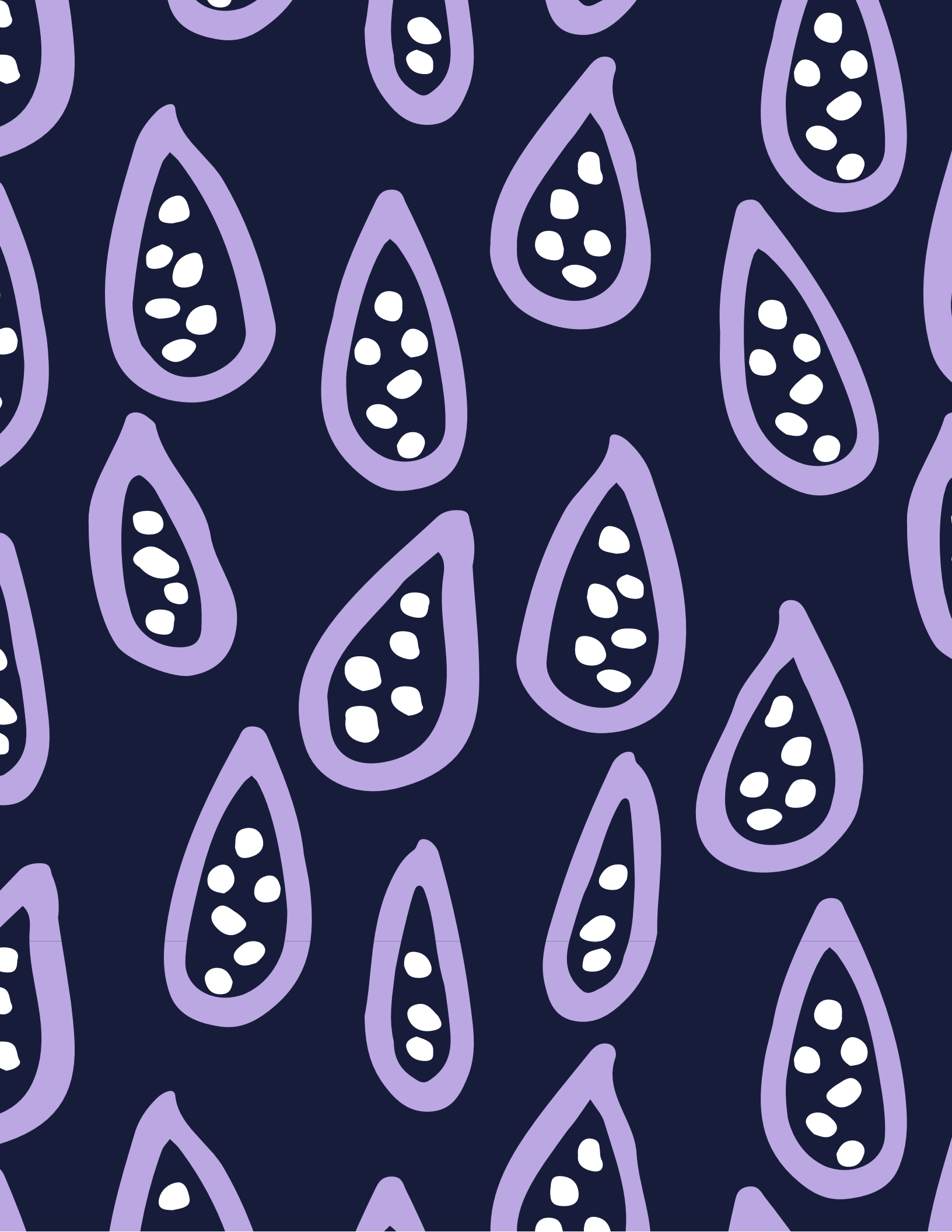


Recall: Thermoplastics → recycle
Thermosets → waste

Term Paper Introduction

General Notes

(i) Decide Vertical vs. Horizontal Approach
(ii) Published, Peer reviewed articles are expectation
(iii) No date limit on citations but you must read it

No-nos

(i) Do not cite web addresses as references
(ii) Try to avoid writing a review article based on summarizing a review article, or book chapters ← books not strictly prohibited, but they should not dominate
(iii) Any more than 50 consecutive word match violates copyright law

Possible Term Paper Subjects

(i) Vitrimers: A chemical group that can be broken apart under certain conditions, while having thermoset characteristics at room temp
Can be considered a dynamic bond
Green Mindset, improved recycling

(ii) Green Flame Retardants: Traditionally Highly Toxic or produce toxic chemicals when heated. Cancer Causing usually. This focuses on developing one that isn't as toxic.

(iii) Biochirals: Making nm x nm crystals with no defects. This small size warranted this time
Example: Carbon Nanotubes
Needle Like crystals which can be prepared from cellulose, kitty, or otters
Defects lead to reduced material strength bio origin
Biodegradable

(iv) MXene: 'Max-ene'. Layers can be separated. Such as graphite being separated into individual layers of graphene. Incredible Aspect Ratio

(v) Glass Transition Temperature: Super easy to measure. Popular topic of polymer studies but not really Known. Nobel Prize worthy.
How can we predict glass transition temperature without any assumptions?

(vi) Collection of Rare Metals:
Natural Oil Resources running out. Fracking helps us, but harmful to environment
↳ Contaminates water, causes natural disasters. Metals much harder to replace. Using by textbooks will exhaust before oil. Found in low concentration in sea water.

(vii) Porous Materials: Used to assist in topic of (vi). Aerogels used on space shuttles. Very brittle/fragile but remarkably strong resistant. Carbon or Polymers
Can create non-metal catalysts with porous nets!
related

(viii) Extreme Temperature Polymers
Mach 7 → Boeing Scramjet can fly in very thin air at fast speed. Falcon
Mach 22 HTV-2 also incredibly fast, compared to current record of Mach 3. Used for weapons, but can turn into passenger travel, reduces trips to other continents to matter of hours.
Polymer needs to be developed to survive 750-1000°C friction temps that is low density to allow safe, stable travel.

(ix) Non-metallic Carbon Catalyst: Carbon's surface has defects → acts as catalytic centers. Can add other atoms to defects → more effective

(x) H-bonding (Supramolecular synthesis): Technique to let monomers contact in non-covalent manner and lets you selectively design polymerization (usually random)
Catalyst allows polymers to align in a desired way → crystalline properties.
Can align through H-bonding and then you can apply desired polymerization

Pages: 1 page to 10,000 pages. 1 page is harder to write. Subject Chosen dictates length.
Rough Draft: Acts as a checkpoint along with other milestones outlined in syllabus

Ask Questions!

Ishida Knows his shit, don't plagiarize or copy references word-for-word!

Chapter 1

Goal: Refresh information from ENGR145

Concepts and Nomenclature

Polymer = poly + mer (multi + unit) } Repeating Units required 2-4 units to be considered a true polymer

Oligomer = oligo + mer (a few + unit)

Plastics ← πλαστικός (greek for plastikos) means to 'mold into'

Sub Category

Macromolecules: Contain both polymeric and non-polymeric large molecules

Rubber (AKA elastomers): polymers that deform elastically and to very large strains

↳ become glassy at low temperatures → become brittle (glass transition temperature)

How many units to be polymer?

⊗ Not repeating

○○ ||

○△○ ||

○△△○ Beginning of structure

Structure of Polymer Chains

Copolymers

- AAAAA
- AAAAABBB
- AAAAA
  BBB
- ABABABA alternating copolymer
- ABBBABA random copolymer

Homopolymer

A,B-diblock polymer

graft polymers

Given Properties of homopolymers A and B

- Can you predict copolymer properties?

properties of A on one side, B on other : like soap

results different properties

even "mix" of properties : AB can be considered a monomer

un balanced "mix" of properties : true random mixture

↳ can be determined roughly with % of each

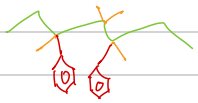
Conformation vs. Configuration

Conformation: Structural change caused by chain rotation. Can be changed easily (reversable) by changing temp

trans: 'zig-zag' chain on a plane gauche: chain rotates +60° or -60°

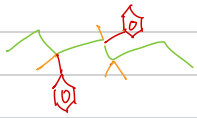
Configuration: Permanent structural difference caused during synthesis. Mild temp change does not affect this

a) Head-to-Head



Less likely to occur as this is energetically demanding

b) Head-to-Tail



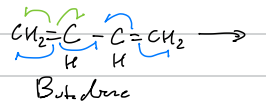
Much less steric hinderance → thermodynamically more stable

Stereoregularity (stereoisomers)

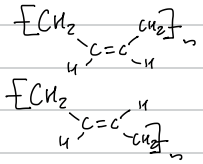
Isotactic Can crystallize ↳ Material looks Hazy Syndiotactic

Amorphous Atactic (Random/Not predictable) ↳ Doesn't crystallize → looks very glass-like

Regioisomers



1,2 polybutadiene



cis-1,4-polybutadiene

'cis' dropped usually

trans-1,4-polybutadiene

IUPAC Naming

- Add 'poly' to start of monomer name

Not accurate! Polybenzoxazine is not wrong!

Tensile Strength

Cut 1×10^5 MW in half, much weaker

Viscosity

Small addition of gums to ice cream makes it feel premium due to 1% high MW gums added

Precipitation

Higher MW polymers precipitate first in a centrifuge. Direct Correlation.

Molecular Weight

Provide MW in Paper

Number Avg MW: $M_n = \frac{\sum N_x M_x}{\sum N_x}$ Related to tensile strength

Basic average idea

Weight Avg MW: $M_w = \frac{\sum W_x M_x}{\sum W_x}$ Here, $W_x = N_x M_x \rightarrow M_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$

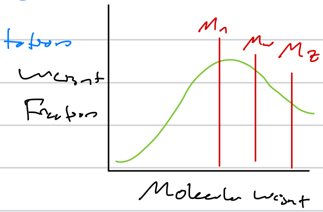
Average from weight perspective

related to viscosity

Z-average MW: $M_z = \frac{\sum N_x M_x^3}{\sum N_x M_x^2}$ Related to precipitation

Poly Dispersal Index (PDI): $PDI = \frac{M_w}{M_n}$

↳ Higher PDI → broader M_w



$M_n < M_w < M_z$

Molecular Weight & Macromolecules

Various MW Measurement Methods

Method	Type	M.W. type	MW range
Colligative properties		Mn	
Boiling point elevation	Absolute	Mn	$< 10^4$
Freezing point depression	Absolute	Mn	$< 10^4$
Vapor pressure lowering	Absolute	Mn	$< 10^4$
Osmotic pressure	Absolute	Mn	$2x10^4 - 10^6$
Terminal group concentration	Absolute	Mn	$< 10^4$
Light scattering	Absolute	Mw	$10^4 - 10^8$
Sedimentation	Absolute	Mw, Mz	$10^2 - 5x10^6$
Intrinsic viscosity	Relative	Mv	$10^3 - 10^8$
Size exclusion chromatography(SEC)	Relative	Mn, Mw, Mz	$10^2 - 10^7$

will be discussed with 'Macromolecules'

Notes accurate but most convenient

Colligative Property (example)
- Add NaCl to water to lower Freezing Point

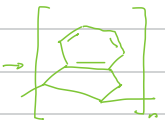
Property related to number

Staudinger's Dinger

Hypothesis: stronger-proportioned molecules consists of aggregates of molecules → size of aggregates should change as chemical structure of molecules is altered

Approach: Hydrogenation of regular Benzene into a positive Saturated cyclohexyl ring

Materials Used: Relatively small oligomers of polyindene →

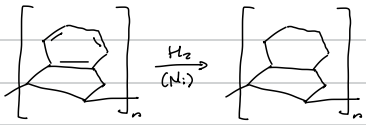


Meas. Method: Colligative property Measurement

Did not use Degree Polymerization as they thought it was aggregate of molecules

Staudinger's Experiments

Initial: Colligative Property Measurement



n	# of particles	m
20	About the same with respect to error	21
30		29
50		46

He was criticized for using small molecules

Final: Acetylation and regeneration of cellulose; viscosity measurement

Hydrophilic → phobic

Cellulose $\xrightarrow[\text{Pyridine}]{\text{Anhydrous acetic acid}}$ Acetylcellulose $\xrightarrow[\text{methanol}]{NaOH}$ Cellulose

n	to	m	to	p
260		250		–
500		500		490
1215		1190		1200

Directly from his paper, so messy value probably measurement error

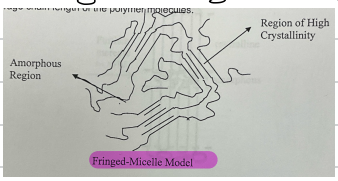
Critics stuck as this rebutted all they were arguing Covalent Bonds provided as structure constant

Viscosity is more sensitive to larger MW molecules than smaller ones (like using cheap gum to make "premium" ice cream)

Morphology

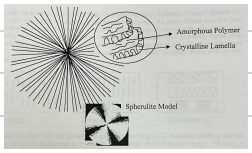
Def: Study of forms of polymer chains, such as crystal structure

→ Polymer crystallinity

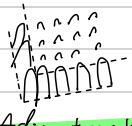


→ Spherulites

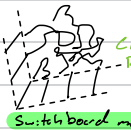
Polarized light reveals a maltese cross (✠)



→ Lamella Structure



Adjacent reentry model
- thought to occur due to energy preference

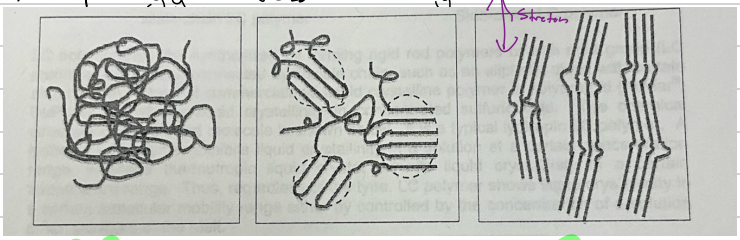


Switchboard model

Today Adjanti is a more favorable explanation

Chaotic, Random

Morphology Control: Stretching

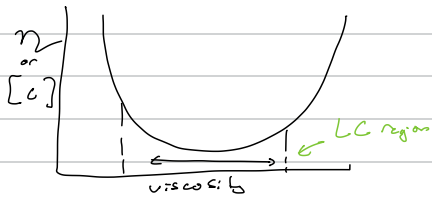


Amorphous Polymer | Semi-crystalline polymer bulk | Semi-crystalline polymer fiber

Stretching
- Molecules realign along stretching direction.
- ↑ stretching → ↓ intermolecular distance
  - ↳ leads to crystalline region formation
- Crystals are also aligned along stretching direction
  - ↳ Thus the fibers or stretched films are stronger along stretching direction

Liquid Crystalline (LC) Polymers

liquid = amorphous
crystal = perfectly ordered
} Two opposing words combined to express unusual material that is neither completely amorphous nor ordered



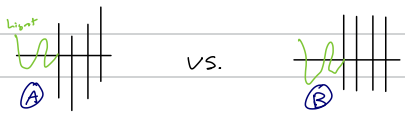
Types of LC Polymers

Nematic LC — No alignment of chain ends

Smectic LC — Chain ends are aligned

Cholesteric LC — Oriented chain planes rotate

Used for LC displays



Light passes through A as it travels transverse alignment

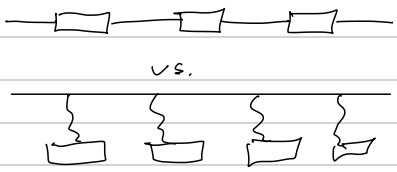
Sustaining an orients the layers so light can rotate up and out

Allows microwaveable tupperware

Thermotropic LC: formed between certain temperature range ex: Aromatic Polyester

Lyotropic LC: formed between certain concentrations range ex: Poly(p-phenylene phthalimide), polyaramid Kevlar

only dissolves in conc. sulfuric acid



Main-chain type LC

Side-chain type LC

□ : LC chromophore

Advantages

(i) Lower viscosity in LC state than random melt solutions

(ii) Molecular alignment even in liquid state → strong fibers

even bullet proof

Chapter 2

Goal: Learn what and when to apply certain analytical techniques

Chapter 2

Goal: Learn what and when to apply certain analytical techniques

You should always start by determining if its a mixture or pure substance

"If you continue into chemical studies, purify, purify, purify, and most importantly purify" - Ishida