

UNIT – III STRUCTURE AND PROPERTIES OF POLYMERS:

Morphology and order in crystalline polymers

Morphology and Order in Crystalline Polymers

1. Introduction to Morphology and Order:

- Crystalline polymers exhibit ordered arrangements of polymer chains in repeating patterns.
- Understanding morphology and order is crucial for tailoring material properties.

2. Polymer Crystallinity:

- Crystallinity refers to the degree of molecular order within a polymer structure.
- Higher crystallinity results in more ordered structures and improved mechanical properties.

3. Morphological Characteristics:

- Lamellar Structure: Polymer chains arrange in stacked layers, forming lamellae.
- Spherulites: Globular structures composed of many lamellae, visible under a microscope.
- Crystalline Nucleation: Initiation of crystalline growth from amorphous regions or nucleating agents.

4. Factors Affecting Morphology:

- Polymer Chain Length: Longer chains promote crystallization due to increased entanglement.
- Temperature and Cooling Rate: Influence crystal size, shape, and degree of perfection.
- Polymer Composition: Different monomers and copolymers lead to varied crystalline structures.

5. Techniques for Morphological Characterization:

- X-Ray Diffraction (XRD): Determines crystalline structure and orientation.
- Differential Scanning Calorimetry (DSC): Measures thermal transitions associated with crystallinity.
- Electron Microscopy: Provides high-resolution images of morphological features.

Applications of Understanding Morphology and Order:

1. Material Design and Engineering:

- Tailoring crystalline morphology enables control over mechanical, thermal, and barrier properties.
- Designing polymers with specific morphologies for applications in packaging, textiles, and biomedical devices.

2. Processing Optimization:

- Understanding crystallization kinetics aids in optimizing processing conditions for desired morphologies.
- Improving efficiency and reducing defects in polymer manufacturing processes.

3. Property Enhancement:

- Manipulating morphology enhances properties such as strength, stiffness, and transparency.
- Development of advanced materials with tailored properties for diverse applications.

4. Structure-Property Relationships:

- Correlating morphology with material performance facilitates structure-property relationships.
- Guiding the design of next-generation polymers with superior properties.

5. Fundamental Research:

- Studying morphology deepens understanding of polymer behavior and structure-function relationships.
- Advances in fundamental knowledge drive innovation in polymer science and technology.

Configurations of polymer chains

Configuration refers to the spatial arrangement of atoms within a polymer chain, independent of overall chain size or shape.

- **Rotational freedom** around single bonds allows chains to adopt various conformations (local arrangements).
- **Restrictions:**
 - Excluded volume effect: Chain segments cannot occupy the same space.
 - Steric hindrance: Bulky groups limit rotation around some bonds.

Types of Configurations:

- **Random Flight:** Simplified model, each segment adopts a random orientation independent of others (not entirely realistic due to excluded volume).
- **Real Chain Configurations:** More complex, account for excluded volume and steric effects leading to a more coiled structure than random flight.

Applications:

- **Material Properties:** Configuration affects a polymer's flexibility, strength, density, and crystallinity.
 - Flexible polymers have more random configurations.
 - Rigid polymers have more extended configurations.
- **Crystallization:** Highly ordered packing of polymer chains in a crystal lattice.
 - Crystallinity depends on chain stiffness and regularity.
 - Crystalline regions contribute to strength and stiffness.
- **Polymer Processing:** Configuration influences how polymers flow, deform, and respond to stresses during processing (e.g., extrusion, molding).

Crystal structures of polymers

Crystal Structures of Polymers in Polymer Chemistry

- **Crystalline vs. Amorphous Polymers:**
 - Crystalline polymers have regions with ordered, aligned polymer chains. These regions are called lamellae.
 - Amorphous polymers lack ordered chain packing.
 - Most polymers are semi-crystalline, with a mix of crystalline and amorphous regions.
- **Factors Affecting Crystallinity:**
 - Polymer chain stiffness: Straighter, more rigid chains pack better.
 - Intermolecular forces: Strong interactions (e.g., hydrogen bonding) promote crystallization.
 - Presence of branching: Disrupts chain packing and reduces crystallinity.
- **Crystallization Techniques:**
 - Cooling from melt
 - Solvent casting
 - Mechanical stretching
- **Applications of Crystal Structure Knowledge:**
 - Understanding and tailoring mechanical properties (strength, stiffness)
 - Predicting thermal behavior (melting point, glass transition temperature)
 - Controlling barrier properties (gas permeability)
 - Designing polymers for specific applications (e.g., high-performance fibers)

Strain-induced morphology

Strain-induced morphology:

- Refers to the changes in a polymer's microscopic structure (morphology) due to applied stress or strain.
- Occurs when polymer chains become aligned and ordered under mechanical deformation.

Key factors influencing strain-induced morphology:

- **Polymer structure:** Regular, stiff chains with strong intermolecular forces crystallize more readily under strain.
- **Temperature:** The process typically occurs above the glass transition temperature (T_g) for increased chain mobility.
- **Deformation:** Greater strain (elongation, stretching) generally leads to higher degree of crystallization.

Applications of strain-induced morphology:

- **Enhancing mechanical properties:** Strain-induced crystals can improve strength, stiffness, and toughness of polymers. This is crucial for materials like fibers, films, and engineering plastics.
- **Tailoring performance:** By controlling strain conditions during processing, manufacturers can optimize the final properties of polymer products.
- **Crystallization control:** Strain can be used to induce crystallization in polymers that wouldn't crystallize otherwise, leading to new material properties.

Crystalline melting point:

Crystalline Melting Point (T_m):

- The temperature at which a crystalline polymer transitions from a solid to a liquid state.
- Represents the breakdown of the ordered arrangement of polymer chains in the crystal lattice.
- Unlike small molecule melting points, it's not always a sharp transition but a range.

Applications of Crystalline Melting Point:

- **Material Selection:** Helps choose polymers for specific applications based on their thermal properties. For example, high T_m polymers are suitable for high-temperature environments.
- **Processing:** Optimizing processes like extrusion, injection molding, and blow molding by understanding the melt behavior of the polymer.
- **Polymer Characterization:** Used to determine the degree of crystallinity in a polymer. Higher T_m often indicates greater crystallinity.
- **Understanding Polymer Properties:** Crystallinity and T_m influence mechanical properties like strength, stiffness, and chemical resistance.

T_m - melting points of homogeneous series

T_m - Melting Points of Homogeneous Series in Polymer Chemistry

Points:

- T_m refers to the melting temperature, the temperature at which a solid polymer transitions to a liquid state.
- In polymer chemistry, T_m is particularly relevant for **homologous series**, which are groups of polymers with the same repeating unit but varying chain lengths.
- For most homogeneous series, T_m exhibits a **general trend** with chain length: T_m increases as the chain length increases. This is because longer chains have stronger intermolecular forces due to increased van der Waals interactions and chain entanglement.
- However, T_m doesn't infinitely increase with chain length. At very high chain lengths, the theoretical T_m approaches an **asymptotic value**, which represents the melting point of a perfect crystal of the polymer.
- There are mathematical models to describe this relationship, like the **Chickos equation**, which helps estimate T_m for different chain lengths within a homologous series.

Applications:

- Understanding the relationship between T_m and chain length is crucial for **polymer processing**. Polymers are often processed in their molten state. Knowing the T_m allows scientists and engineers to choose appropriate processing temperatures for different polymers.
- T_m can be used to **characterize the degree of crystallinity** in a polymer. Highly crystalline polymers will have a sharper T_m peak compared to those with lower crystallinity.
- By comparing T_m of copolymers with their homopolymer counterparts, scientists can gain insights into the **intermolecular interactions** between different monomer units and how they affect the overall packing and order in the crystalline phase.

Effect of chain flexibility and other steric factor

Chain Flexibility and Steric Factors in Polymer Chemistry

Effects:

- **Chain Flexibility:**
 - **Increased flexibility:**
 - Enhances chain mobility: easier movement of segments
 - Lower glass transition temperature (T_g): easier transition from rigid to rubbery state
 - Better processability: easier to form films, fibers, etc.
 - More chain entanglement (at high chain lengths): affects mechanical properties
 - **Decreased flexibility:**
 - Reduced chain mobility: hinders segment movement
 - Higher glass transition temperature (T_g): harder to transition to rubbery state
 - Poorer processability: more difficult to form desired shapes
 - Less chain entanglement: can affect mechanical properties
- **Steric Factors (bulky side groups):**
 - **Increased steric hindrance:**
 - Limits chain mobility due to repulsion between bulky groups
 - Increases glass transition temperature (T_g)
 - Affects packing density and crystallinity
 - Can improve some mechanical properties (e.g., stiffness)

Applications:

- **Designing polymers for specific properties:**

- Tailoring chain flexibility and steric factors to achieve desired T_g , processability, and mechanical properties. (e.g., flexible polymers for films, rigid polymers for structural applications)
- **Rubber elasticity:**
 - Highly flexible chains with low T_g are essential for elastomeric behavior.
- **Plastics engineering:**
 - Balancing chain flexibility and steric factors to create strong, yet processable plastics.

Entropy and Heat of Fusion

Entropy (S):

- Represents the degree of disorder or randomness in a polymer system.
- Higher entropy corresponds to a more disordered state.
- In polymer chemistry, entropy is crucial for understanding:
 - Polymer chain flexibility and mobility
 - Glass transition temperature (T_g) - Entropy change plays a role in the transition from the rigid, glassy state to the rubbery state.
 - Miscibility of polymers - Blending of polymers with high entropy of mixing can lead to favorable interactions and stronger materials.

Heat of Fusion (ΔH_f):

- The amount of energy absorbed per mole of a polymer during melting (solid to liquid transition).
- Represents the energy required to overcome intermolecular forces and increase disorder in the system.
- In polymer chemistry, heat of fusion is important for:
 - Determining the degree of crystallinity - Higher ΔH_f indicates a more crystalline polymer with more ordered regions.
 - Understanding processing behavior - The energy needed to melt a polymer is related to its processing temperature.
 - Material selection - Polymers with high ΔH_f can offer better dimensional stability due to their well-defined crystalline structure.

Applications:

- **Designing polymers with tailored properties:** By understanding the relationship between entropy, ΔH_f , and polymer structure, scientists can design materials with desired flexibility, thermal properties, and miscibility characteristics.
- **Understanding polymer processing:** Knowledge of ΔH_f helps optimize processing conditions like temperature and pressure for efficient melting and shaping of polymers.
- **Developing new materials:** Blending polymers with complementary entropy and ΔH_f values can lead to novel materials with improved properties.

The glass transition temperature, T_g , relationship between T_m and T_g

Glass Transition Temperature (T_g):

- **Definition:** The temperature at which an amorphous (non-crystalline) polymer undergoes a transition from a rigid, glassy state to a rubbery state.
- **Physical Changes:** Below T_g , the polymer chains have minimal mobility, making the material stiff and brittle. Above T_g , the chains gain some mobility, allowing the polymer to become more flexible and rubbery.
- **Importance:** A crucial property for determining a polymer's usability at various temperatures. It affects mechanical strength, stiffness, and other properties.
- **Factors Affecting T_g :**
 - Chemical structure: Polymers with stiffer chains or more intermolecular interactions tend to have higher T_g .
 - Molecular weight: Generally, T_g increases with increasing molecular weight.

Melting Temperature (T_m):

- **Definition:** The temperature at which a crystalline polymer transitions from a solid to a liquid state.
- **Physical Change:** At T_m , the ordered arrangement of polymer chains in the crystalline regions breaks down, and the polymer melts.
- **Importance:** Determines a polymer's processability and suitability for applications requiring high-temperature stability.

Relationship Between T_g and T_m :

- **General Trend:** T_g is typically lower than T_m for most polymers.
- **Rule of Thumb:** For many symmetric polymers, T_g is roughly half of T_m ($T_g \approx 0.5 T_m$). This is an estimate and can vary depending on the specific polymer.
- **Deviation from Rule:** Highly asymmetric polymers or those with strong intermolecular interactions may deviate from this rule.

Applications:

- **Material Selection:** By considering T_g and T_m , engineers can choose polymers suitable for specific applications. For example, a cup needing to withstand hot liquids would require a polymer with a T_m above the intended use temperature.
- **Processing:** Knowing T_g and T_m helps determine the appropriate processing temperature for shaping polymers. Processing typically occurs above T_g but below T_m for most polymers.
- **Polymer Design:** Understanding the factors affecting T_g allows scientists to design polymers with tailored properties for specific applications.

Effect of molecular weight, diluents, chemical structure, chain topology, branching and crosslinking

Molecular Weight:

- Higher molecular weight generally leads to:
 - Increased viscosity (thicker, more resistant to flow)
 - Improved mechanical strength (stronger, more elastic)
 - Higher melting point
 - Poorer processability (more difficult to mold or shape)

Diluents (Solvents or Plasticizers):

- Diluents can:
 - Reduce viscosity (easier to process)
 - Affect mechanical properties (can decrease strength)
 - Plasticizers increase flexibility at lower temperatures

Chemical Structure:

- The chemical makeup of the polymer chain heavily influences:
 - Physical and chemical properties (strength, electrical conductivity, resistance)
 - Reactivity (how readily it interacts with other substances)
 - Thermal behavior (melting point, glass transition temperature)

Chain Topology (Linear vs. Branched vs. Network):

- Chain topology refers to how the polymer chains are arranged:
 - Linear chains: Easy to pack, often crystalline, good strength
 - Branched chains: More difficult to pack, less crystalline, good processability
 - Network polymers (crosslinked): Rigid, insoluble, excellent chemical resistance

Branching:

- Increased branching can:
 - Reduce packing efficiency, leading to lower crystallinity and strength
 - Improve processability due to lower melt viscosity

Crosslinking:

- Crosslinking creates permanent bonds between polymer chains, forming a network:

- Dramatically increases viscosity (becomes a gel or solid)
- Improves mechanical strength and chemical resistance
- Limits elasticity and processability

Applications:

- Understanding these factors allows scientists to tailor polymers for specific applications:
 - High molecular weight for tire rubber (strength)
 - Branched polymers for films (processability)
 - Crosslinked polymers for coatings (durability)
 - Specific chemical structures for biocompatible materials (medical implants)