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## Introduction: Polymer Morphology

### General Issues

**Morphology: Generally consider at least 2 coexisting phases.**

**A phase is defined by distinguishable physical features:**

**density, optical density, orientation. A distinguishable physical feature is something you can measure, so the definition of a phase implies that there is some measurable feature. Generally phases are considered to be basically fixed in structure at least on the time scale of normal observation.**

**Coexistence means that two phases are present in the same material. This can be due to thermodynamic equilibrium or due to kinetic or topological constraints on the system. A phase's structural shape and size is generally governed by a balance of thermodynamics and kinetics. Polymer systems are fairly unique in that kinetically dominated systems are the normal situation. Most commonly used polymer systems involve kinetically dominated structures.**

**Morphology involves the relative arrangement of phases in space.**

### **Structural Levels.**

**The observed morphology is a strong function of the level of magnification at which a material is observed. For instance a sheet of high-density polyethylene (milk jug material) is macroscopically two phase since it is turbid while a film of metallocene PE macroscopically is single phase since the crystallites are extremely small. If magnified 1000 times HDPE displays spherulites while MPE shows single phase. If Magnified  $1e6$  both display lamellar structures on a colloidal scale. If magnified to atomic dimensions both display identical crystalline and amorphous structures.**

**Most materials display basic levels of structure in magnification where distinct features can be observed. It is important to consider that morphology can be described at different levels in this way.**

**EXAMPLE: Spherulitic polymer crystals (HDPE).**

**Level 1: Crystal**

**Level 2: Lamellae**

**Level 3: Fiber Bundles**

**Level 4: Intermediate Features**

**Level 5: Spherulites**

### Polymer Morphology:

**1) The main morphological feature distinguishing polymeric systems from**

**Metals, Ceramics and even biological materials is disorder. They are materials inherently governed by statistics, entropy and kinetics.**

**2) Polymer morphology differs from other materials since one often is describing statistical averages of morphological features. *Every morphological feature of a polymer has an associated statistical distribution associated with it.***

**Example: XRD peaks for polymers are always broad with a large amorphous background. i) small-crystallites/Scherrer Effect, ii) always semi-crystalline, iii) lateral growth shows polydispersity, iv) Levels 3,4,5 above are highly inhomogeneous.**

**As a result of the inherent disorder in polymer morphology, indirect characterization techniques are often preferable and are more powerful than direct techniques. To fully understand such systems a combination of direct and indirect techniques are necessary.**

**Morphology is observed using structural characterization techniques.**

**Direct Observation: AFM, STM, TEM, SEM, OM  
user bias, limited spatial averaging, relationship between structural levels is not clear, for disordered systems general features of system are often obscured.**

**Indirect Observation: Structural versus Non-Structural**

**i) Structural: XRD, SAXS, USAXS, SALS**

**Good for global averaging of statistical systems. Relies on a good model usually based on direct techniques.**

**ii) Non-Structural:**

**a) Thermodynamic: DSC**

**e.g. Avrami Kinetics from isothermal crystallization**

**b) Kinetic: DMTA**

**e.g. BCP ODT**

**GENERALLY "ii" is VERY TRICKY BUSINESS.**

**With This In Mind What is Polymer Morphology?**

### **A) MORPHOLOGIES OF MOLECULAR ORDER AND ABOVE**

**-Semi-crystalline morphology: Spherulitic, Single Crystalline, Fibrillar, Low-Crystalline Systems, and Many Others.**

**-Liquid-Crystalline morphologies: Side Chain, Main Chain, Liquid Crystalline Transitions, Meso-phases.**

### **B) MORPHOLOGIES OF COLLOIDAL ORDER AND ABOVE**

**-Block-copolymers: (Relies on thermodynamics from next category.)**

### **C) MORPHOLOGIES OF MACROSCOPIC ORDER**

**-Amorphous/Amorphous phase separation: Spinodal/Nucleation and Growth**

### **D) FILLED SYSTEMS**

**-Polymer/Inorganic**

**-Polymer/Polymer**

**NEXT TIME:**

**2. Semi-Crystalline Morphology:**

**I. XRD for Polymers.**

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