

Structure-Property Relationships in Polymer Systems

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Polymers are a class of organic (mostly composed of C, H, O, N) molecules usually featuring a backbone chain of repeating units (mers, or monomers) connected by covalent bonds, and weak secondary bonding between these chains. Though termed “plastics”, polymers exhibit a huge range of behaviors beyond plasticity that depend on their composition, synthesis method, and environmental conditions (e.g. temperature).

Structure

Chain Structure

Polymer chains can exhibit various structures depending on how the chains are covalently bonded with each other and macroscopically arranged. Their structure affects how easily chains can slide past each other upon loading (chain mobility), which in turn, determines much of their properties. Polymers fall into 3 classes based on chain mobility/arrangement: thermoplasts, thermosets, and elastomers.

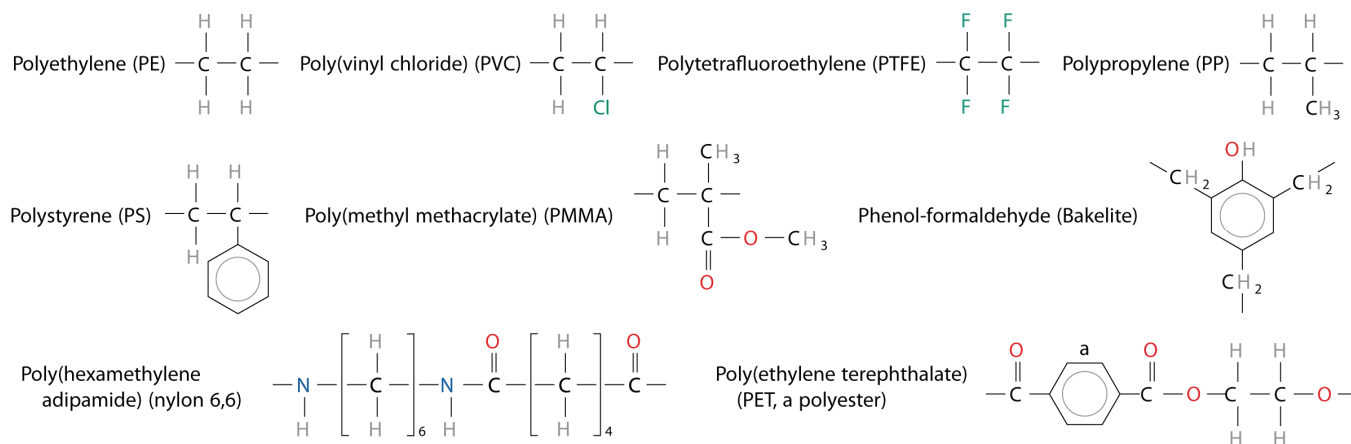
Chain mobility also determines a material’s recyclability. The classical definition of a recyclable material is one that can be melted and remolded (e.g. for chains to be able to flow relative to each other).

Structure	Example	Class	Recyclable?	Chain mobility
linear	HDPE	thermoplast	Y	Greatest
branched	LDPE			Good, but less than linear
cross-linked	epoxy	thermoset	N	None
network	phenol-formaldehyde			None
coiled cross-linked	polyisoprene (rubber)	elastomer	N	No inter-chain sliding, but chains can uncoil and recoil*

* an elastomer will recoil because: 1) steric hindrance due to *cis* double-bond configurations causes the natural shape of the chain to be kinked/coiled; 2) a stretched chain will want to return to a higher-entropy state (also read p. 589 regarding vulcanization)

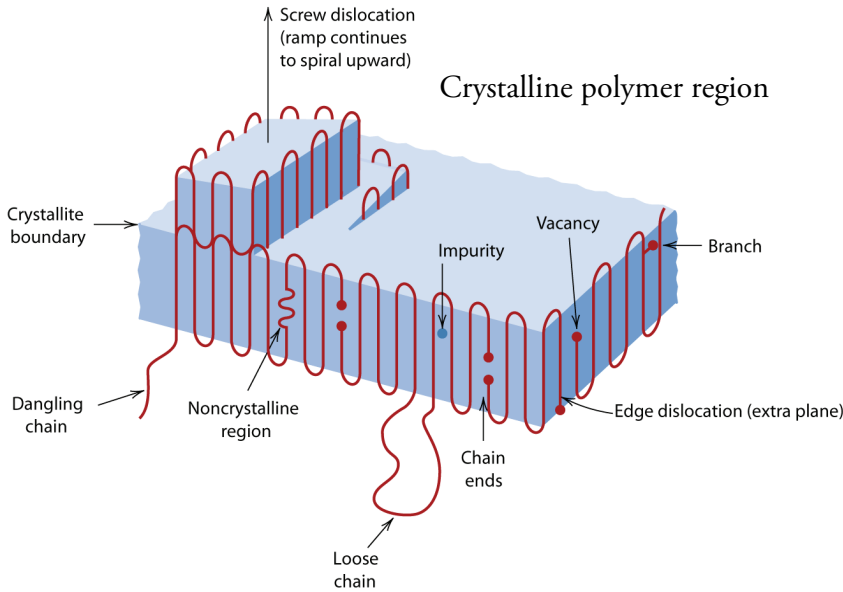
Copolymers

Polymers with two or more distinct repeating backbone units are termed copolymers. Different types of copolymer arise based on the relative arrangement of these different units: block, alternating, random, graft.

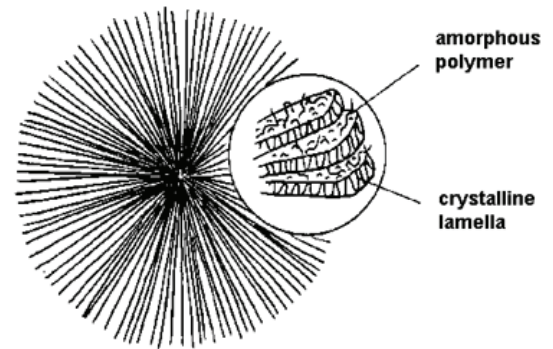


Crystallinity

Certain polymers can become crystalline when certain regions of chains are folded and arranged parallel to each other. These regions are usually platelike (~10nm thick, 10µm long), and can either arrange into a multilayer structure separated by amorphous polymer strands, or into spherulite structures, which have the platelike regions radiating outwards from a nucleation site.



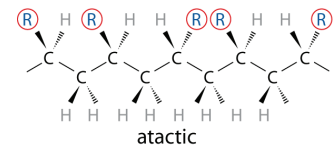
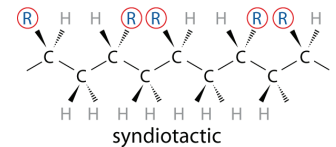
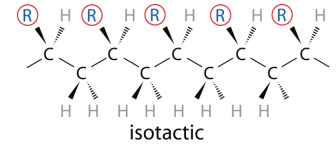
Any aspect of a polymer's structure that hinders/obstructs chain packing/mobility will negatively affect a polymer's ability to form crystalline regions.



(memorize!)

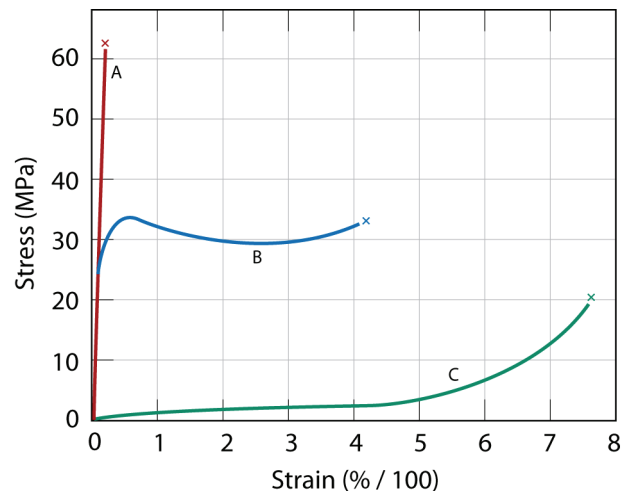
POLYMER STRUCTURES THAT ENCOURAGE CRYSTALLINITY

- 1) No cross-linking (thermosets do not crystallize!)
- 2) Small side groups
- 3) No chain branching
- 4) Iso-/syndiotacticity (regular arrangement of sidegroups)
- 5) Simple repeating units
- 6) If copolymer: alternating or block type

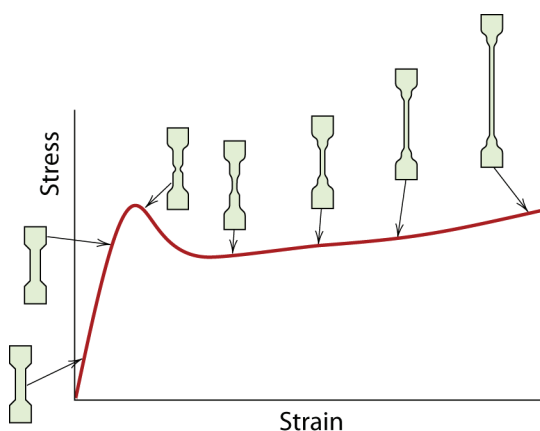
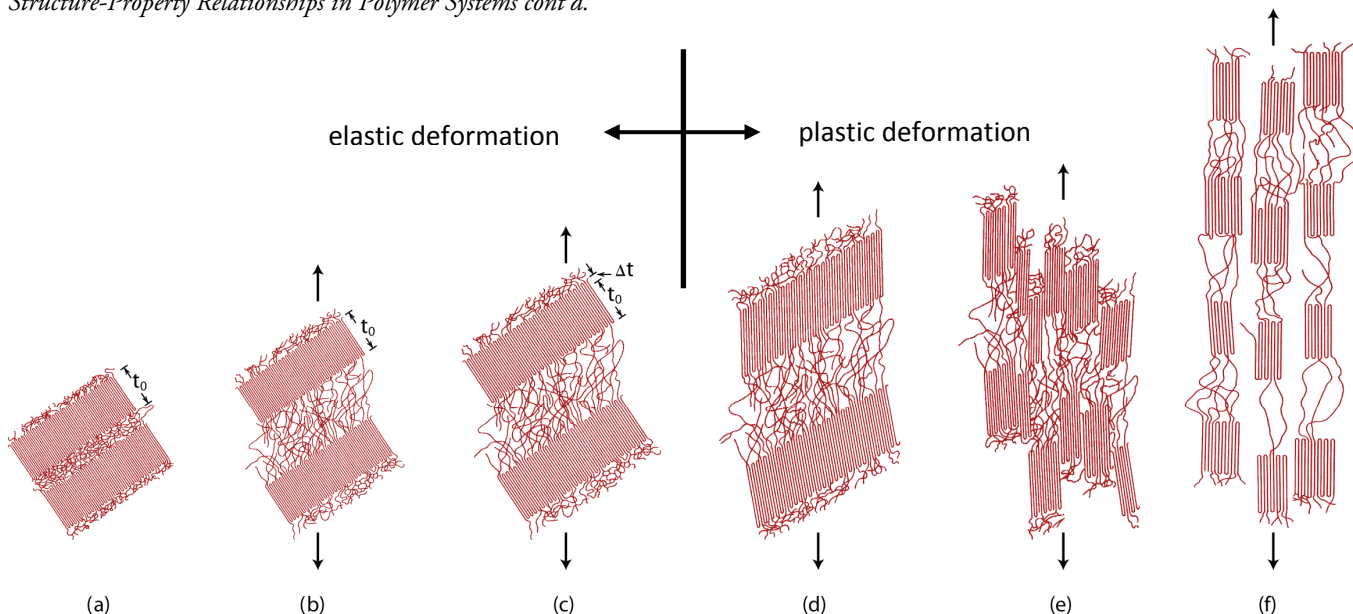


Properties

Polymers can exhibit a range of mechanical behavior from brittle to extremely elastic (elastomeric). Similar to slip, polymer chains must be able to move relative to one another in order for plastic (non-reversible) deformation to occur. Plastic deformation in polymers occurs, however, with a much different mechanism than in metals.



Stress-strain behavior for brittle (A), plastic (B), and elastomeric/highly elastic (C) polymers.



Elastic deformation involves stretching of amorphous regions first, followed by some elongation of crystalline regions.

As plastic deformation begins (at necking), polymer chains in the crystalline region align themselves to the applied load. Eventually, as necking worsens, sections of the crystalline region will break apart into smaller segments.

The glass transition temperature of a polymer is a measure of the ability of polymer chains to move past one another upon heating. A polymer's yield strength is a measure of the ability of polymer chains to withstand inter-chain motion upon applied loading.

To be discussed: viscoelastic behavior (time-dependent strain due to relaxation).

Polymer Terms and Definitions

Weight-average molecular weight [g/mol]: $\bar{M}_w = \bar{m} \times n$, \bar{m} : mer molecular weight

n : degree of polymerization (# of repeat units)

For copolymers, $\bar{m} = \bar{m}_{copolymer} = f_1 \bar{m}_1 + f_2 \bar{m}_2$, $f_1 + f_2 = 1$, f_x : the weight fraction of backbone species x