EMAC 276

Lecture 11 : The Polyolefin Family

Polyethylene – PE: Part 3: PE Short Chain Copolymers

Polypropylene - PP

Poly(1-butene) – Polybutylene – PB

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February 14, 2025

EMAC 276 - Homework Assignment #2

Due: <u>TODAY!</u>, February 14, 2025

Dr. Olah

During our classes we identified several common polymers that when initially discovered were described as "value-less", "impossible to process", "a useless mass", etc. We also identified several methods ("tricks") that were subsequently utilized to develop these polymers into successful products; many which are still with us today.

Your exercise is to select one polymer (either from our in-class discussion or from outside our class discussion) and describe 1) the polymer and the initial performance deficiency, 2) the action taken to overcome this deficiency, and, 3) the ensuing product(s) developed from this modification.

If you choose to use an "in class" example your maximum score will be 10.

If you choose to use an "outside the class" example your maximum score will be 12. (i.e., final score +2)

Your answer shall be short comprising between one-half to one page.

Your answer is shall be structured accordingly:

Paragraph #1: Identify and describe the polymer and it's initial deficiency **(3 Points)**

Paragraph #2: Identify the modification or "trick" which was utilized to overcome this deficiency. **(5 Points)**

Paragraph #3: Identify the commercial product or products resulting from this modification. **(2 Points)**

These Variations of Polyethylene Lead to a Diversity of Products

Linear Versions:

High density polyethylene (HDPE)

Ultra-high molecular weight polyethylene (UHMWPE)

Branched Versions:

Low-density polyethylene (LDPE)

Linear low density polyethylene (LLDE)

Medium-density polyethylene (MDPE)

Very-low-density polyethylene (VLDPE)

High-molecular-weight polyethylene (HMWPE)

Ultra-low-molecular-weight polyethylene (ULMWPE)

Chlorinated polyethylene (CPE)

Bimodal and Trimodal Polyethylene

Cross-linked polyethylene (PEX): four forms (PEX-a, PEX-b . . etc)

Simplest of Molecular Structures Can Lead to a Large Diversity of Structures.

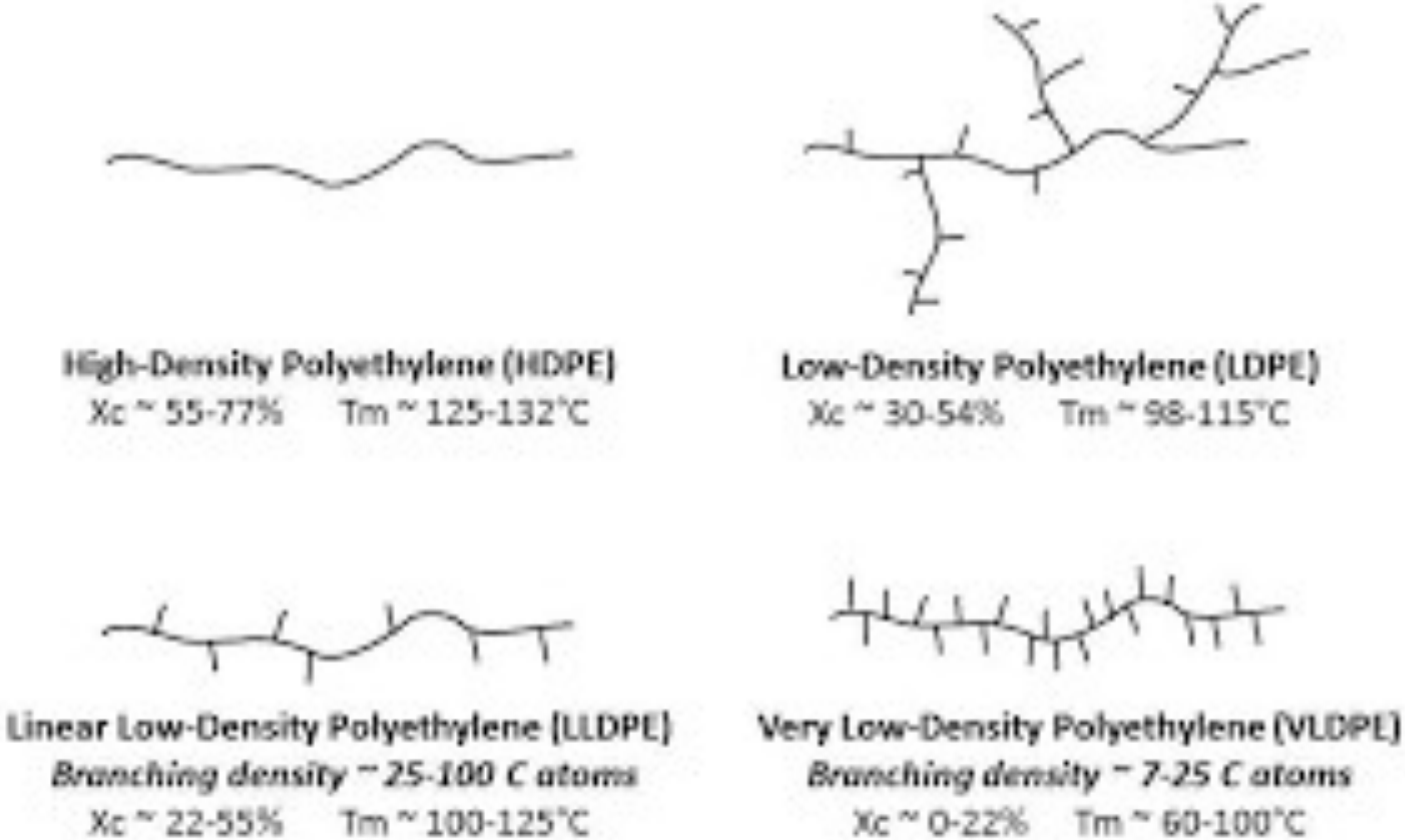
Three fundamental features of polyethylene leading to the diversity of structures and in turn performance are:

a. Short chain and long chain branching.

b. Co-monomer content and distribution.

c. Molecular weight and molecular weight distribution.

The Variance of Most Polyethylene Products is Based on Branching



The Comonomers used with PE Determine the Short Chain Branch Structure

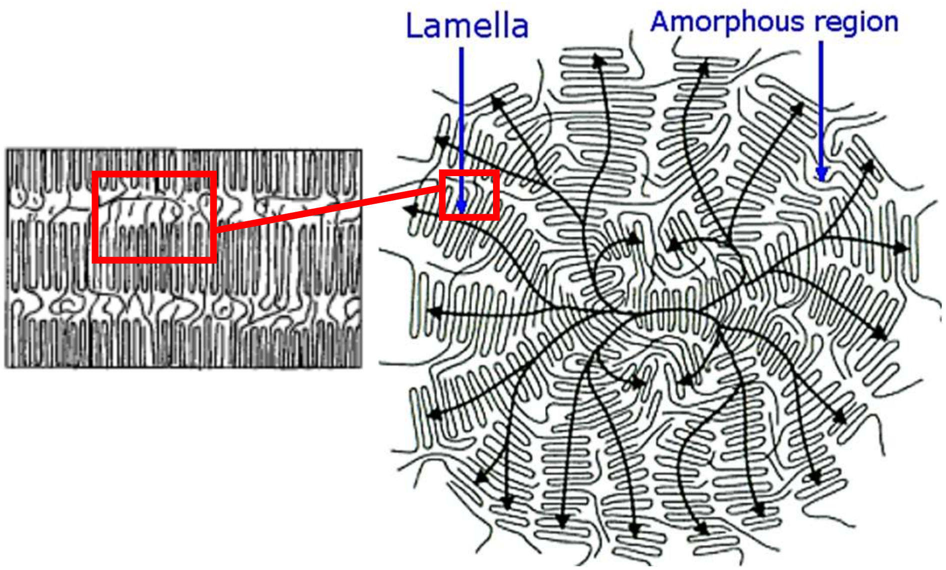
- **Copolymers of Polyethylene :** m>>n

$(CH_2{=}CH_2)_m$	$+ (CH_3\text{-}CH{=}CH_2)_n$	Propylene
	$+ (CH_3\text{-}CH_2\text{-}CH{=}CH_2)_n$	n-Butene
	$+ (CH_3\text{-}(CH_2)_3\text{-}CH{=}CH_2)_n$	n-Hexene
	$+ (CH_3\text{-}(CH_2)_5\text{-}CH{=}CH_2)_n$	n-Octene

- **Heterogeneous Catalysts for the Synthesis of Polyethylene Copolymers:**

  i. Ziegler – Natta Catalyst
  ii. Constrained Geometry Catalyst Technology (CGCT)
  iii. “Shuttle” Technology

Morphological Property Dependence of PE



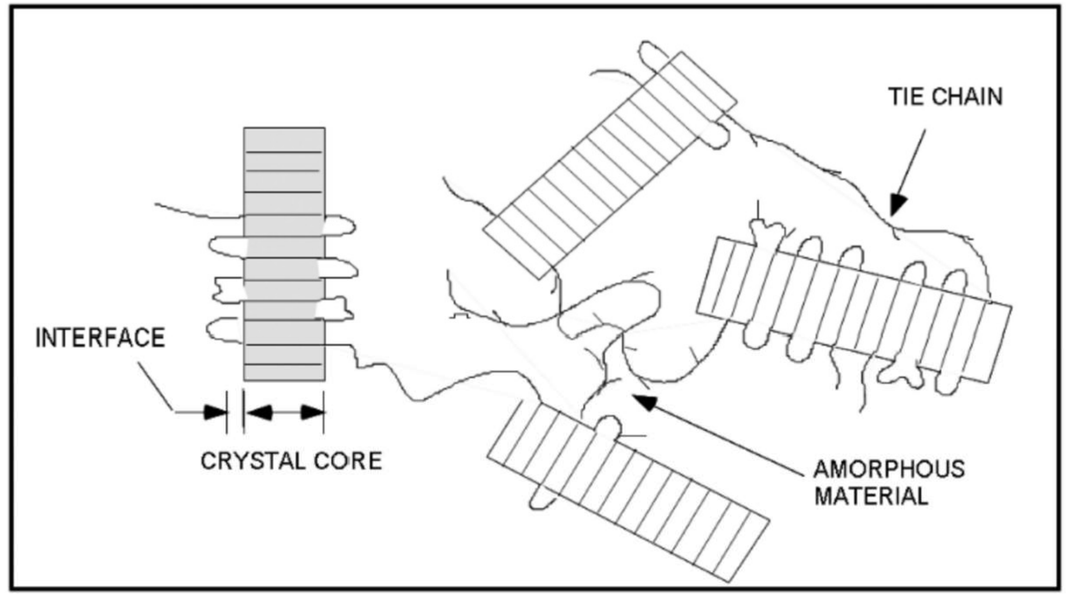


Figure 1. Graphical description of tie chains.

The critical morphological structure that determines most of the properties is the semicrystalline structure of polyethylene.

The molecular connectivity between the amorphous phase and the crystalline phase and the interconnected nature of the crystalline network defines most of the physical properties.

Octene Comonomer Provides the Highest Concentration of Tie Chains in Polyethylene

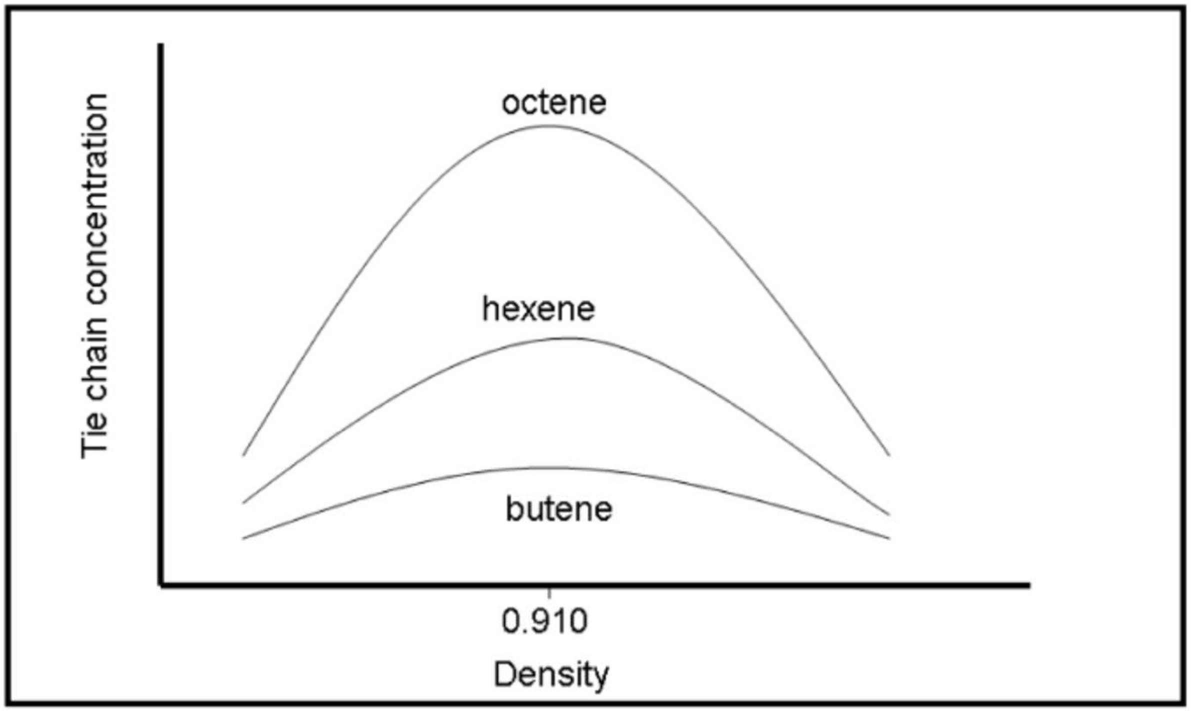
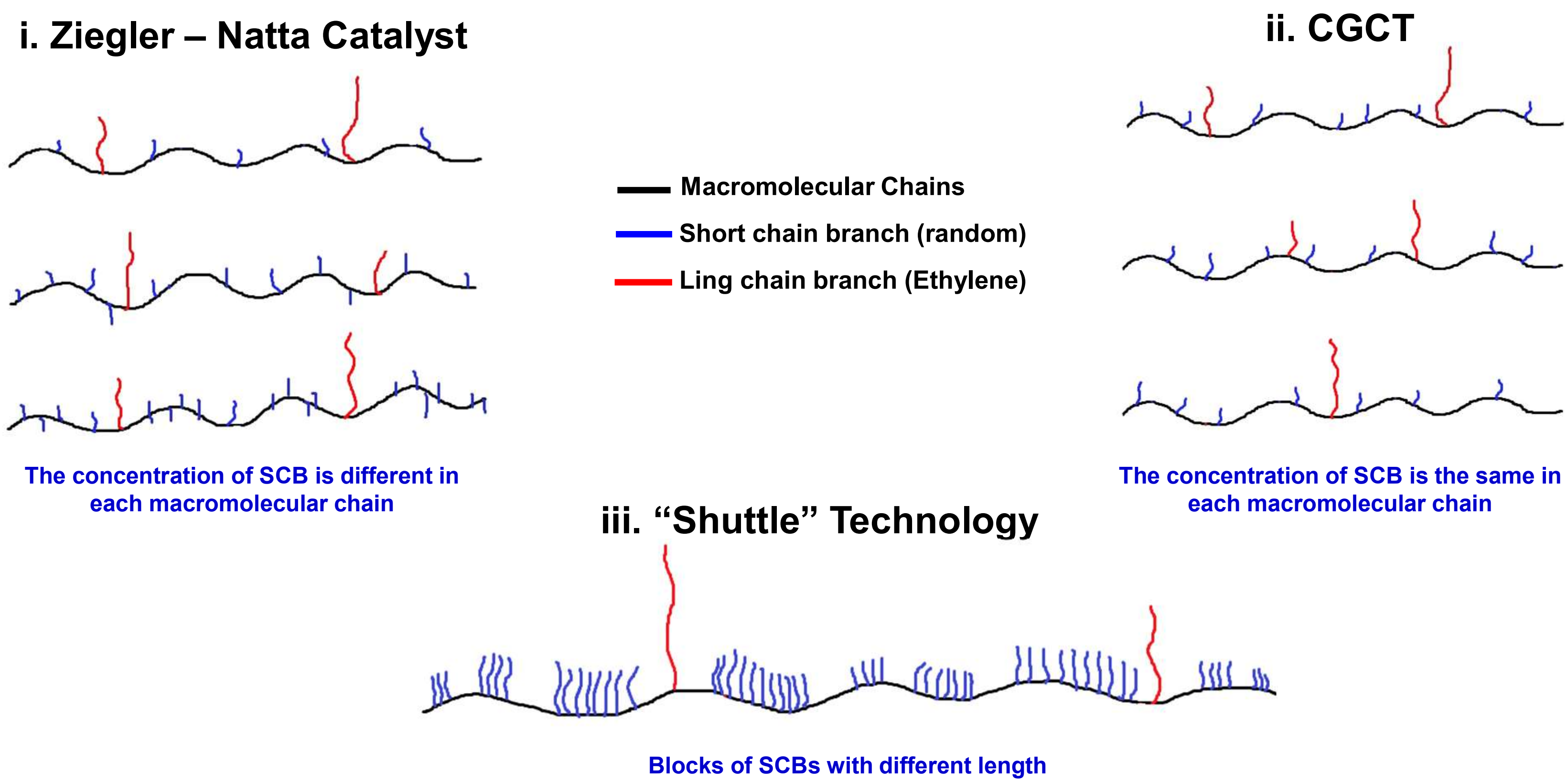


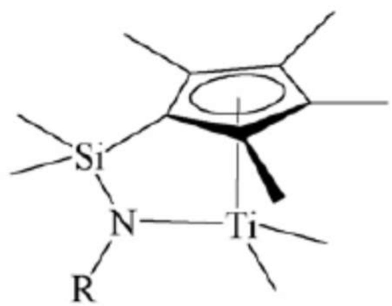
Figure 2. Tie chain concentration vs. density for common alpha olefin comonomers.

Heterogeneous Catalysts



Constrained Geometry Catalysis is a Metallocene Type of Catalyst

Constrained Geometry Catalysts



Example of CGC catalyst for high temperature solution polymerization of olefins having controlled levels of long-chain branching

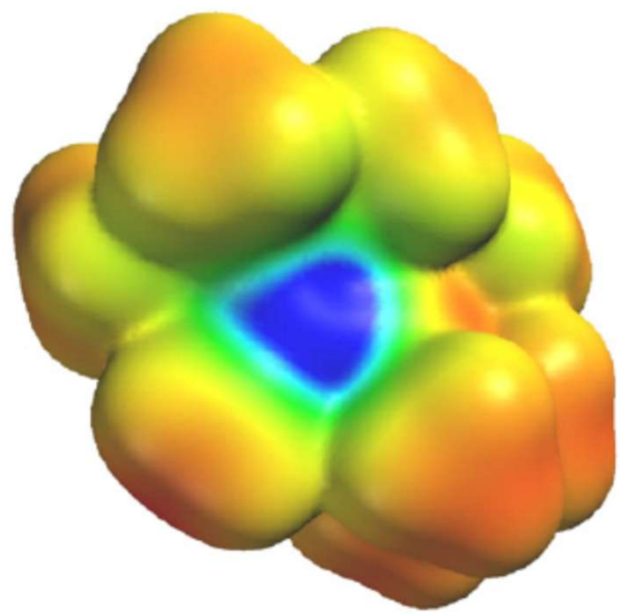


Fig. 7. Constrained geometry catalysts (CGC) technology developed by Dow.

Benefits of CGCT for Polyethylene Copolymerization

Metallocene technology allows for the production of polyolefin copolymers with tailored molecular structures that can be modeled. The constrained geometry catalyst (CGC) technology in a solution process developed by The Dow Chemical Company in the early 90s, Trademarked INSITE® technology, has the most flexibility of the various technologies in its ability to control polymer structure design due to its simplicity of a one-phase system. This technology produces simple, homogeneous structures which can be characterized and modeled relating the structure to the physical properties.

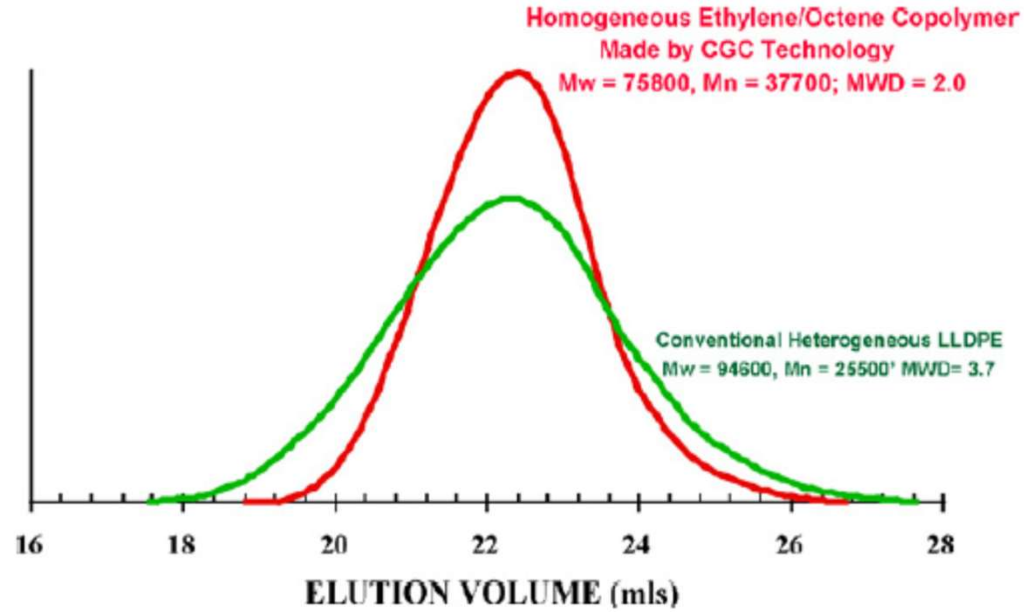
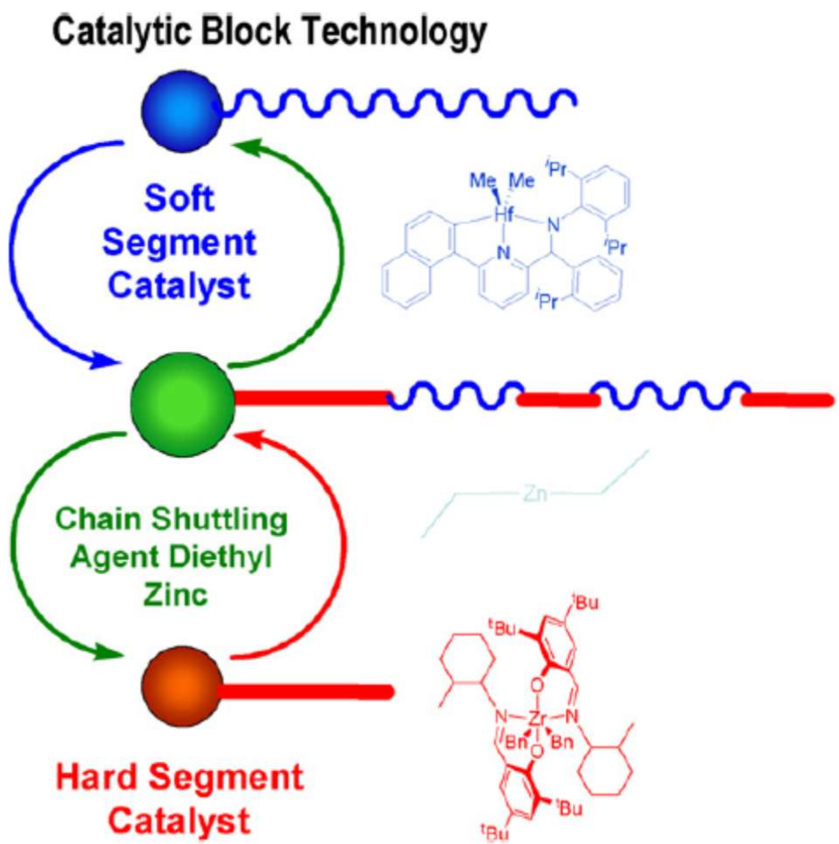


Fig. 11. GPC molecular weight distribution comparison of 2 ethylene–octene copolymers with density 0.920 g/cm^3.

Chain Shuttling Polymerization of Ethylene - Octene



Dow Chain Shuttling System

- Coupled, reversible chain transfer between 2 different catalysts in one reactor
- High catalyst efficiency
- Excellent control of average block lengths
- Excellent control of number of blocks per chain
- Compatible with a wide variety of low cost monomers (octene, butene, etc.)
- Made in Dow's solution process

Fig. 26. Chain shuttling technology for olefin block copolymers.

Classification of Homogeneous Ethylene-Octene Copolymers Based on Comonomer Content

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[1]Department of Macromolecular Science and Center for Applied Polymer Research, Case Western Reserve University, Cleveland, Ohio 44106; [2]Polyolefins and Elastomers Research and Development, The Dow Chemical Company, Freeport, Texas 77541

Table I. Constrained Geometry Catalyst Technology (CGCT) Polymers

Polymer Designation	Pellet Density (g/cc)	Mole % Comonomer	I_2 (g/10 min)	I_{10}/I_2
CGCT96-H	0.9550	0	1.0	8.0
CGCT9180-O	0.9158	2.8	1.0	8.7
CGCT9099-O	0.9079	4.0	1.0	9.3
CGCT9016-O	0.9014	5.2	0.9	8.8
CGCT896-O	0.8968	6.2	0.9	11
CGCT8817-O	0.8879	8.2	0.9	8.7
CGCT8730-O	0.8781	10.7	1.1	6.7
CGCT8702-O	0.8724	12.3	0.8	8.1
CGCT8630-O	0.8682	13.6	0.5	n/a

Morphology Dependent Properties

Systematic correlation of copolymer composition with crystallinity, morphology and tensile stress-strain behavior have been obtained using copolymers prepared by Dow's INSITE constrained geometry catalyst (CGCT) and process technology.

A composition of about 7 % octane comonomer (approximately 30% crystallinity) marks a gradual transition in the solid state structure, **characterized by a loss of spherulitic texture and a change in crystal morphology from chain folded lamellar to fringed micellar.**

Morphology Dependent Properties

The transition occurs as random incorporation of increasing amounts of the non-crystallizable comonomer gradually reduces the length of the crystallizable ethylene sequences.

When the comonomer content is high enough the crystallizable sequences are not long enough to chain-fold into lamellar crystals.

In the absence of chain folding the crystallizable sequence length dictates the crystal thickness, the lateral dimensions are restricted by crowding at the crystal-amorphous interface.

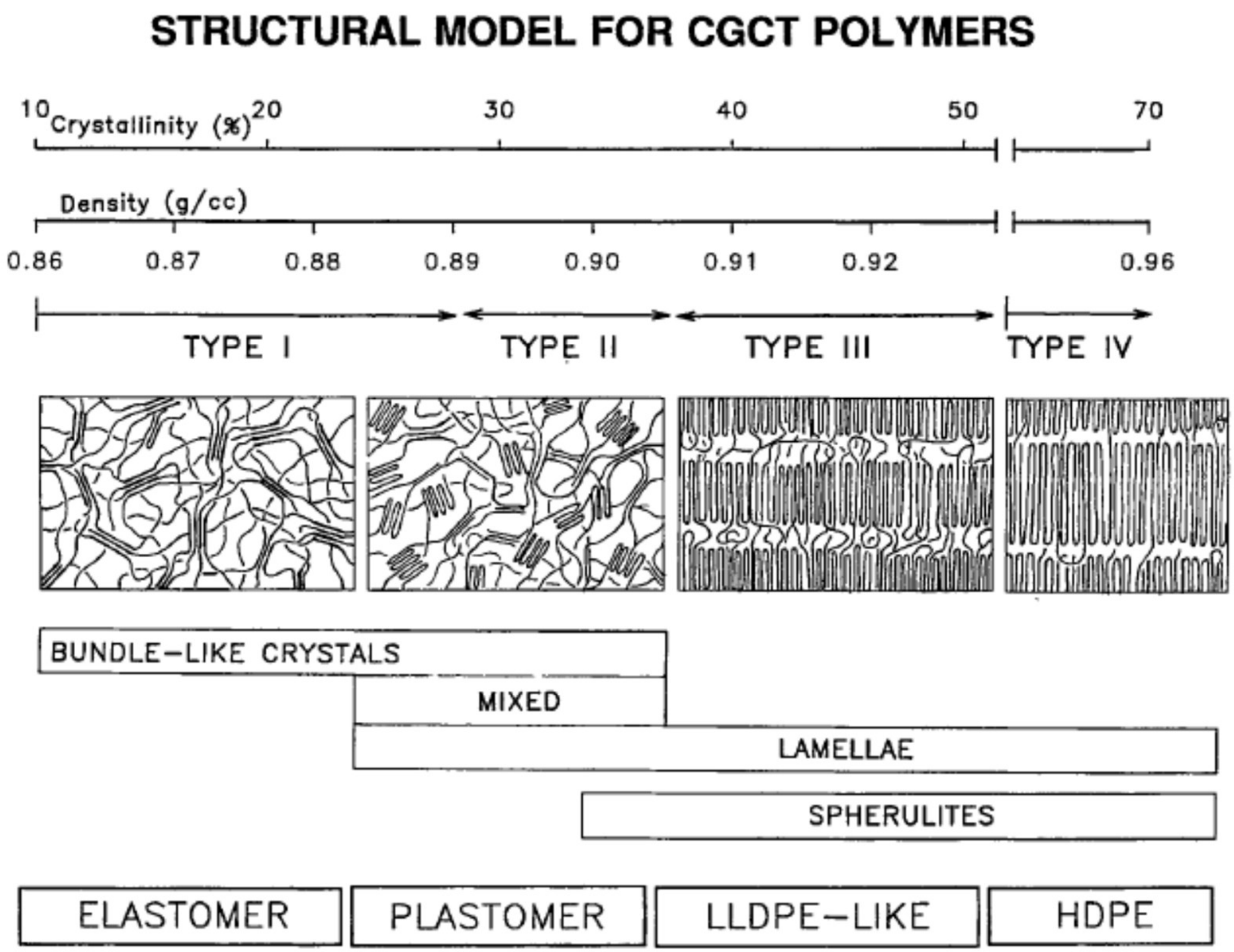

Figure 9. Schematic illustration of the four types of CGCT polymers. The terms elastomer and plastomer are taken from Hwang et al.[7]

What is a plastomer?

- A *plastomer* is a polymer material which combines qualities of elastomers and plastics, such as rubber-like properties with the processing ability of plastic. As such, the word *plastomer* is a combination of the words plastic and elastomer.
- Significant *plastomers* are ethylene-alpha olefin copolymers.

Mechanical Performance as a Function of Octene Comonomer Content

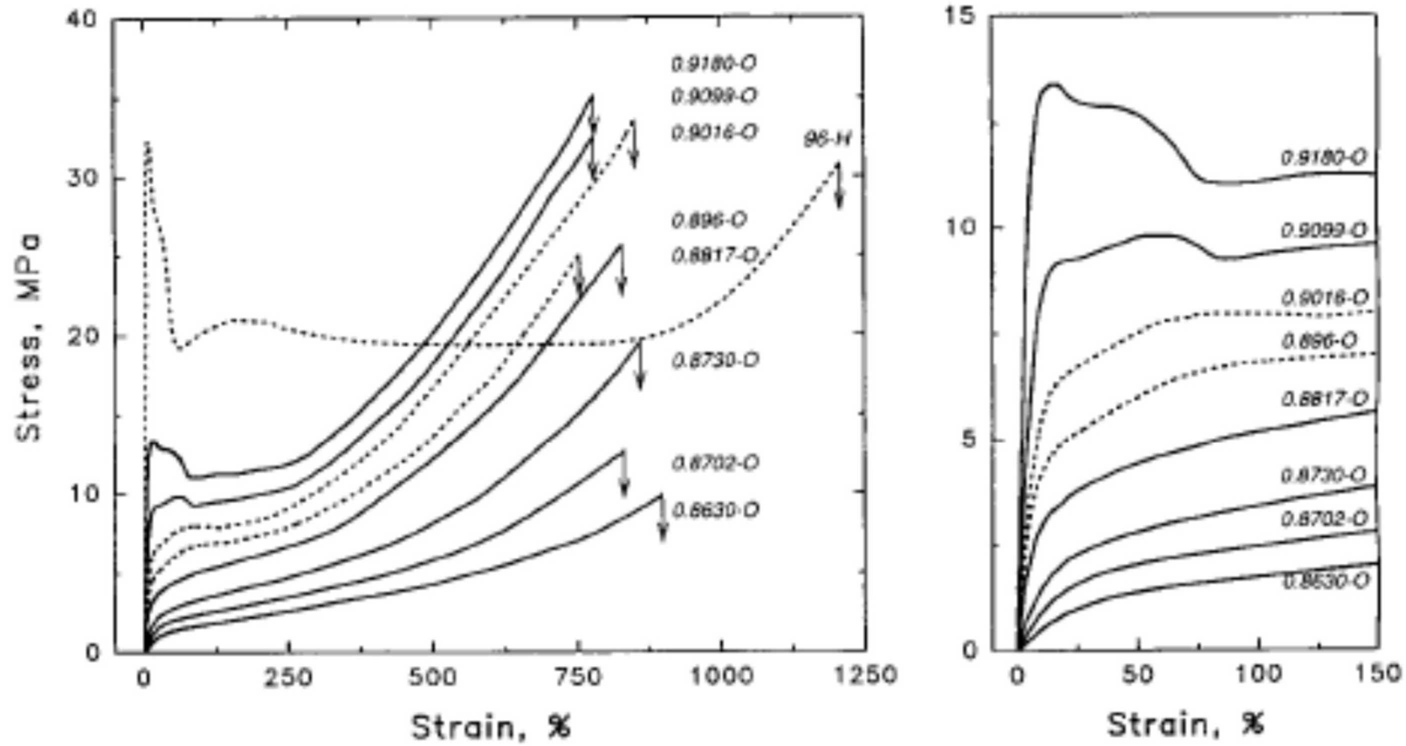

Figure 12. Engineering stress–strain curves of CGCT polymers cooled at 1°C/min with the yield region of the copolymers enlarged. Results for type IV and type II polymers are given by dashed curves, those for type III and type I by solid curves.

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CGCT8630-O	0.8682	13.6	0.5	n/a

Mechanical Performance as a Function of Octene Comonomer Content

Table III. Tensile Properties of CGCT Polymers

Polymer	Cooling Condition	DSC Crystallinity (%)	Elastic Modulus (GPa)	Yield Stress (MPa)	Fracture Stress (MPa)	Fracture Strain (%)
CGCT96-H	1°C/min	77	1.5 ± 0.4	31.7 ± 0.6	25.6 ± 5.2	1088 ± 150
	quenched	62	0.8 ± 0.2	23.5 ± 0.6	36.9 ± 0.7	1332 ± 68
CGCT9180-O	1°C/min	46	0.4 ± 0.1	13.0 ± 0.4	34.6 ± 2.0	755 ± 30
	quenched	42	0.16 ± 0.02	9.8 ± 0.2	31.7 ± 3.6	712 ± 64
CGCT9016-O	1°C/min	33	0.12 ± 0.01	7.8 ± 0.1[a]	30.9 ± 0.2	761 ± 10
	quenched	31	0.055 ± 0.005	7.0[a]	27.8 ± 1.0	664 ± 28
CGCT8702-O	1°C/min	14	0.0065 ± 0.0007	—	12.4 ± 0.6	771 ± 16
	quenched	14	0.0070 ± 0.0004	—	12.5 ± 0.9	757 ± 15

[a] Plateau yield stress.

CGCT96-H = 0% Octene; CGCT9180-O = 2.8% Octene; CGCT9016 = 5.2% Octene; CGCT8702 = 12.3% Octene

Mechanical Performance between Quenched and Slow Cooled Poly(ethylene/octene) Copolymers

CGCT9180 = 2.8% Octene
CGCT8702 = 12.3% Octene

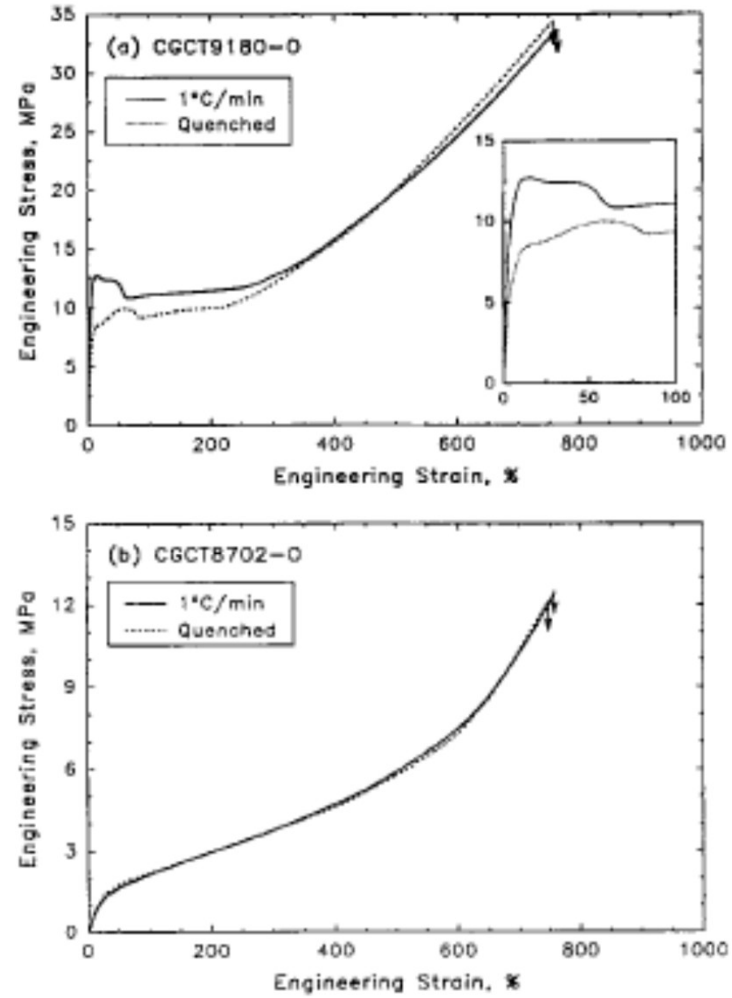


Figure 14. Effect of cooling rate on the engineering stress–strain curve: (a) CGCT9180-O; and (b) CGCT8702-O.

Correlation of Crystallinity from DSC and Density Measurements

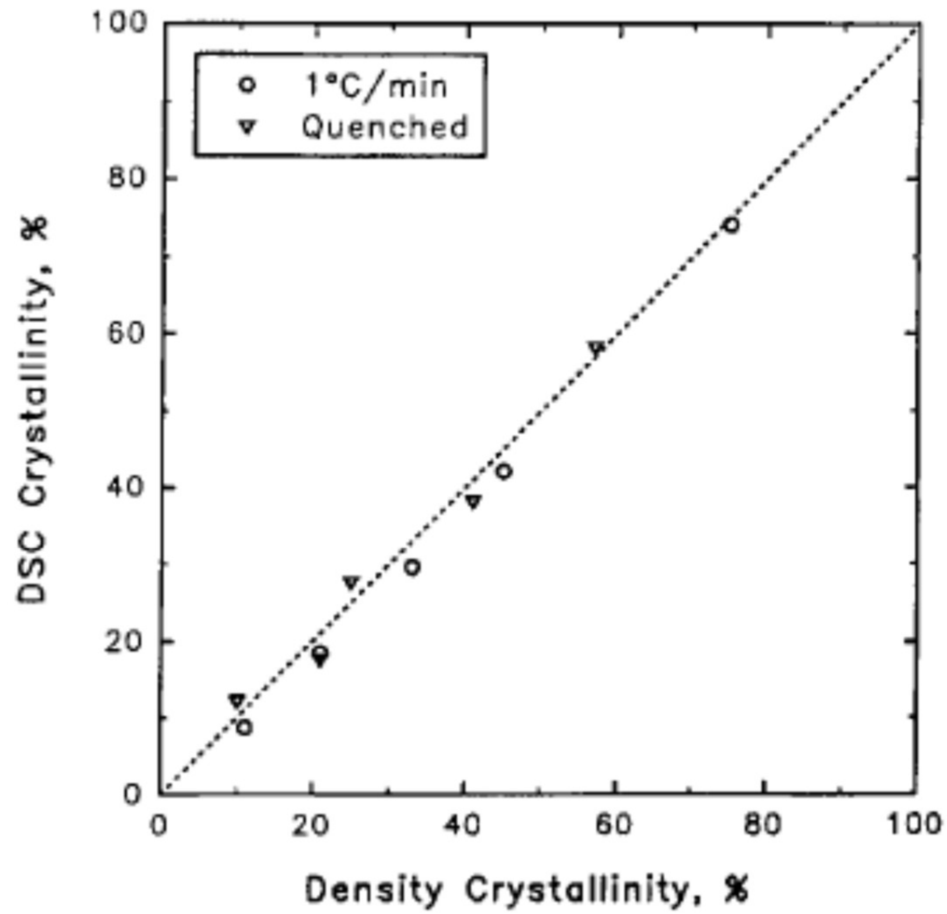
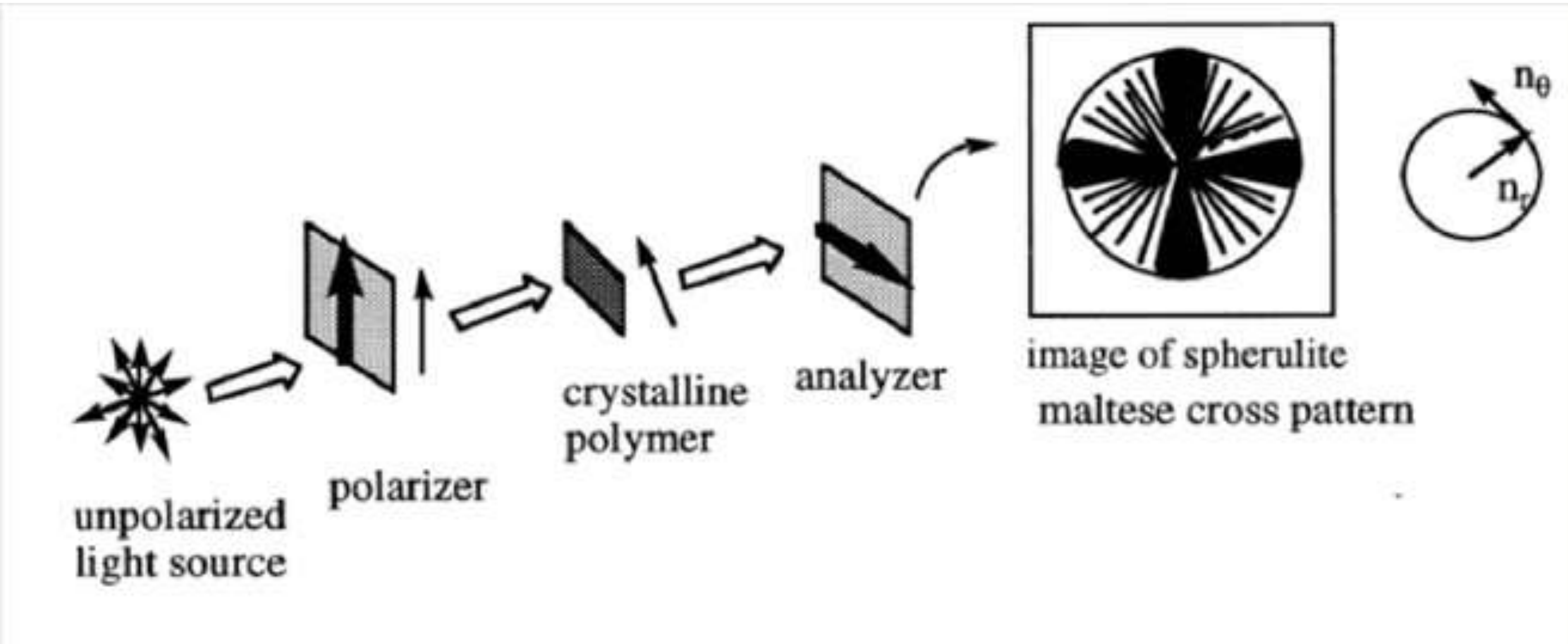
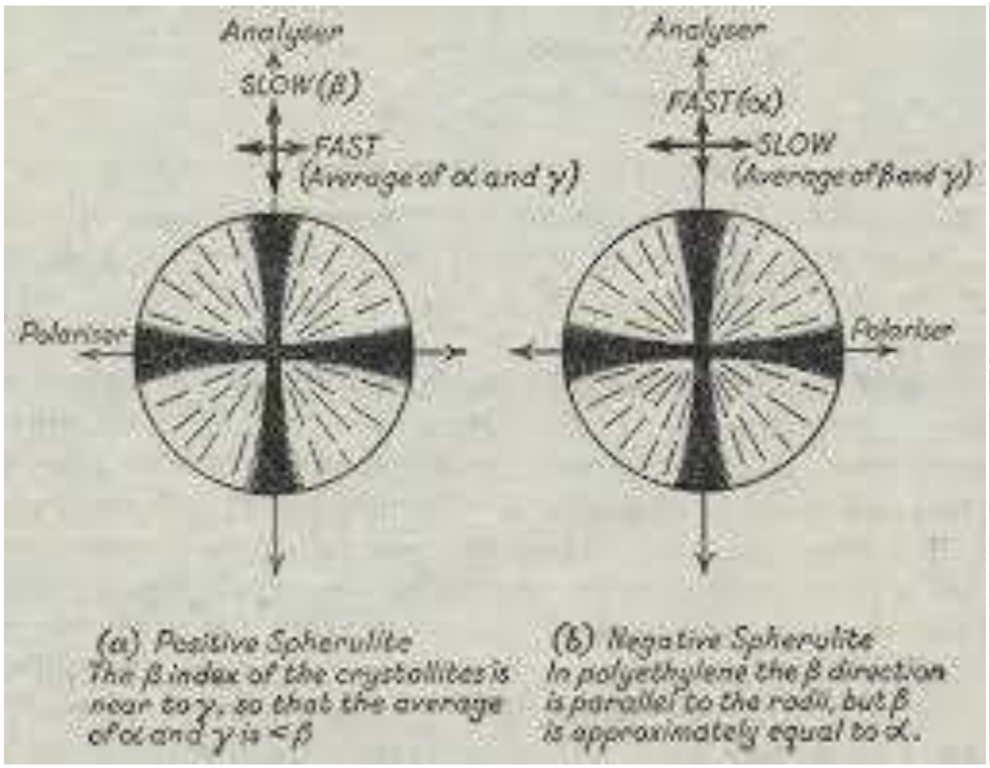


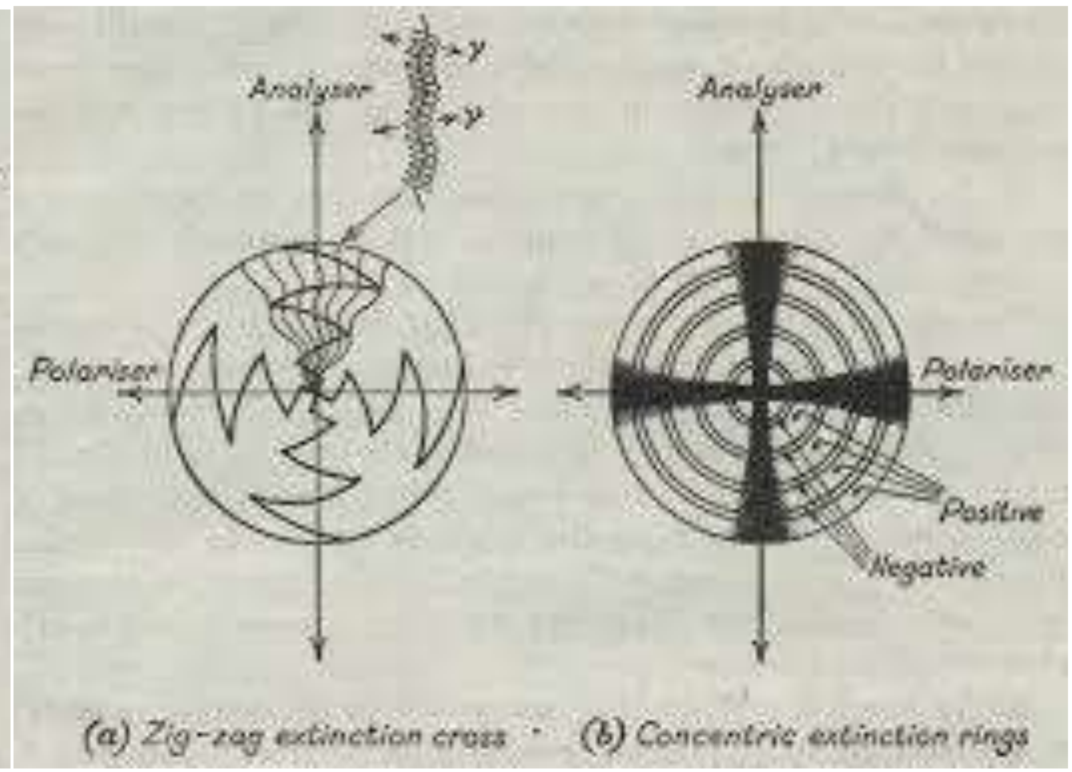
Figure 2. Plot of percent crystallinity from DSC versus percent crystallinity from density: (▽) quenched, and (○) cooled at 1°C/min.

Observation of Spherulites via Polarized Light MIcroscopy

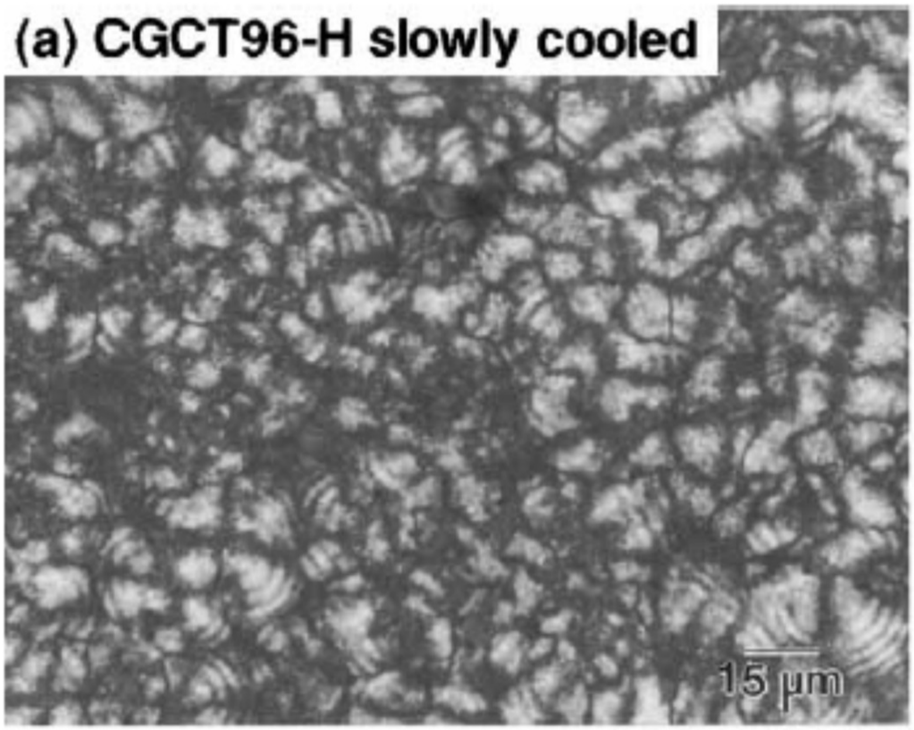


Observation of Spherulites via Polarized Light Microscopy

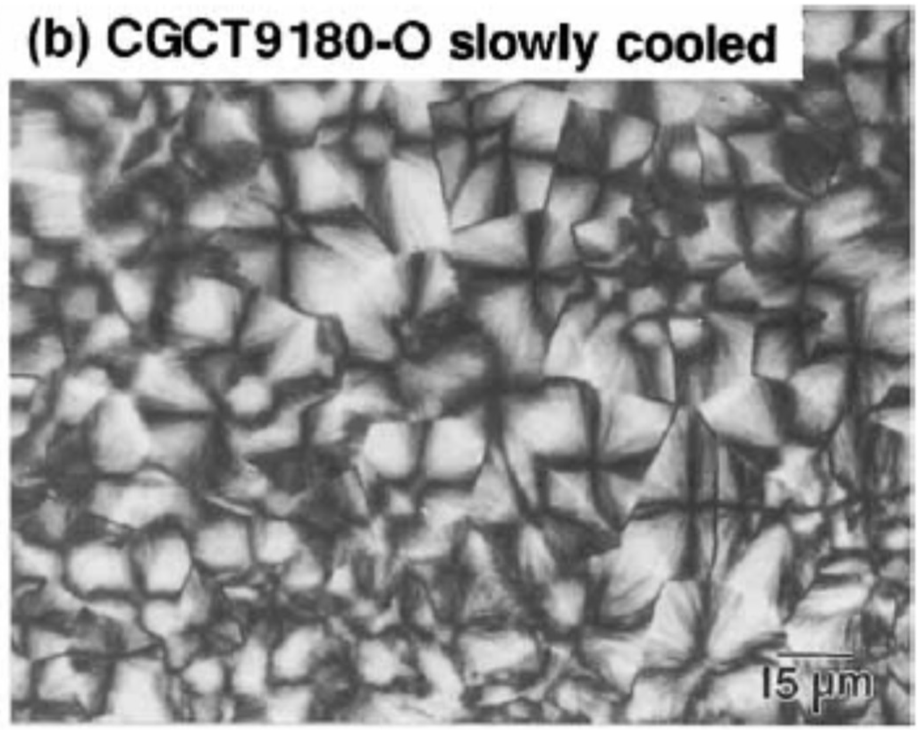




Spherulite Morphology Relative to Cooling Rate

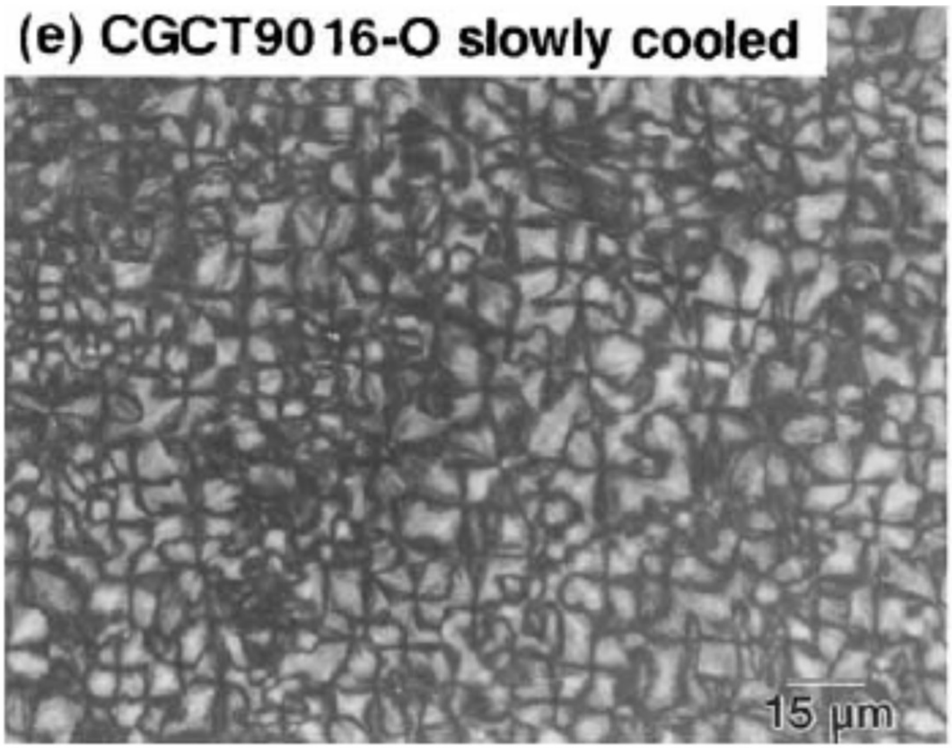


0% Octene Comonomer

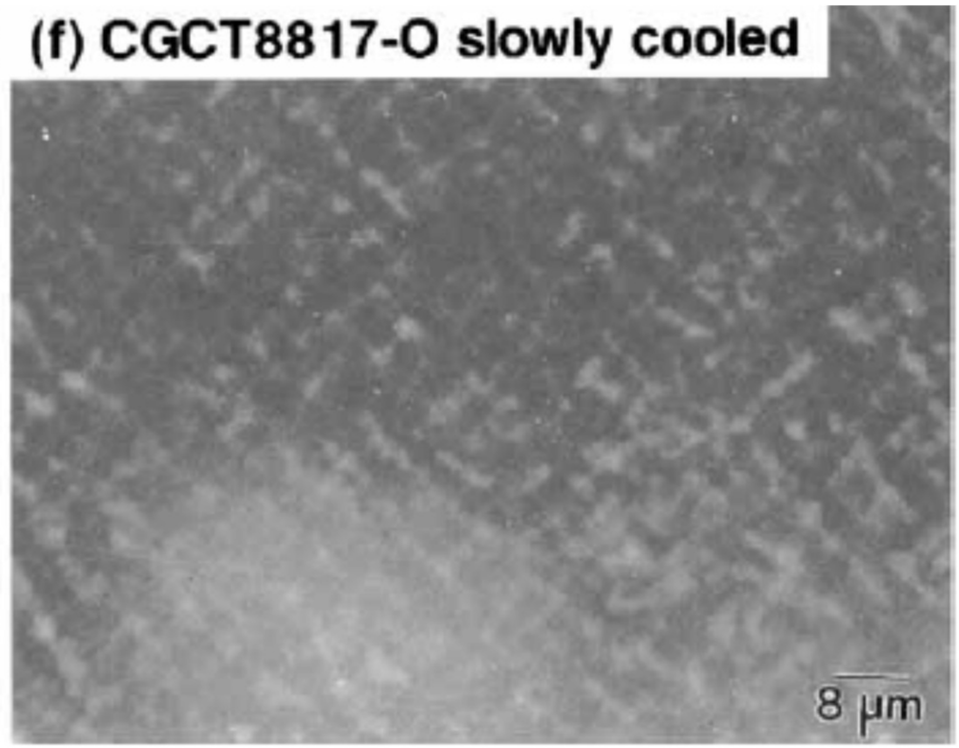


2.8% Octene Comonomer

Spherulite Morphology Relative to Cooling Rate



5.2% Octene Comonomer



8.2% Octene Comonomer

Deformation of Elastomeric Ethylene−Octene Copolymers

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Table 1. Characteristics of Elastomeric CGCT Ethylene−Octene Copolymers

(a) Comonomer Content Variable

polym desig	mol % comonomer	melt index (g/10 min)	density[a] (g/cm^3)	density crystallinity (%)	heat of melting[b] (J/g)	DSC crystallinity (%)
CGCT88	8.2	0.9	0.8883	23	55	19
CGCT87	12.3	0.8	0.8730	12	36	12
CGCT86	13.6	0.5	0.8679	9	27	9

(b) Molecular Weight Variable

polym desig	M_w	M_n	melt index (g/10 min)	density[a] (g/cm^3)	density crystallinity (%)	heat of melting[b] (J/g)	DSC crystallinity (%)
CGCT87−57K	131700[c]	56700[c]	0.8	0.8730	12	36	12
CGCT87−37K	81700	37300	5	0.8757	14	36	12
CGCT87−32K	68600	32000	10	0.8747	14	37	13
CGCT87−26K	52300	26000	30	0.8751	14	32	11
CGCT87−20K	40200	19700	73	0.8763	15	41	14

Influence of Octene Comonomer Content on the Mechanical Performance

CGCT88 = 8.2% Octene; CGCT87= 12.3% Octene CGCT86 = 13.6% Octene

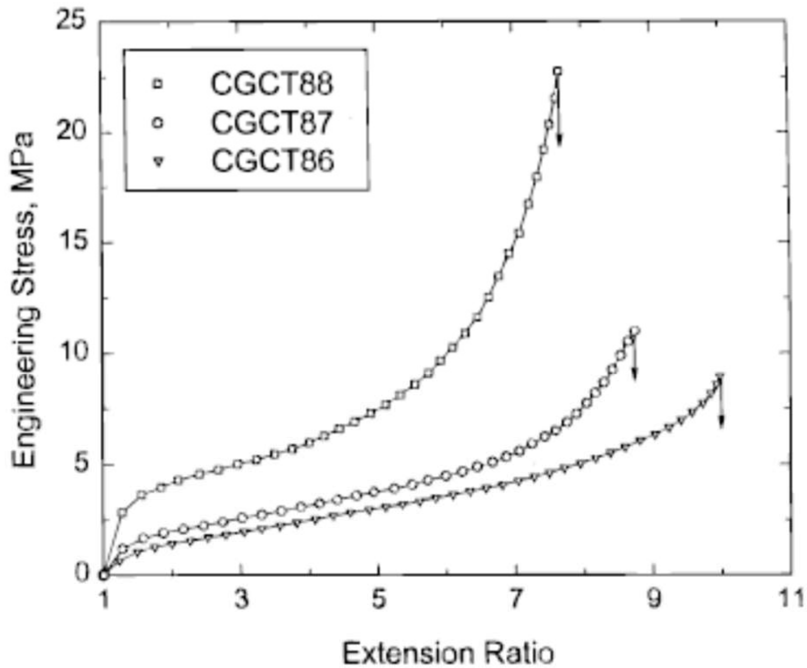

Figure 1. Stress−strain curves of three elastomeric CGCT copolymers at room temperature.

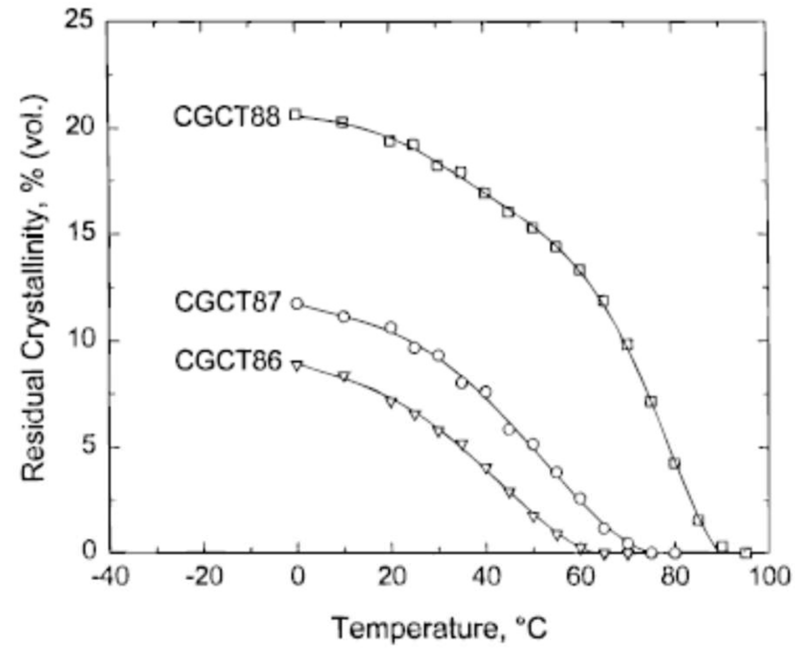

Figure 2. Volume crystallinity as a function of temperature in the melting range.

Influence of Molecular Weight on the Mechanical Performance of Ethylene-Octene Copolymers; 12.3% Octane.

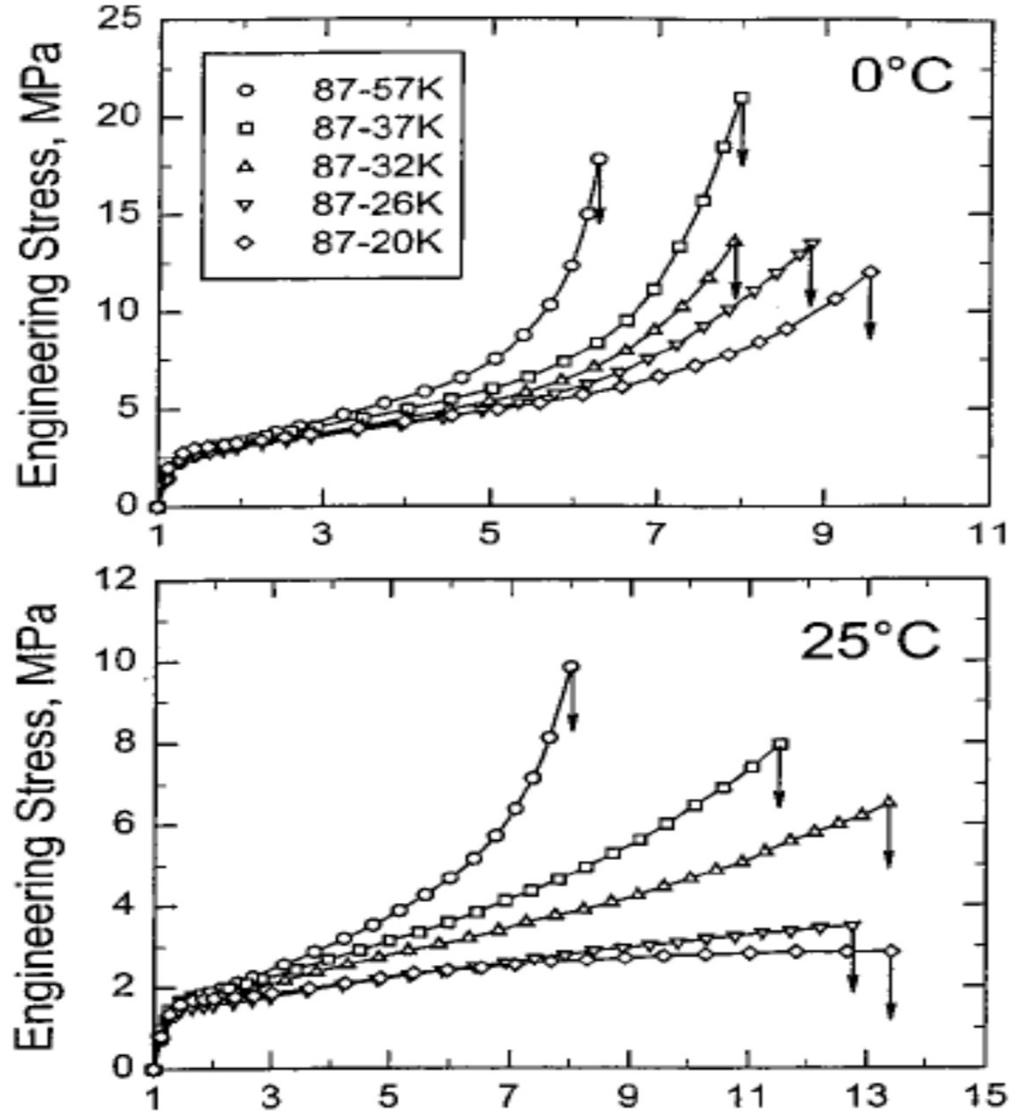

Figure 11. Stress−strain curves of CGCT87 copolymers of various molecular weights: (a) at 0 °C; (b) at 25 °C; (c) at 40 °C.

Slip Link Model for Mechanical Performance

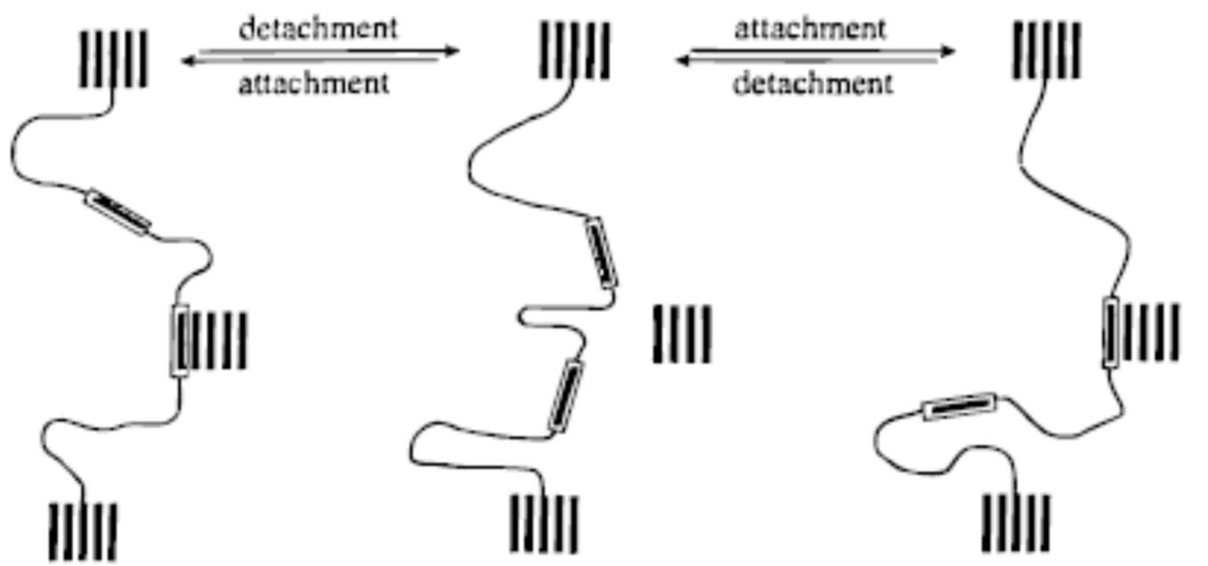

Figure 10. Schematic representation of detachment−attachment of crystallizable chain segments to produce a topological constraint equivalent to a slip-link.

Lesson 11: Polyolefin – PE 3: PE Short Chain Copolymers

Questions?

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If life during Covid was a math word-problem :

"You're going down a river at 2 MPH and your canoe loses a wheel, how much pancake mix would you need to re-shingle your roof?"