Engineering the Microstructure of Semicrystalline Polymers

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Semicrystalline Polymers: Who Cares?

Images from Wikipedia

Kobe, Japan (January 1995)

6000 dead
500000 homes destroyed

Osaka gas:
Iron/steel pipes failed
NO failures in PE pipes

Entire Japanese pipe market (and most of the European and North American markets) for water and natural gas now use polyethylene piping

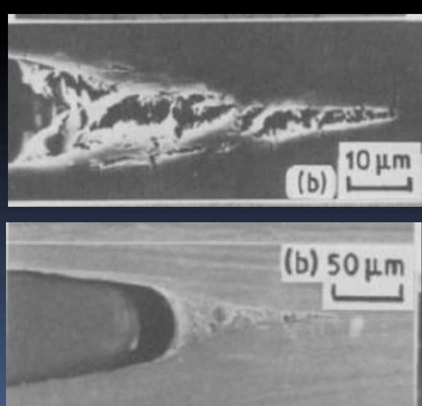
There is polyethylene, and then there is polyethylene…

Semicrystalline polymers ~ 70% of all synthetic polymers
(~225 billion kg/year)

Polyethylene: Example of *semicrystalline* polymer, viz. can crystallize into 3D ordered structure

Microstructure (and properties) can be tailored for same molecule

How does "pipe grade" PE differ from "plastic bucket" PE?



Source: Lu (1988)

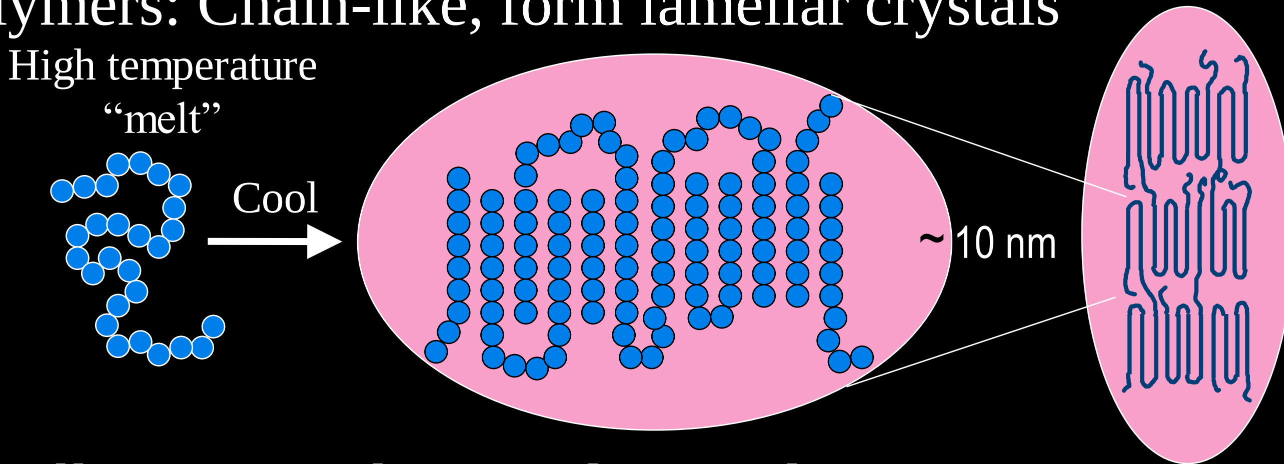
J. Mat. Sci. 1988, 23, 643.

The *microstructure* of pipe grade PE inhibits formation, propagation of cracks

What is *microstructure*, and what controls it?

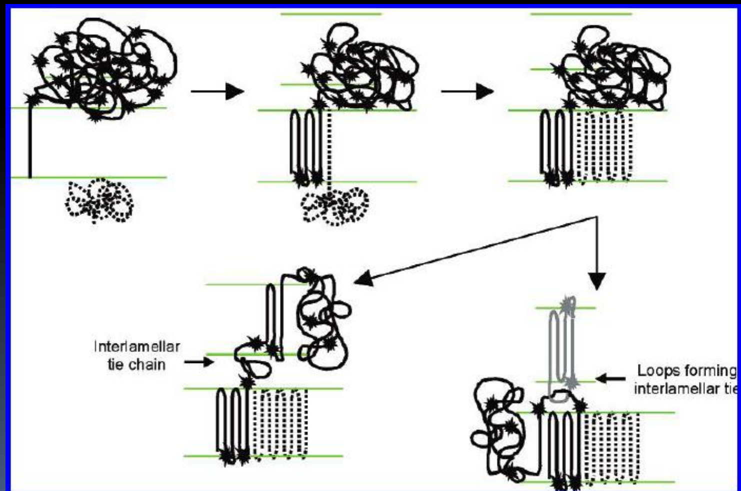
Semicrystalline microstructure

Polymers: Chain-like, form lamellar crystals



Semi-crystalline: Amorphous and Crystal states co-exist
Far from equilibrium: Gibbs phase rule doesn't hold

Source: Krishnaswamy (2008)

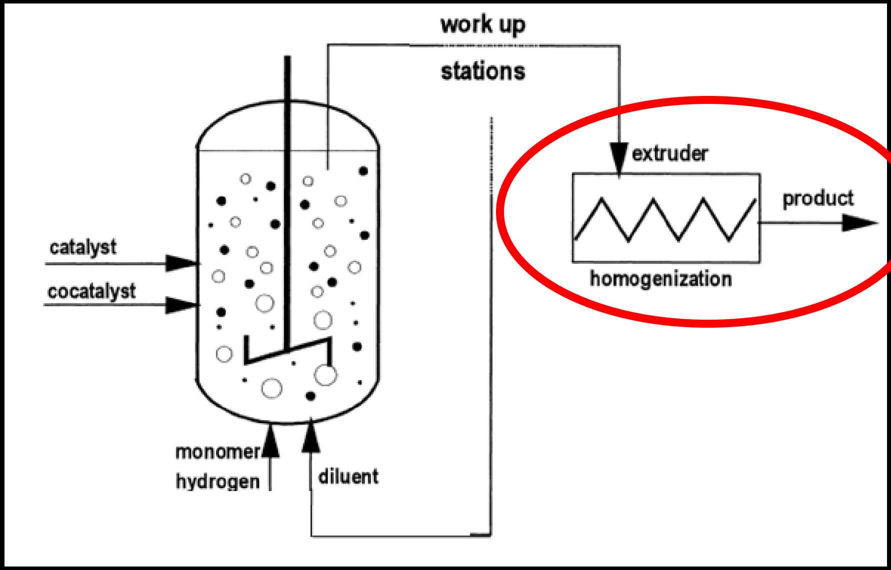


Macromolecules 2008, 41, 1693.

In pipe grade PE
Macro-scale toughness controlled by Molecular attributes (molecular weight distribution, chemical composition along polymer chain)

More "tie" chains that link crystalline lamellae

Controlling semicrystalline microstructure



Changing the chemistry of the polymer: Changes at the reactor level (difficult, expensive): pipe grade PE

Polymer crystallization is non-equilibrium (exploit this!)

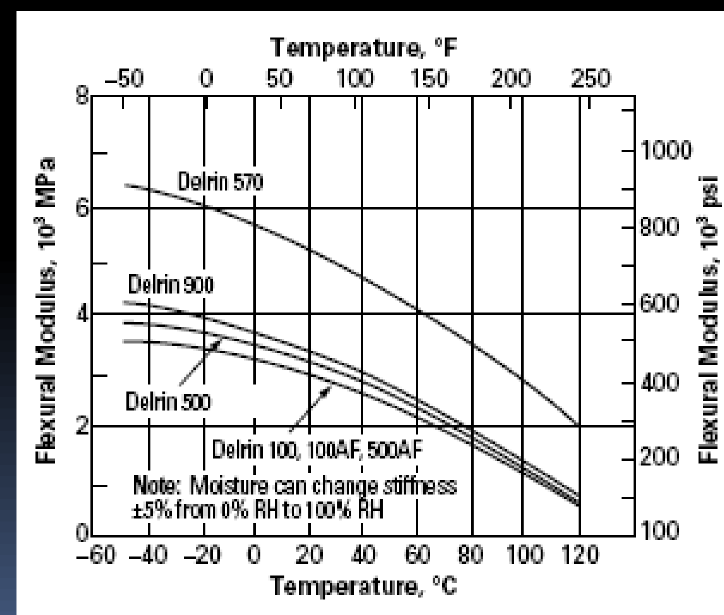
> Process the polymer differently
> Engineer desired microstructure
> Control properties

Challenge: Tools to characterize microstructural development (Still no way of *measuring* tie chain content)

Controlling semicrystalline microstructure

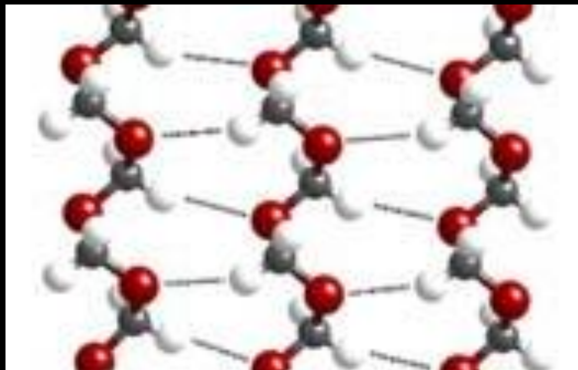
Delrin: Polyoxymethylene $-(CH_2-O)-$ (POM)

- Engineering semicrystalline polymer
- Excellent fatigue properties
- Melts around 175°C, but stiffness deteriorates near 100°C
- Why?? What can we do about this?



DuPont Delrin Design Guide III

Temperature dependent change in stiffness



Acta Cryst. 2007, 63, 190.

Polyoxymethylene forms helical structures that pack into crystals

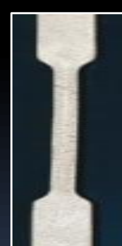
Believed that decreased stiffness on heating due to increased torsional motions of chains (intrinsic to the chain chemistry)

Does the interphase between lamellae play a role?

Compare model semicrystalline microstructures, with same local crystal structure

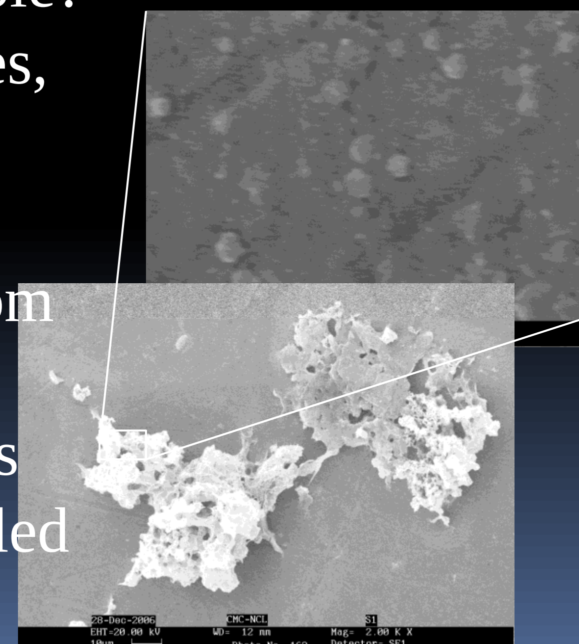
Injection molded from the melt.

Chain entanglements create interphase structure



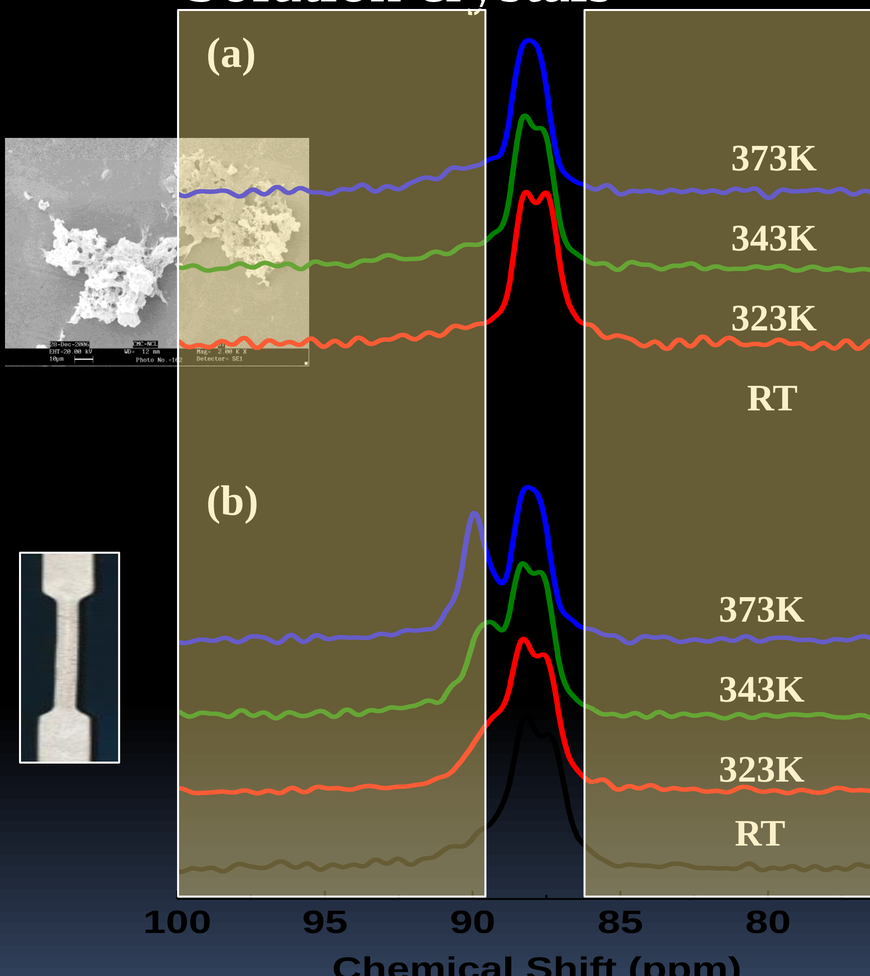
Crystallized from dilute solution.

Isolated crystals from disentangled chains

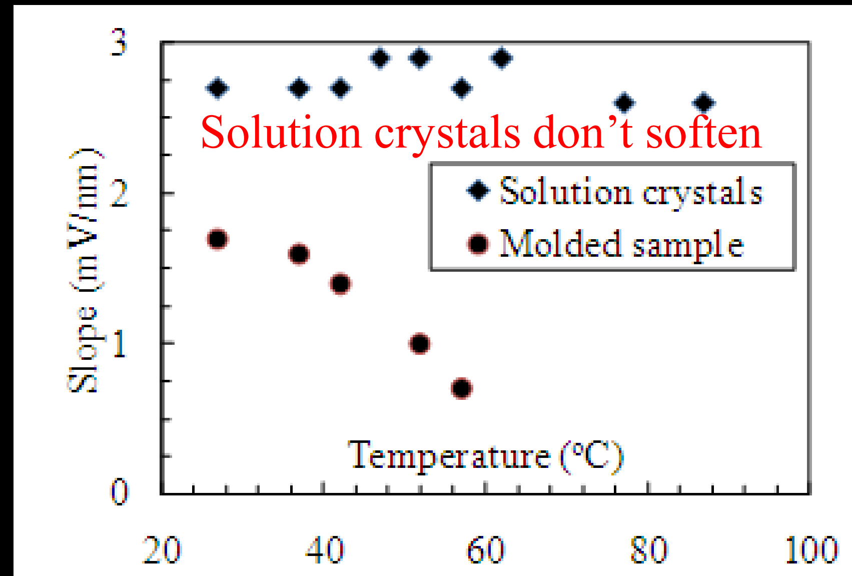


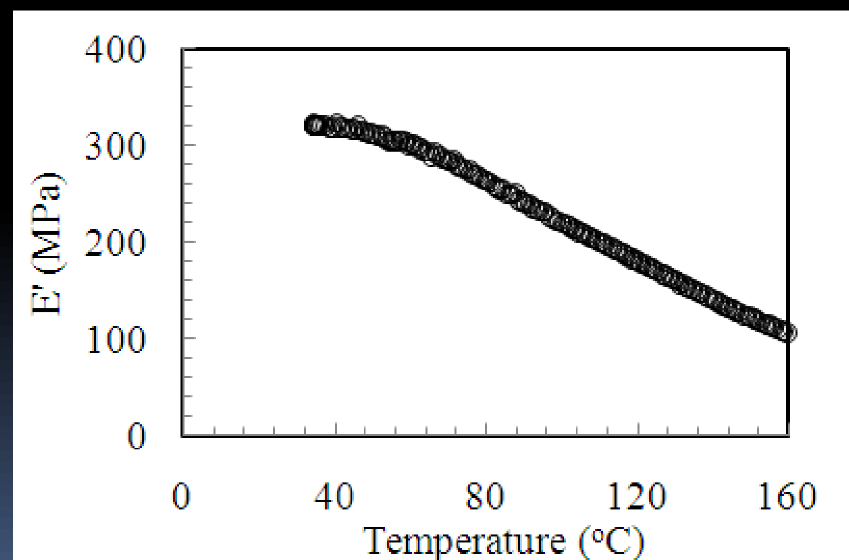
Solid State NMR: Chain mobility in both microstructures

Solution crystals



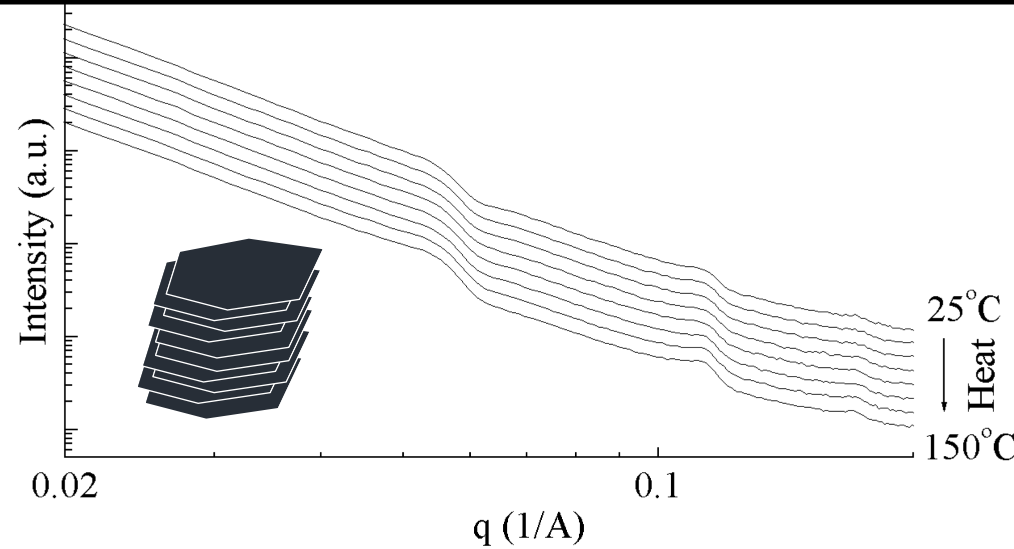
Melt crystallized



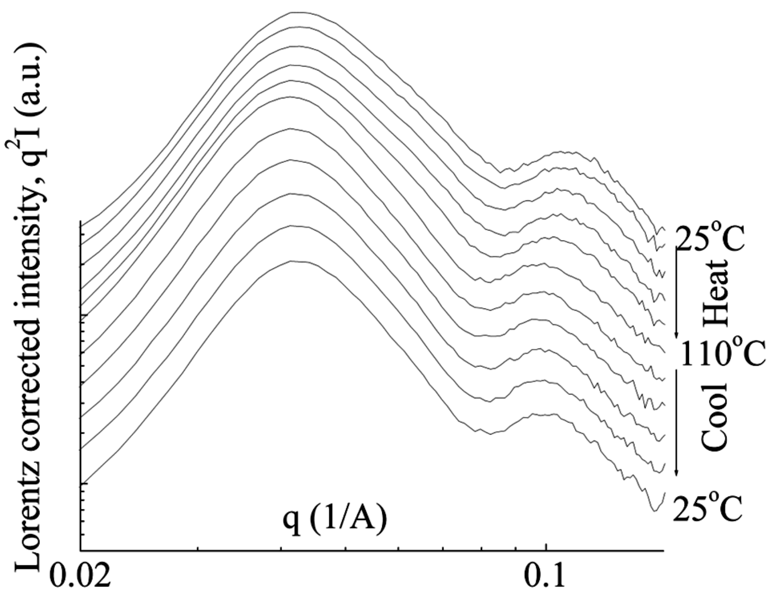


Microstructural changes on heating POM

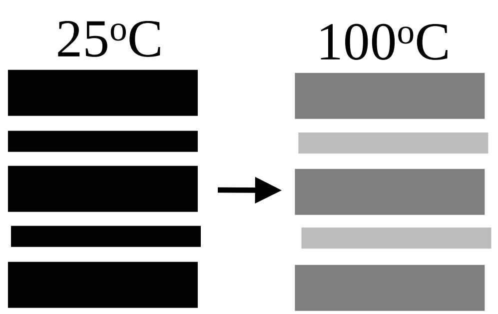
Use Small Angle X-ray Scattering (SAXS) to probe lamellae



Solution crystals are stacks of ~11 nm crystals SAXS does not change on heating to 150°C



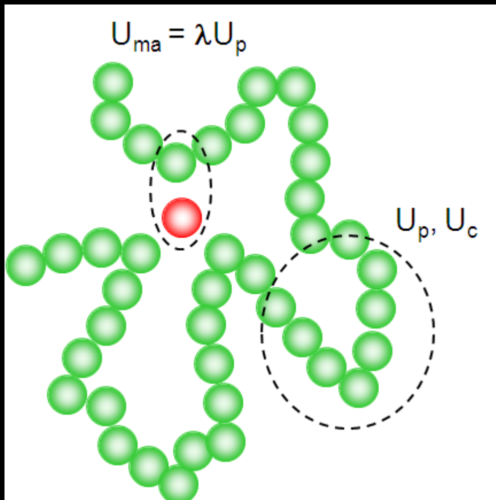
Melt crystals: Polydisperse lamellae stacked together



- On heating to 100°C, interspersed thin lamellae melt

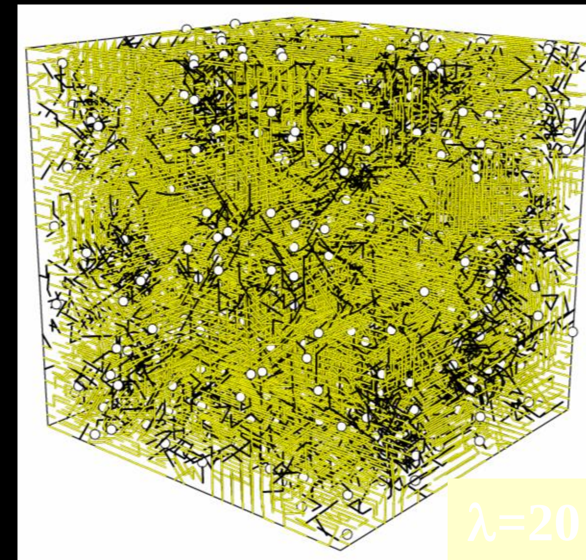
(US patent filed Manuscript in preparation)

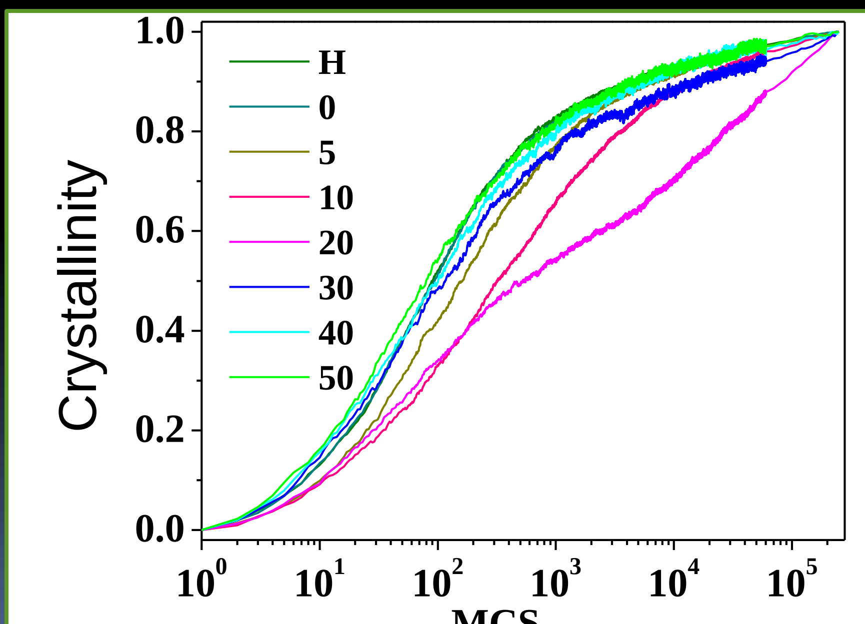
How can we dial-in lamellar structure?



"Sticky" additives that make chains sluggish as they crystallize on cooling

Lattice MC simulations to model crystallization

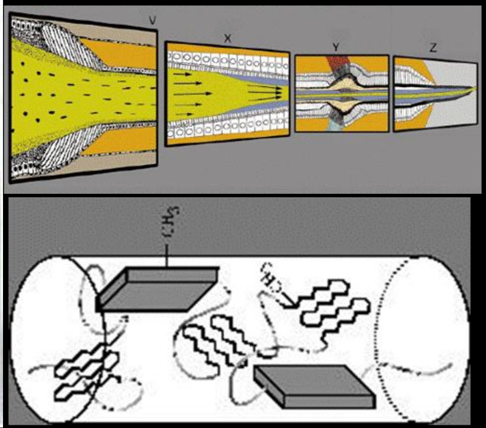




Suitable choice of additives (with intermediate stickiness) can qualitatively change crystallization.

Dasmahapatra, Nanavati and Kumaraswamy
J. Chem. Phys. 2009, 131, 074905

Semicrystalline μ-structure > Orientation (by flow)

Nature 2001, 410, 541; *Science* 1996, 271, 39

High modulus and toughness

SPIDER VERSUS SYNTHETIC

Material	Strength (N/m^2)	Energy to break (J/kg)
Dragline silk	1×10^9	1×10^5
Kevlar	4×10^9	3×10^4

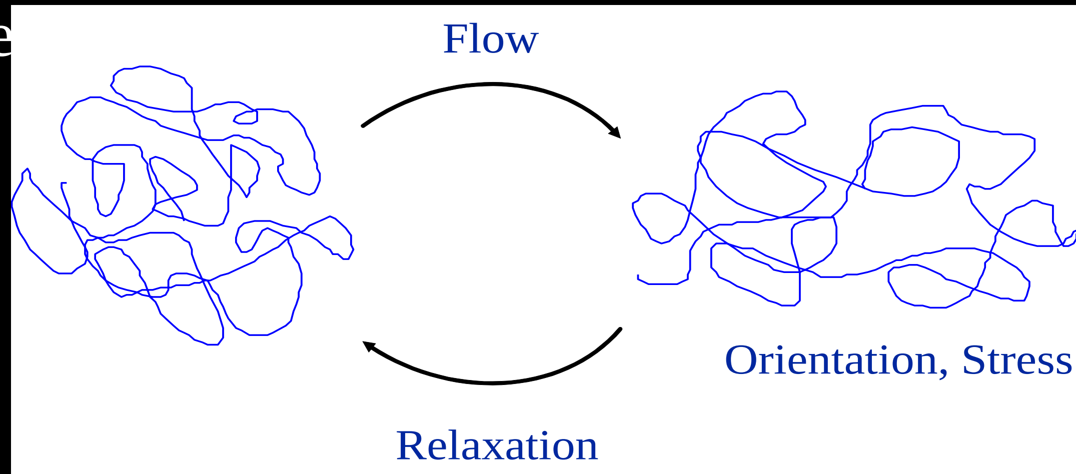
Low viscosity protein "dope" solution spun by the spider through a "hyperbolic die"

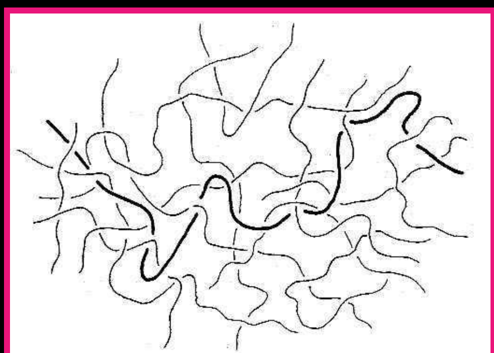
Strong elongational flow induces orientation

What does flow do?

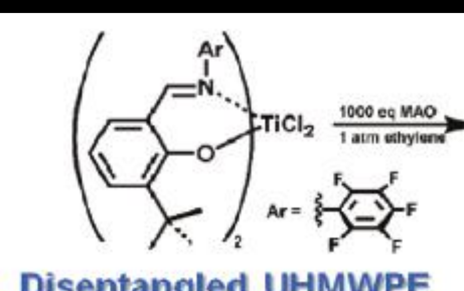
Polymers are liquid-like but relax slowly

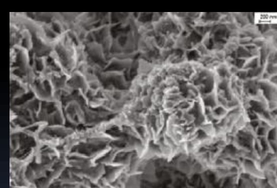
$\tau_{relax} \approx O$ (1-10 ms) at 150^{o}C for PE with MW = 10^5 g/mol

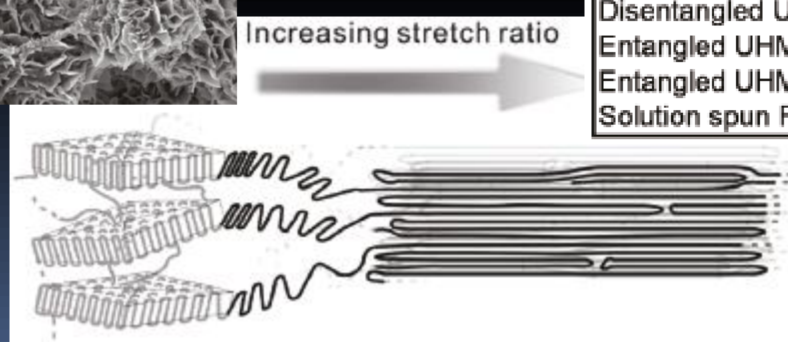




Chain-chain entanglements inhibit drawing





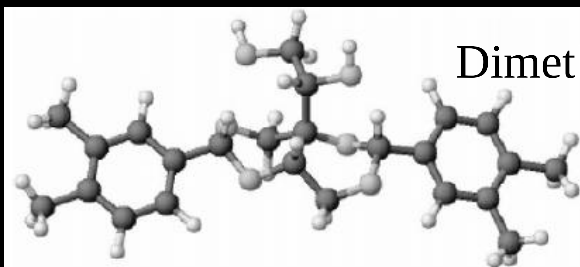


	Tensile Strength [GPa]	Modulus [GPa]
Disentangled UHMWPE	3.75	157
Entangled UHMWPE Grade A	1.95	102
Entangled UHMWPE Grade B	2.30	165
Solution spun Fiber	3.50	135

Macromolecules 2011, 44, 5558

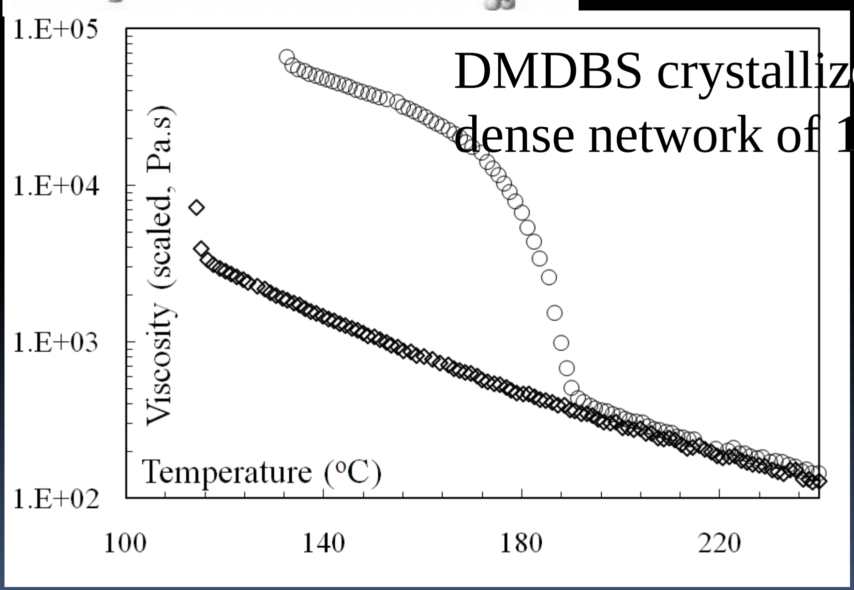
A strategy to induce orientation in PP: Oriented Scaffolds

Generate an oriented scaffold that locally stretches the polymer and forces oriented crystallization

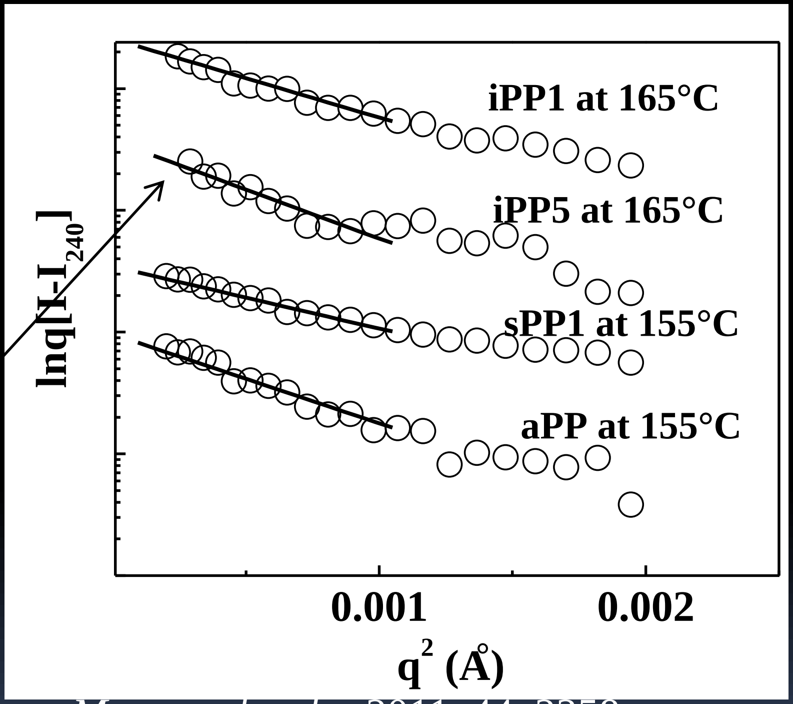


Dimethyldibenzylidenesorbitol

0.8% in PP

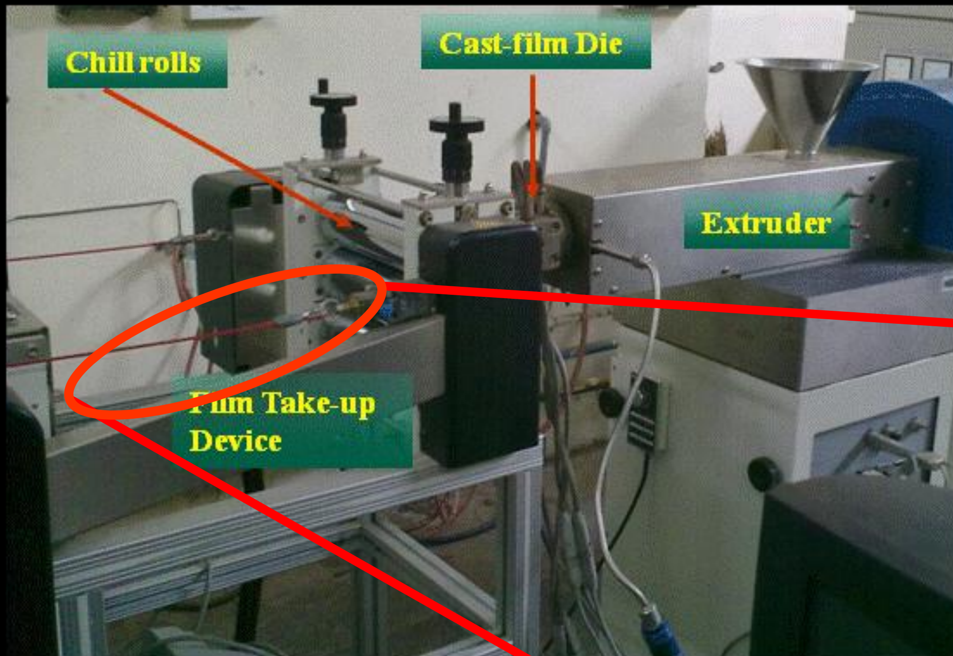


DMDBS crystallizes to form a dense network of 10 nm fibers in PP



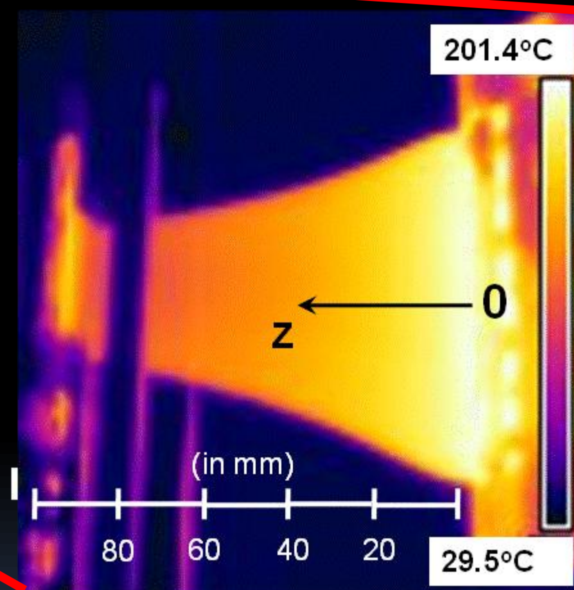
Macromolecules 2011, 44, 2358

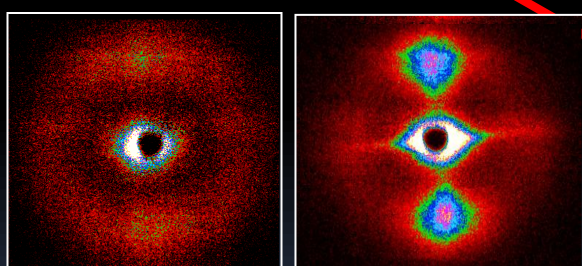
Making oriented films



Cool to form DMDBS network
Pull to orient scaffold

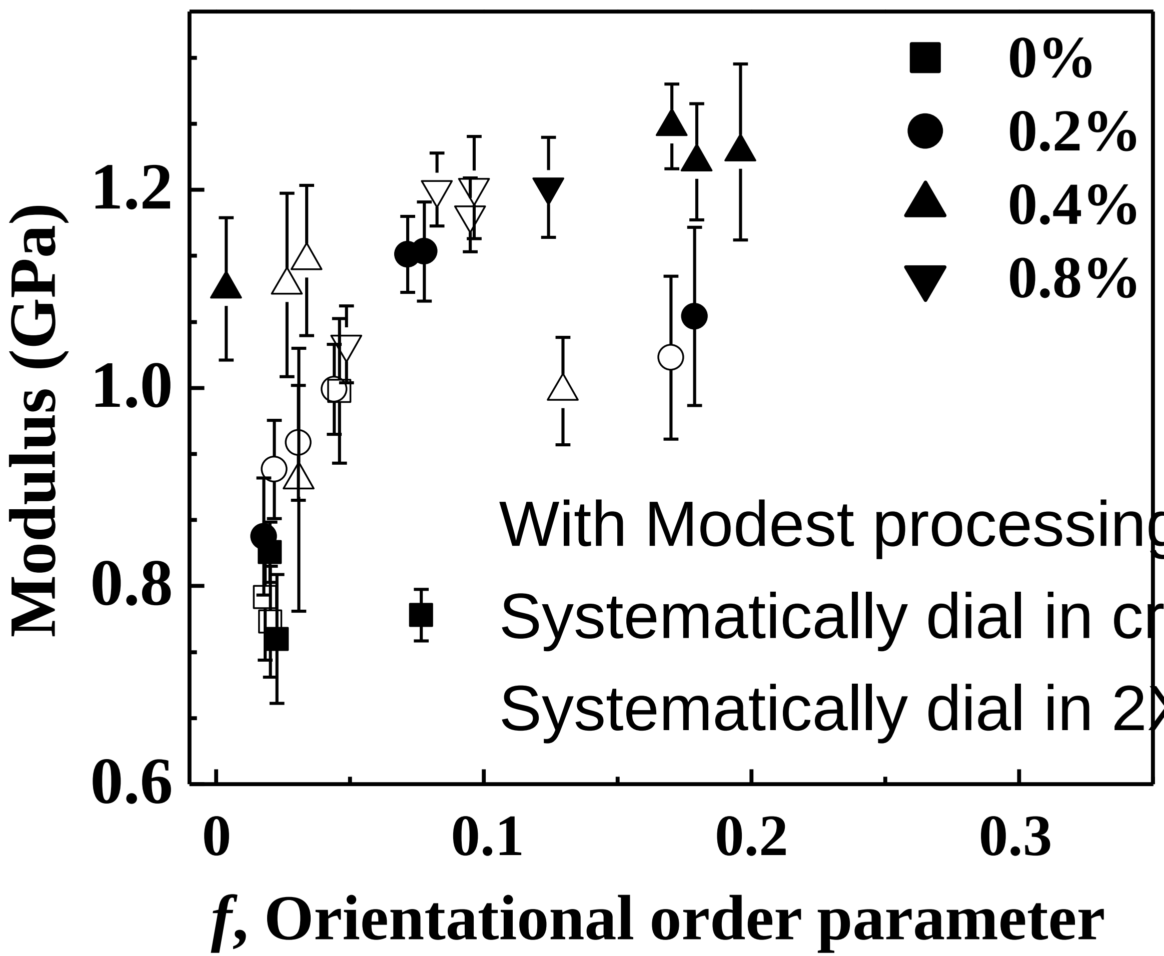
PP crystallizes on oriented scaffold





Modest draw ratios
Unable to orient neat PP
PP/0.8% DMDBS strongly oriented

Can Dial-in Orientation (and Modulus)



With Modest processing draw ratios, can

Systematically dial in crystal orientation

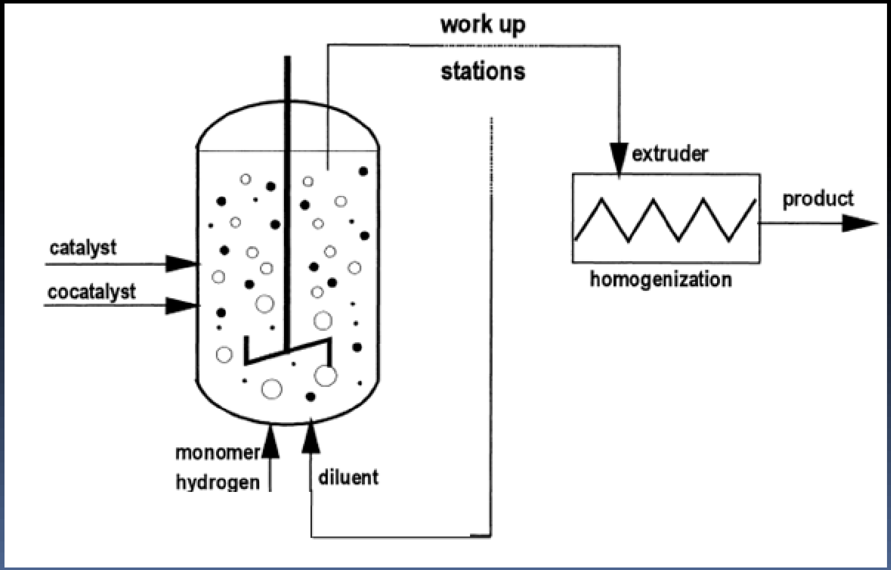
Systematically dial in 2X modulus variation

Polym. Eng. Sci. 2011, 51, 2013

The Frontiers

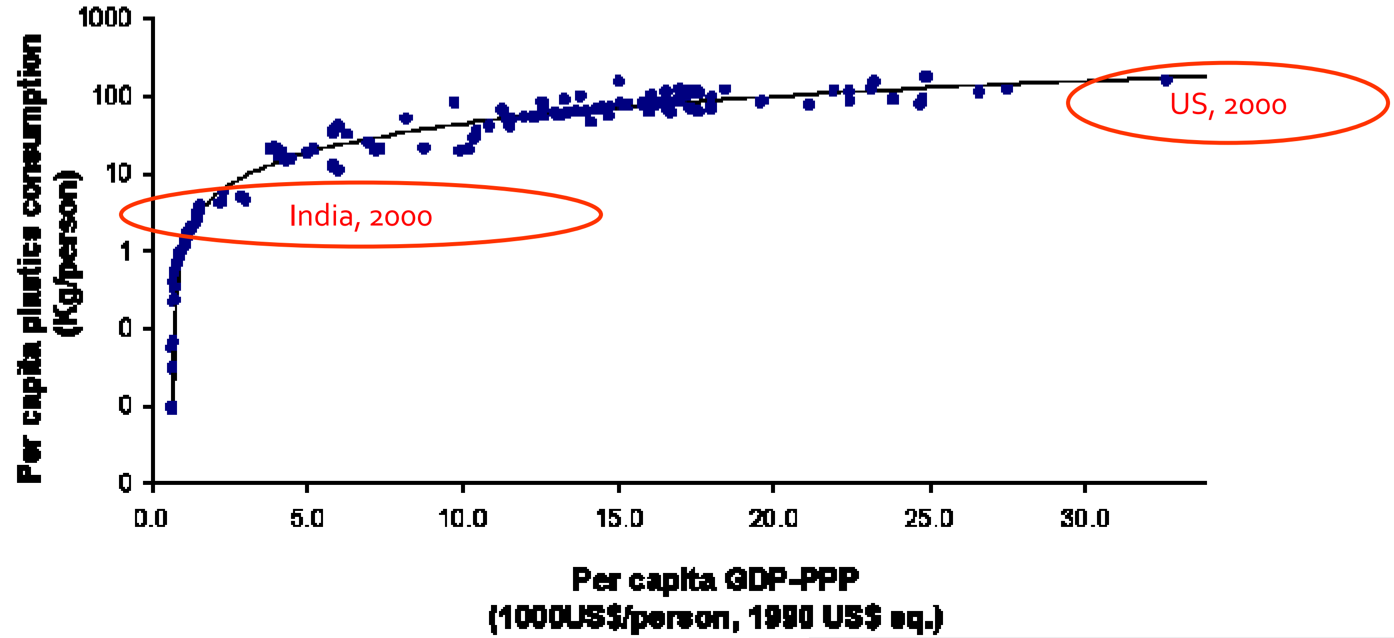
Semicrystalline microstructure is complex

Quantitative measurement of microstructure, and microstructural development, using a combination of experimental tools : insights into connections with properties and with molecular structure



Connecting properties to microstructure to molecular structure to reactor conditions QUANTITATIVELY

Context: Plastics and Quality of Life



Plastics consumption (y, Kg/person, n = 138) with respect to the GDP in purchasing power
Symbols represent data for Australia (1993, 1994, 2000), Austria (1993, 1994), Belgium (199
(2000), Chile (1993,1994), China (1993), Columbia (1993, 1994, 2000), Czech Republic (1993,
2000), Germany (1993, 1994, 2000), Hungary (1993, 1994, 2000), India (1971-2000), Israel (19
1994, 2000), Malaysia (2000), Mexico (1993, 1994), New Zealand (1993, 1994), Romania (199
Slovenia (1993, 1994, 2000), South Africa (1990-2000), South Korea (1993, 2000), Spain (199
(2000), UK (1993, 1994, 2000), USA (1993, 1994, 2000) and Western Europe (1971-2000). The
0.65)1.114 (Coefficient of correlation, R2=0.97)

Figure 5. Relationship between plastics consumption per capita

Resources, Conservation and Recycling 2006, 47, 222

Structure Control in Polymers, Polymer Crystallization

"Soft Matter"

Weak interactions (~$k_B T$, compare with covalent bond energies of 10^2 $k_B T$)
Multitude of interactions
Several examples of out-of-equilibrium systems providing opportunities to *engineer* microstructure and properties

Colloids, Surfactants, Liquid Crystals, Biological fluids, …

Poster: Using Soap Slime to Assemble Nanoparticles