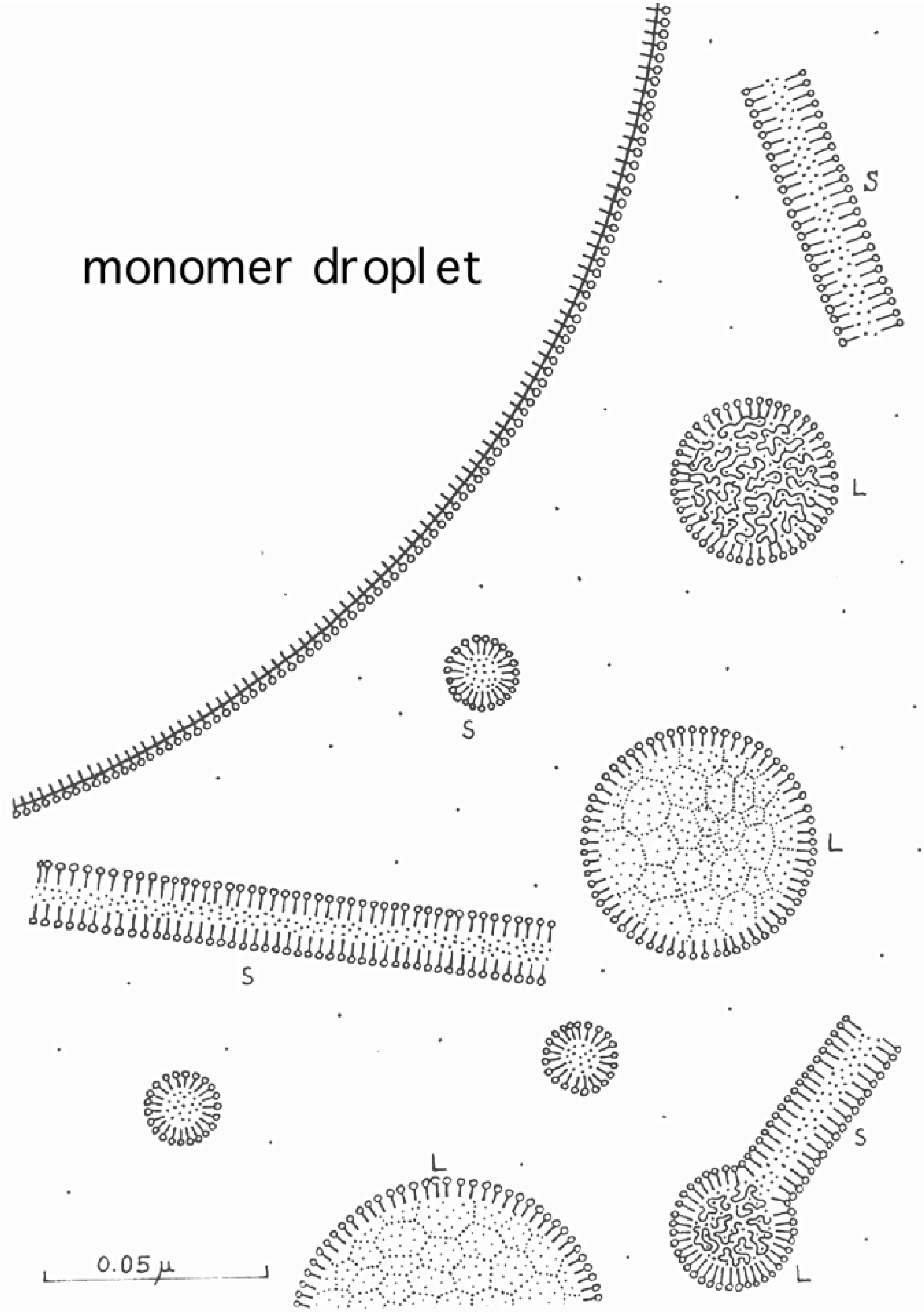
Polymerisation Techniques

Polymerisation techniques used in the production of some commercial polymers.

Polymer	Polymerisation technique
Polyamides	Bulk
Polycarbonates	Bulk
Poly(ethylene terephthalate)s	Bulk
Polysulphides	Suspension
Polyethylene (low density)	Bulk, Solution
Polyethylene (high density)	Solution
Poly(methyl methacrylate)	Bulk, Suspension
Polypropylene	Solution
Polystyrene	Solution
Poly(vinyl acetate)	Emulsion
Poly(vinyl chloride)	Suspension
Polyisoprene	Solution
Styrene-Butadiene copolymer	Emulsion
Polyformaldehyde	Solution
Polycaproamide (Nylon 6)	Bulk

Emulsion Polymerisation



Advantages of emulsion polymerisation

- Easy heat removal and control.
- The polymer is obtained in a convenient, easily handled, and often directly useful form.
- High molecular weigth can be obtained.
- The very small particles formed resist agglomeration thus allowing the preparation of tacky polymers.
- Inverse phase (water in oil) emulsions possible.

Disadvantages of emulsion polymerisation

- Low yield per reactor volume
- A somewhat less pure polymer than from bulk polymerisation, since there are bound to be remnants of the suspending agent(s) adsorbed on the particle surface.
- The inability to run the process continuously, although if several batch reactors are alternated, the process may be continuous from that point on.
- It cannot be used to make condensation polymers or for ionic or Ziegler-Natta polymerisations (anything which reacts with water). Some exceptions are known.

Suspension Polymerisation

Major advantages of suspension polymerisation.

- Easy heat removal and control.
- The polymer is obtained in a convenient, easily handled, and often directly useful form.

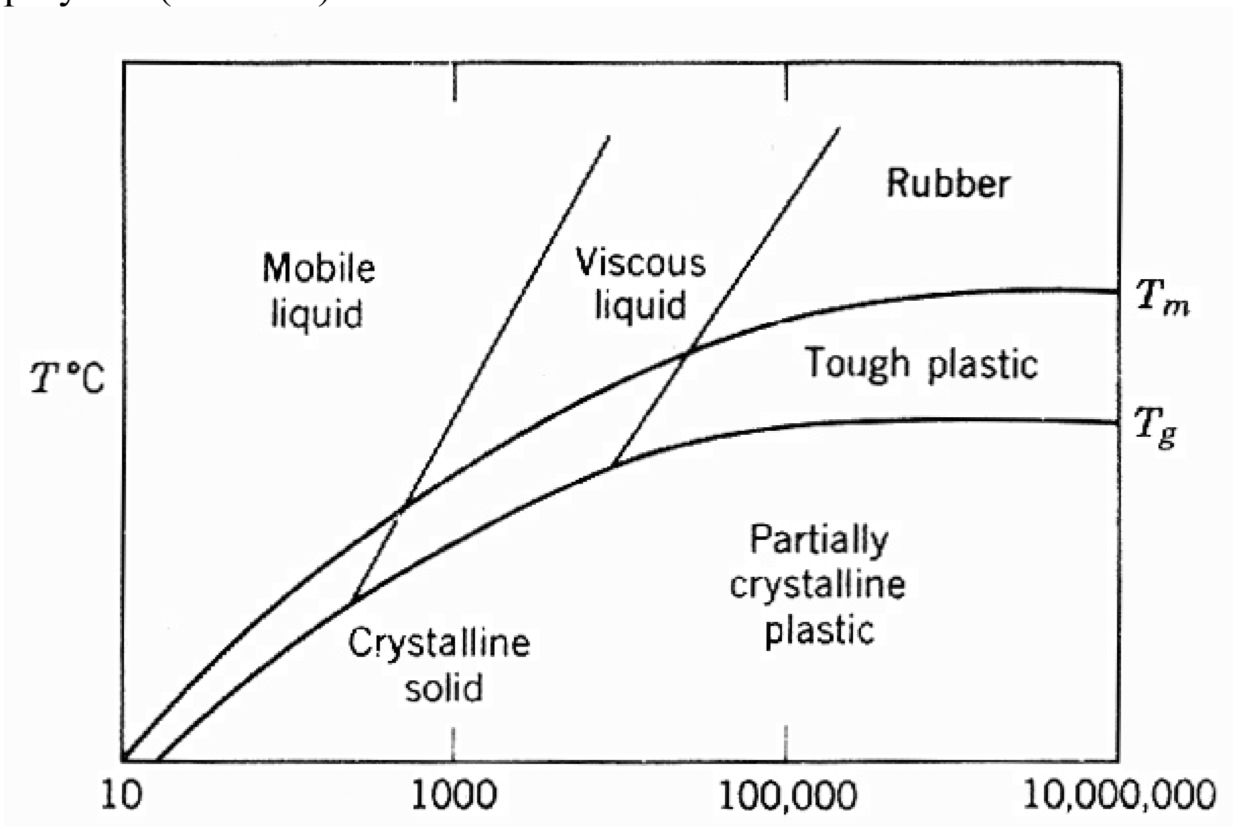
Disdavantages include the following

- Similar to emulsion polymerisation

	aqueous phase	**organic phase**
Emulsion Polymerisation	water surfactant initiator	monomer surfactant
Suspension Polymerisation	water protective colloid	monomer protective colloid initiator

Properties related to Polymer Structure

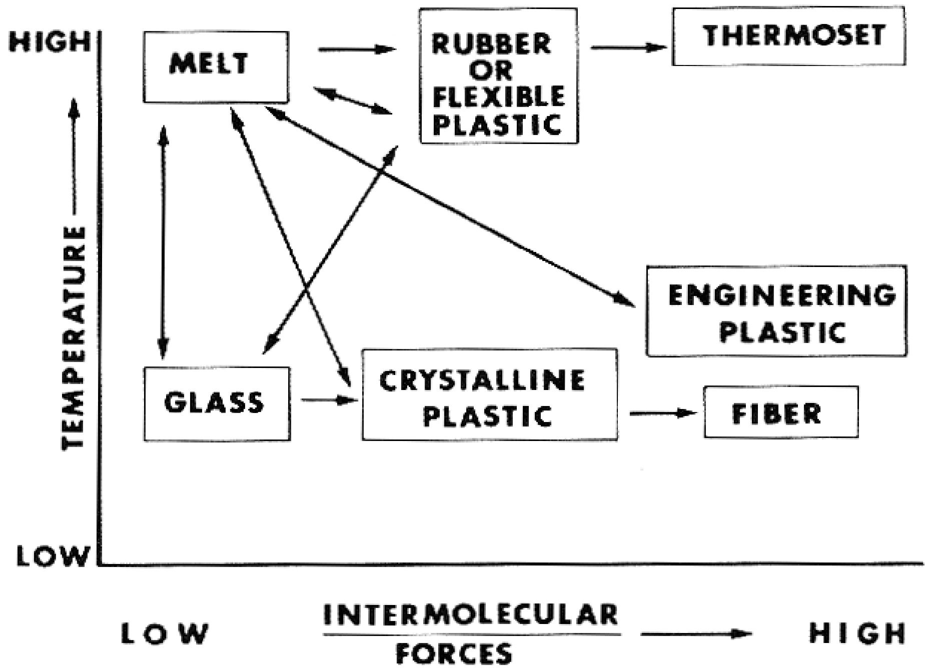
T_g and T_m versus molecular weight (M_n or M_w) assuming a semi-crystalline polymer (most are)



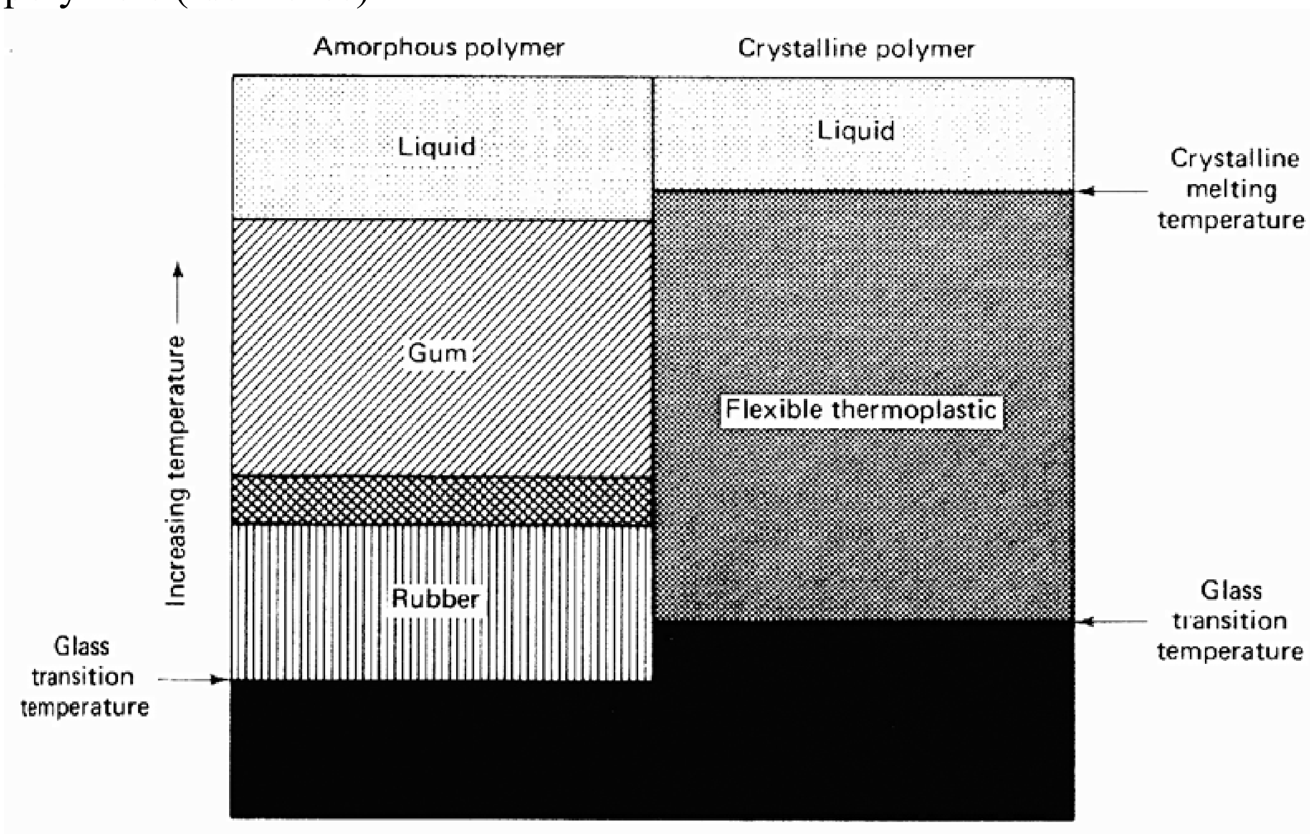
Chemical Bond parameters

Bond Type	Interatomic Distance (nm)	Dissociation Energy (kJ / mol)
Covalent bond	100 - 200	200 - 900
Transition metal bond	200 - 350	200 - 600
Ionic bond	200 - 300	40 - 100
Hydrogen bond	200 - 300	10 - 80
Dipole interaction	200 - 300	5 - 20
van der Waals interaction	300 - 500	2 - 10

Effect of temperature on the physical properties of a polymer related to the strength of the corresponding intermolecular forces.



Juxtaposition of transition behaviour between amorphous and crystalline polymers (ideal case)



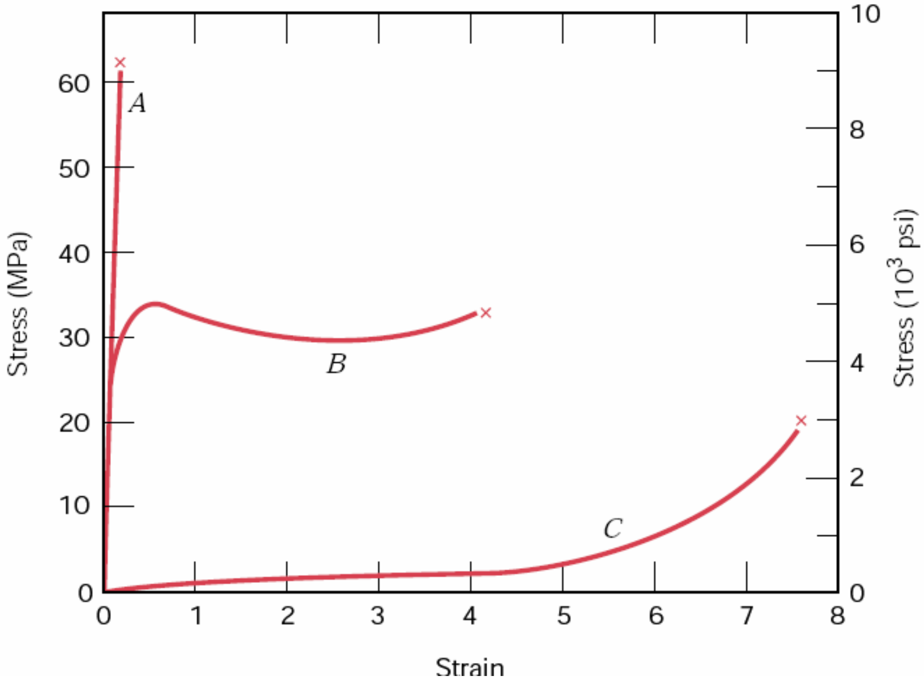


Figure 7.22 The stress–strain behavior for brittle (curve *A*), plastic (curve *B*), and highly elastic (elastomeric) (curve *C*) polymers.

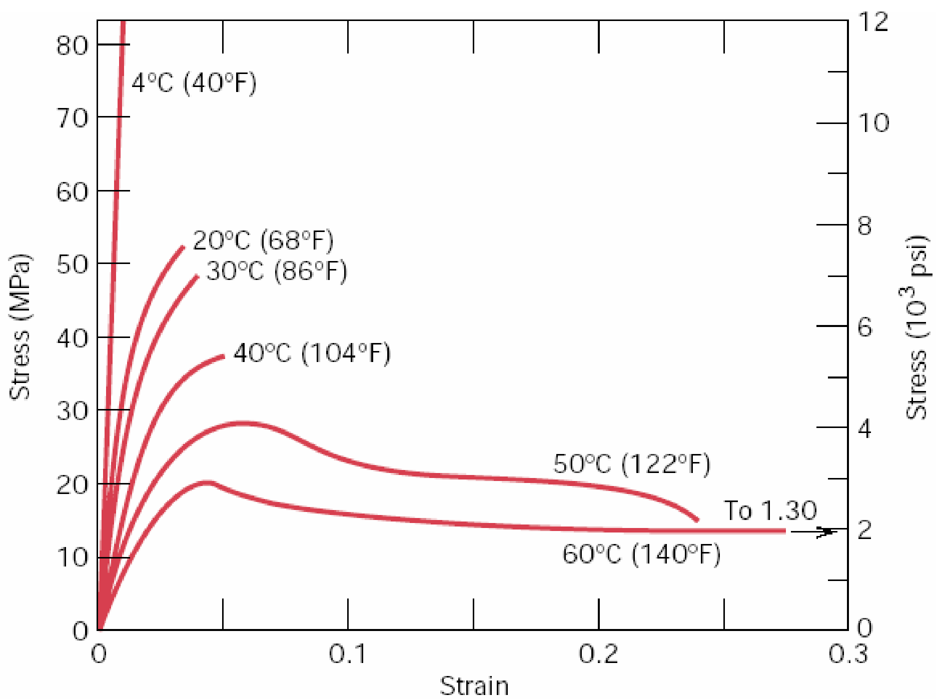
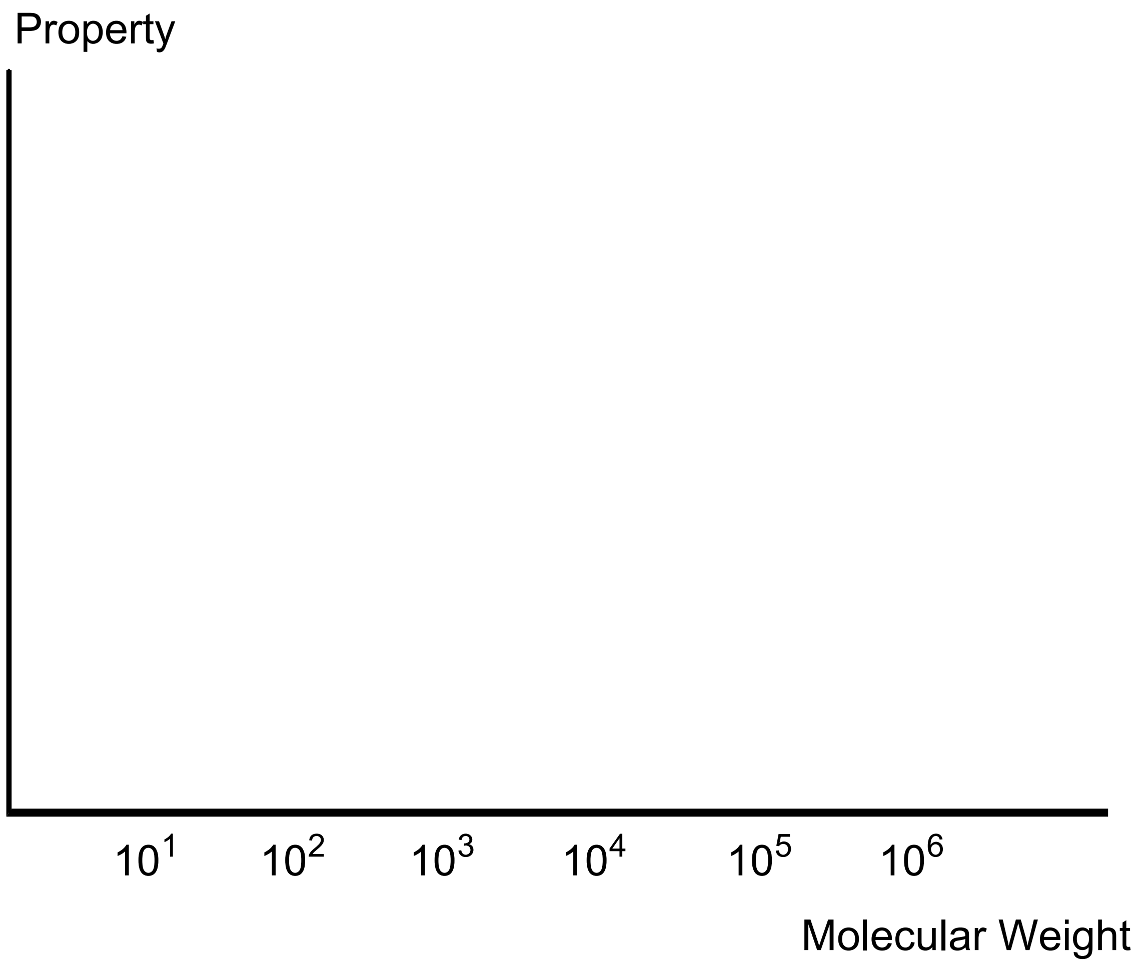
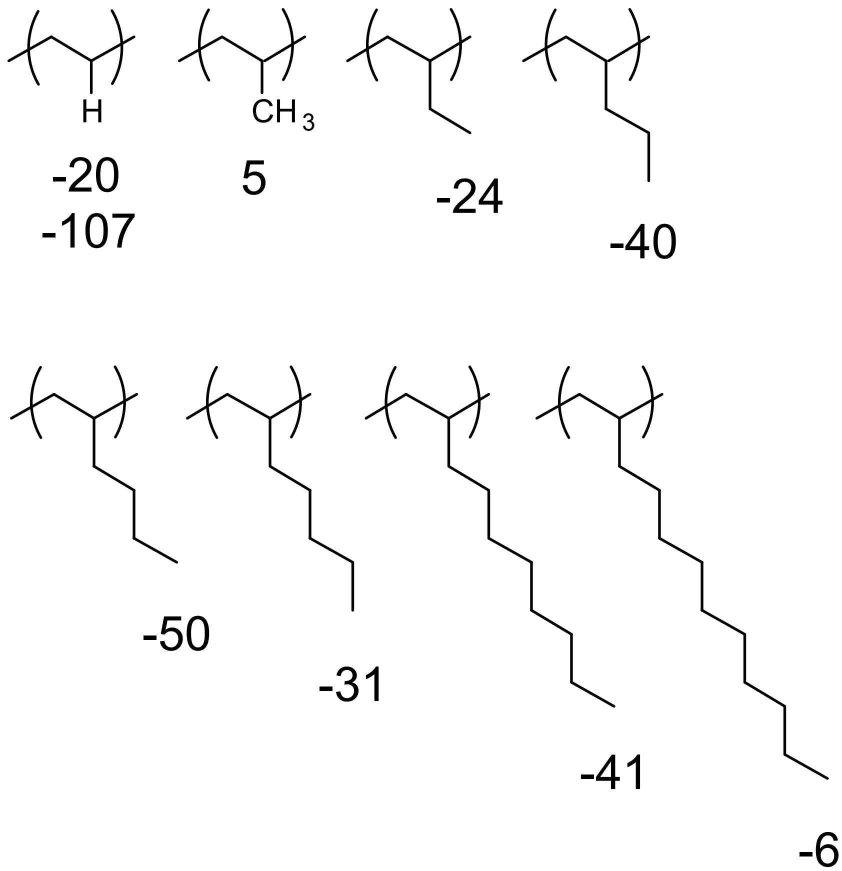


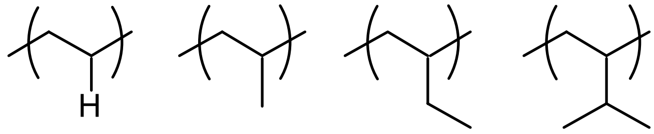
Figure 7.24 The influence of temperature on the stress–strain characteristics of polymethyl methacrylate. (From T. S. Carswell and H. K. Nason, "Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics," *Symposium on Plastics,* American Society for Testing and Materials, Philadelphia, 1944. Copyright, ASTM. Reprinted with permission.)

General Relationship of Molecular Weight vs Polymer Properties

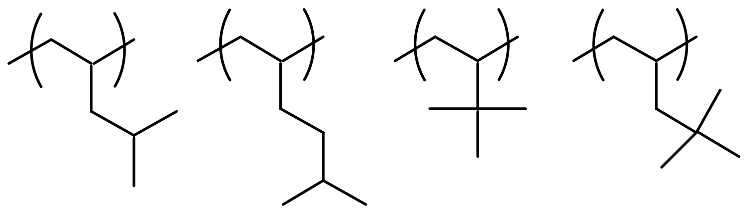


Glass Transition Temperature: Relation to Structure

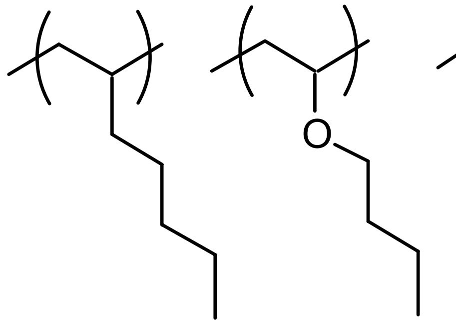


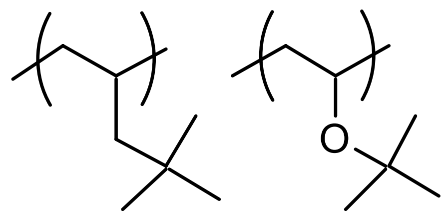


-20 -107   5   -24   50



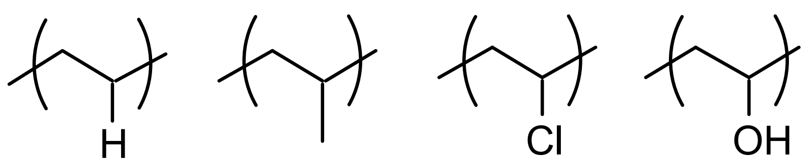
29   -14   64   59





59   88

-25   -55

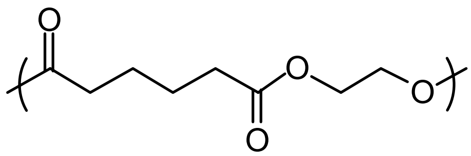


-20   5   81   85

Tacticity control of polymer properties

Polymer	Tg (^oC)		
	syndiotactic	atactic	isotactic
poly(methyl methacrylate)	145	105	45
poly(ethyl methacrylate)	65	65	12
poly(t-butyl methacrylate)	114	118	7
poly(propylene)	~ 40-60	-6 no T_m	-18 T_m = 165
poly(styrene)	100	100	99

Influence of segmental length of polymer main chain



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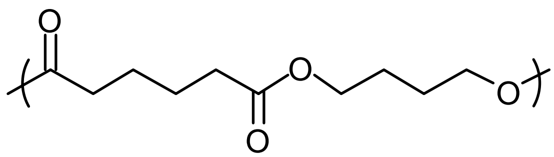

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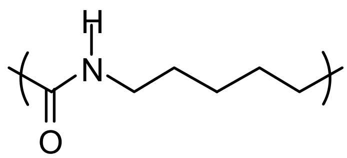

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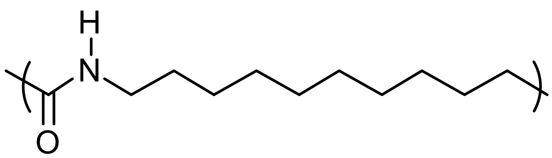

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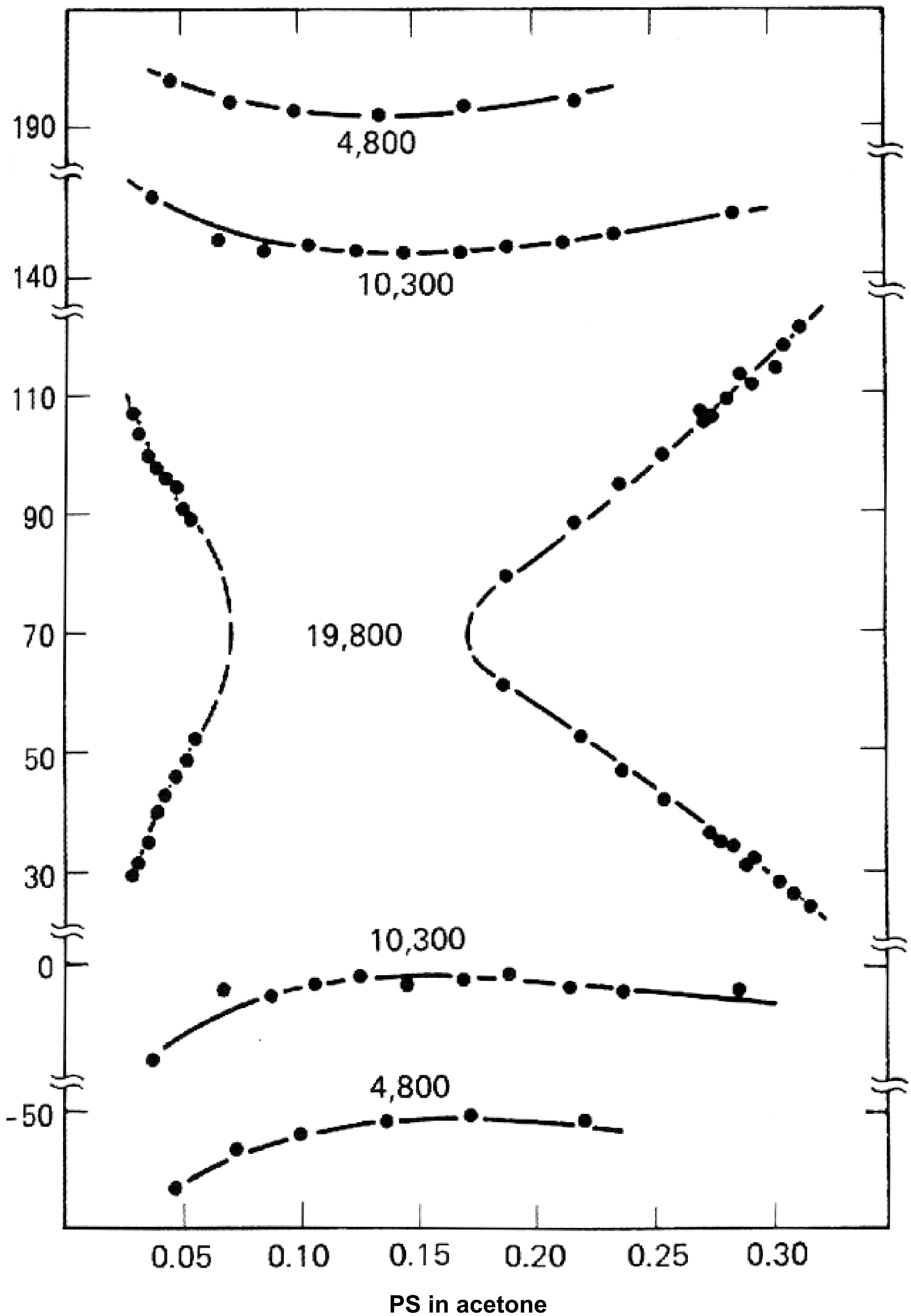
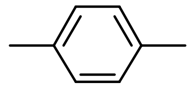
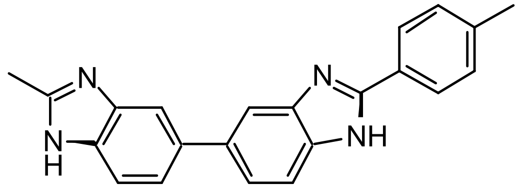
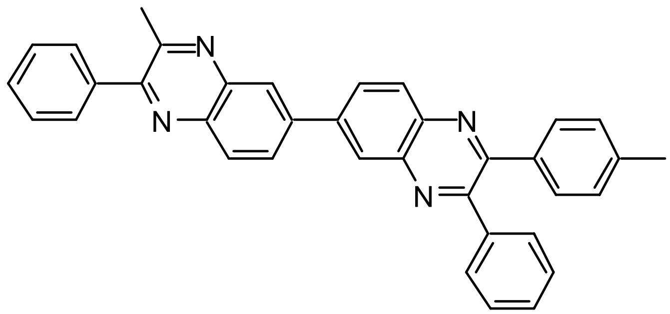
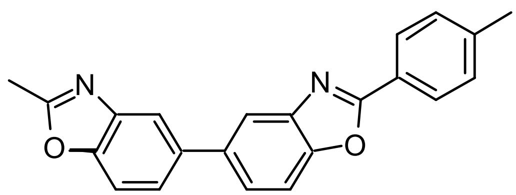
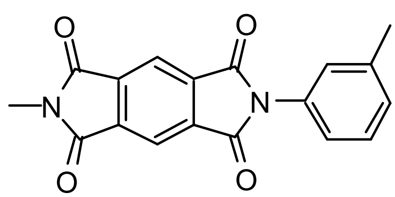
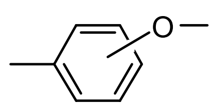
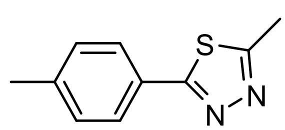
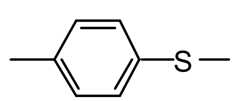
Critical Solution Temperatures

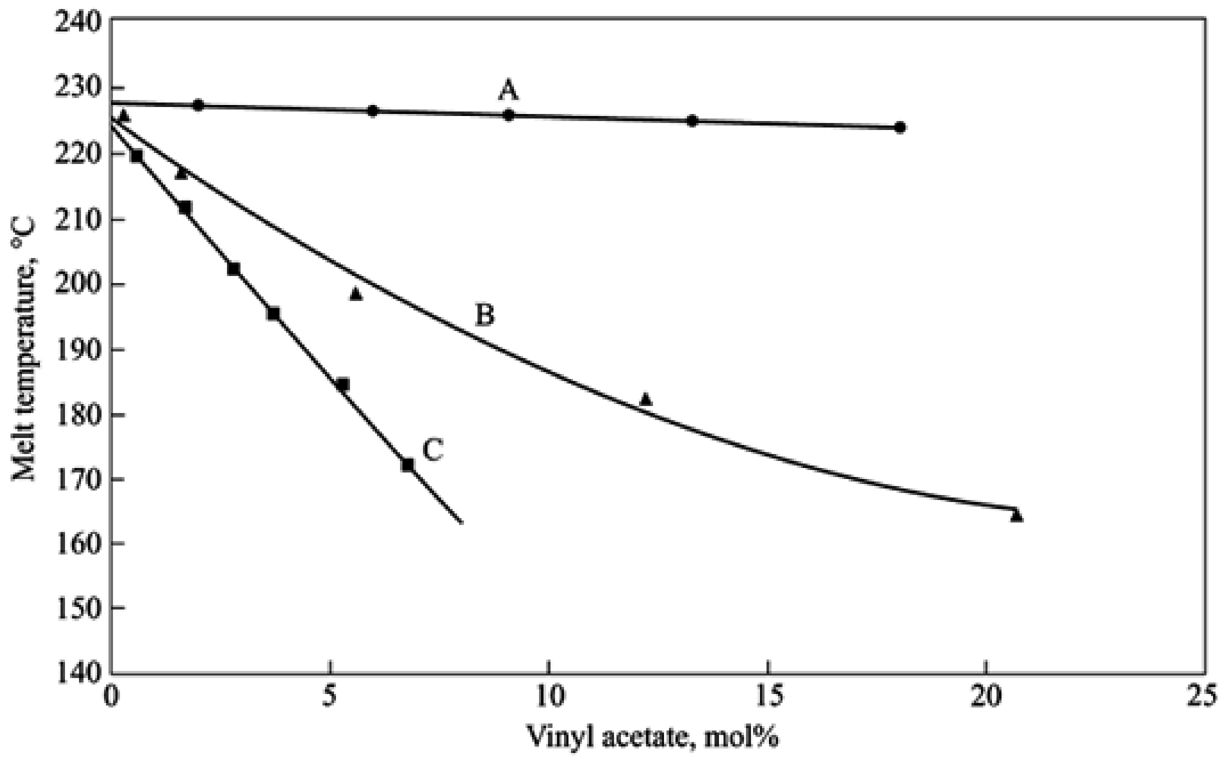


Thermal stability

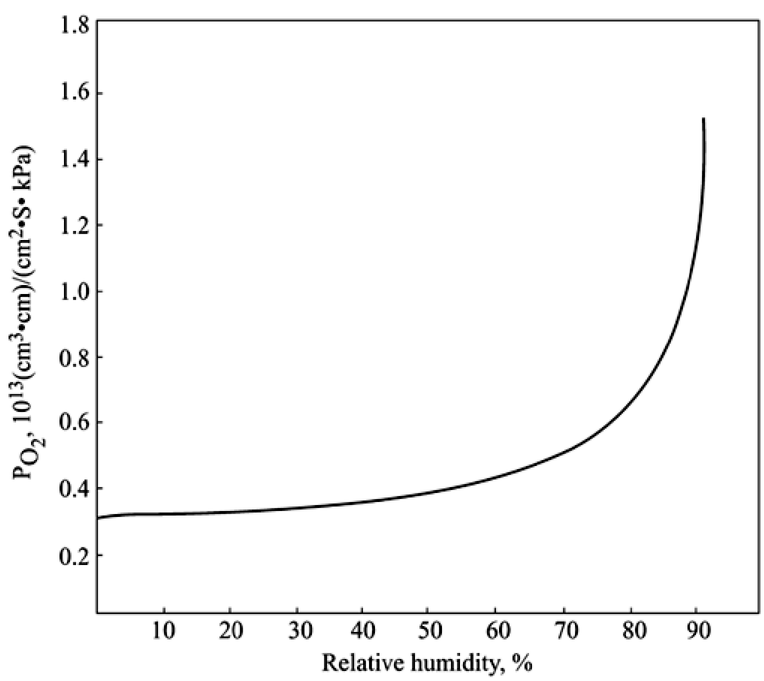
poly(p-phenylene)		660
polybenzimidazole		650
polyquinoxazoline		640
polyoxazole		620
polyimide		585
poly(phenylene oxide)		570
polythiadiazole		490
poly(phenylene sulfide)		490

Case Study Polymers

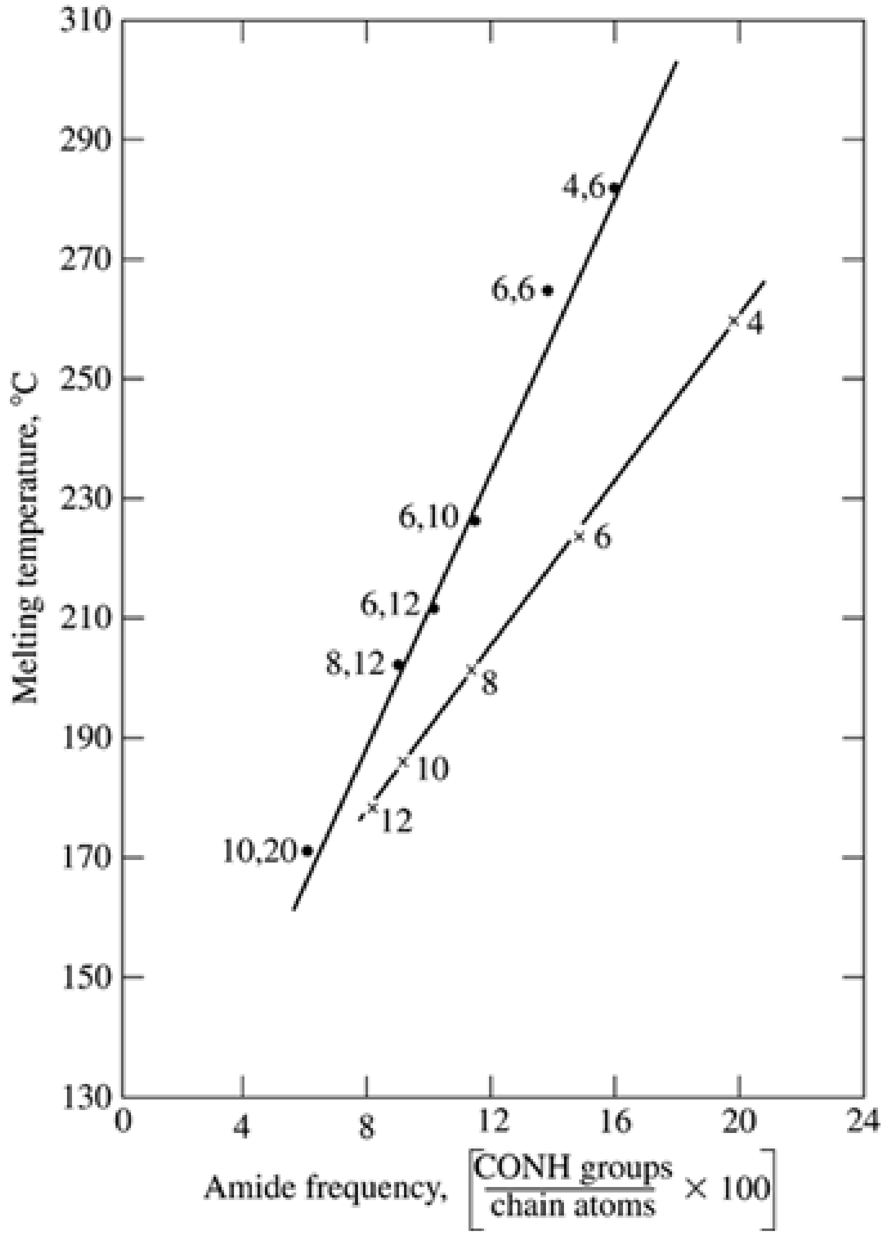
Influence of vinyl alcohol–vinyl acetate copolymer composition on melting temperature (44), where A represents block copolymers (higher blockiness); B, block copolymers (lower blockiness); and C, random copolymers.



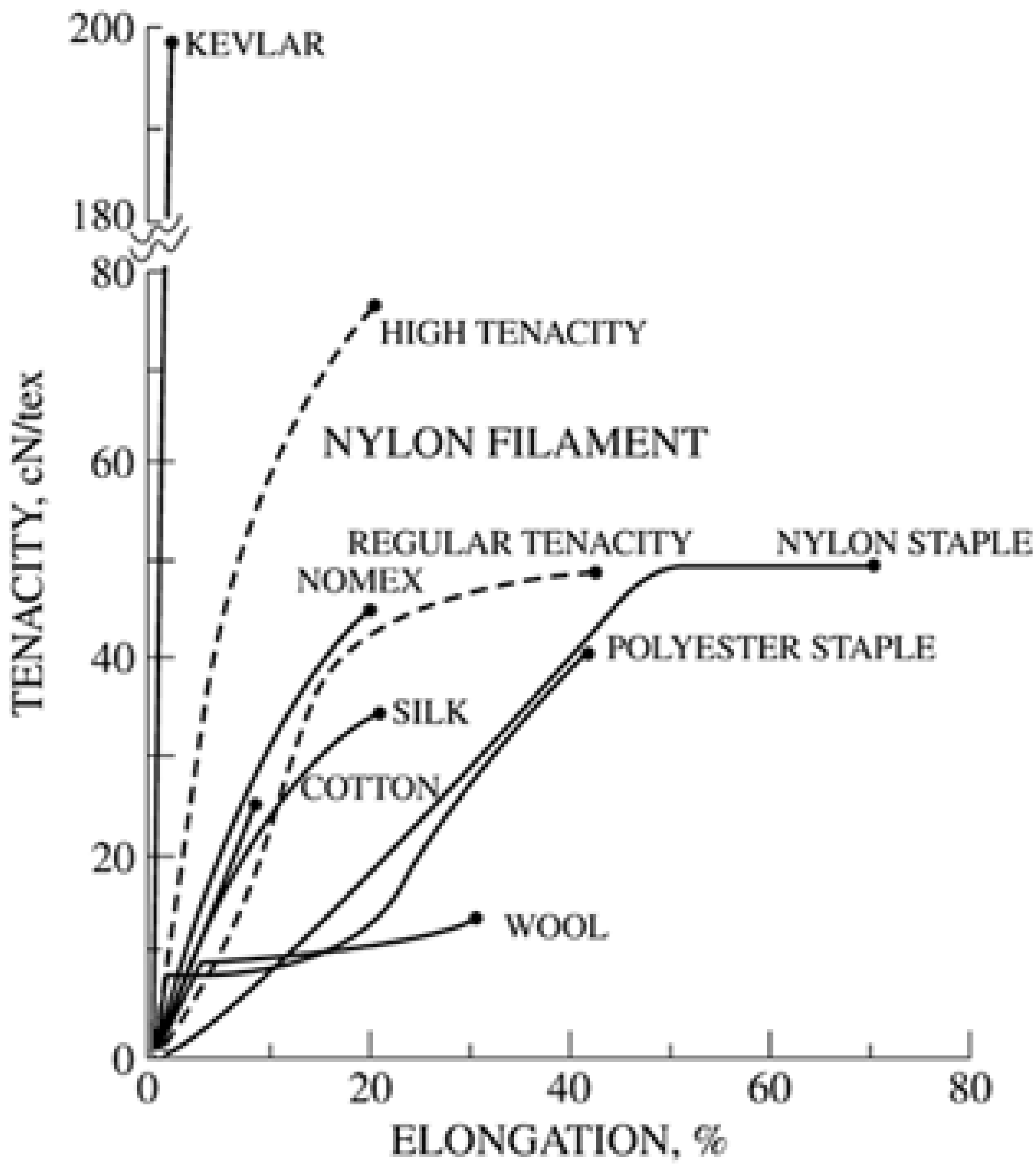
Oxygen permeability of PVA as a function of humidity; degree of hydrolysis, 99.9 mol%, DP = 1750 (47).



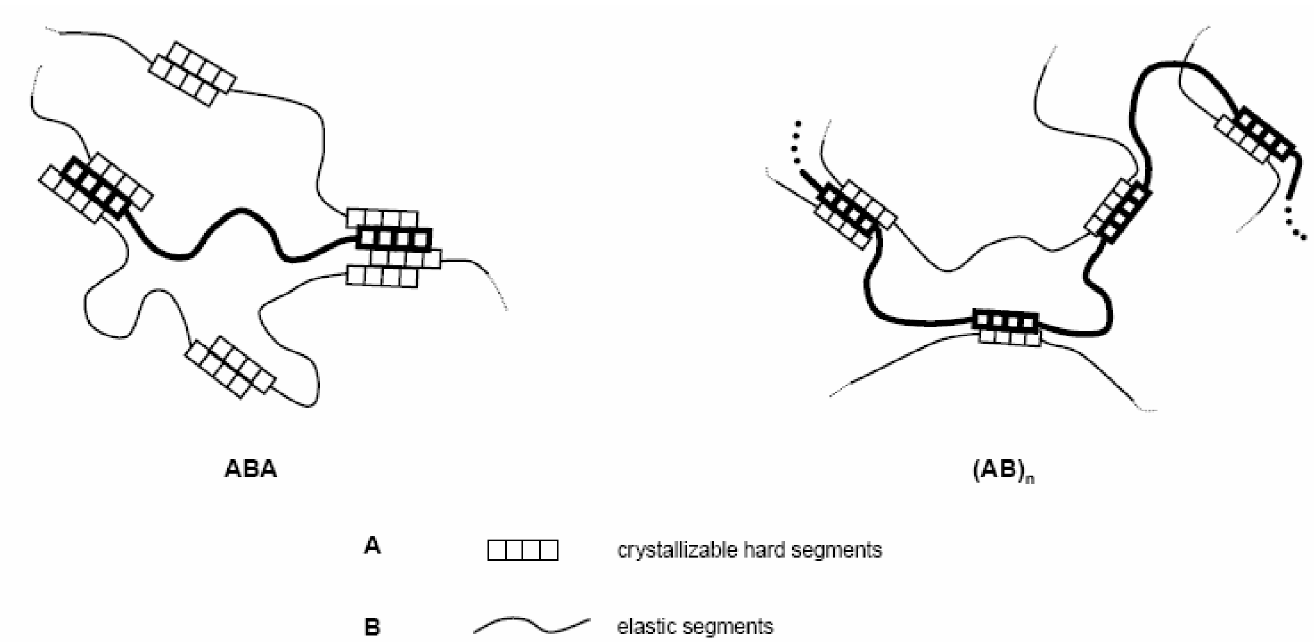
Effect of amide frequency on the melting points of AB-type (×) and AABB-type (•) polyamides. The number on the curves indicate the specific nylon.



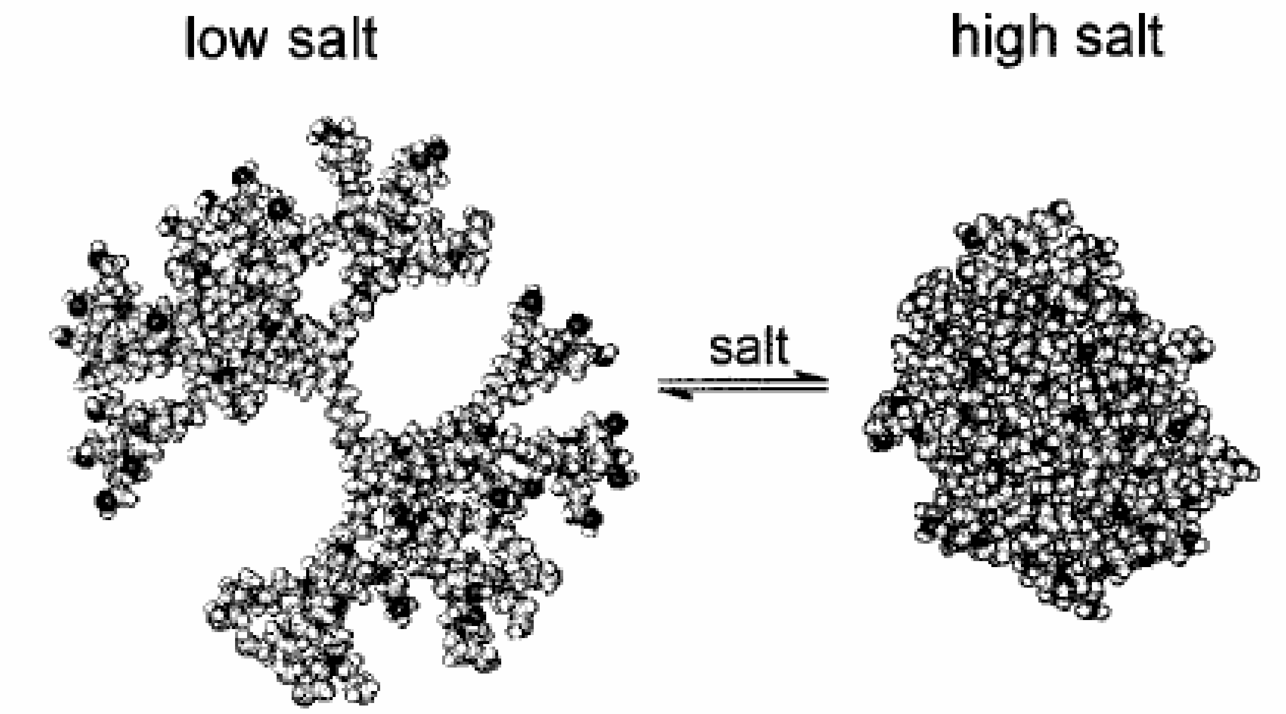
Stress–strain curves of some textile fibres (22).



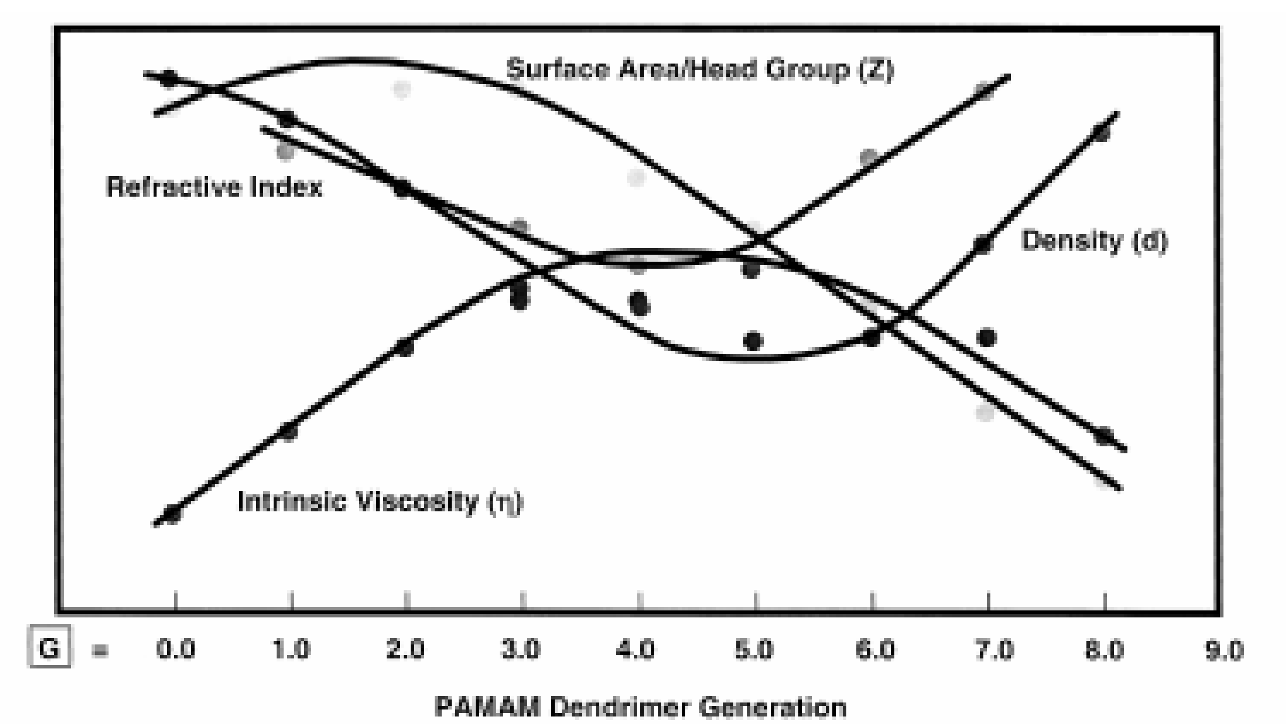
ABA vs AB_n elastomeric network formation



Influence of dielectric constant of solvent on denrimer conformation



Some structure/property relationships for PAMAM dendrimers



PPV-Solubility