Supporting material for students registered to subject:

Macromolecular chemistry S112003

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Sources:

Prokopová I.: Makromolekulární chemie, VŠCHT Praha, 2007. (educational text in Czech)
Merna J.: Polymers Instantly, educational text in English, freely accessible from
http://merna.eu/teaching/macromolecular-chemistry/
Encyclopedia of Polymer Science and Technology, J.Wiley Sons, Interscience, Publ., New York, 1964-1991

Supramolecular (physical) polymer structure- polymer morphology

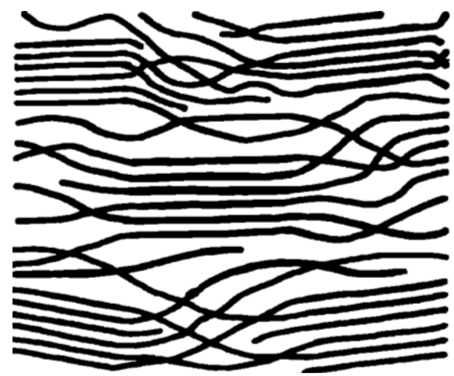
Amorphous polymers : macromolecules are randomly entangled

Semi crystalline polymers: some degree of regular arrangement of macromolecules

Semi-crystalline polymers:

fringed micelle model

non-oriented



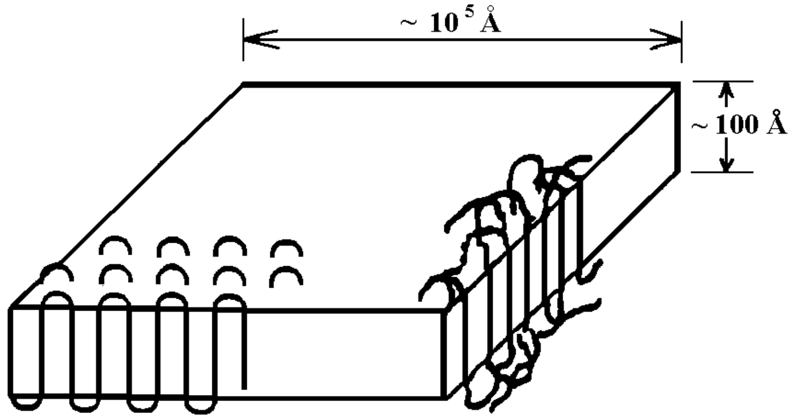
oriented (fiber drawing)

Structural requirements for crystalline polymers

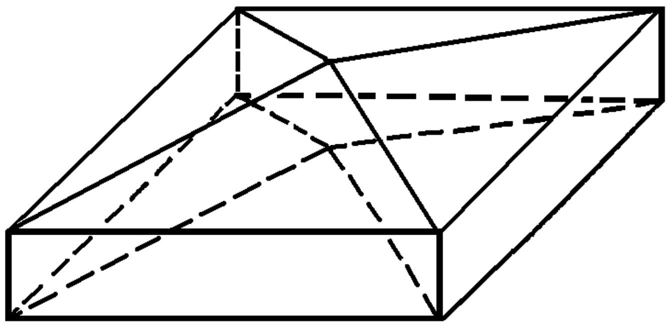
- Polymer chain regularity
- Polymer chain flexibility
- Intermolecular interactions

Structure of polymer monocrystal

(from diluted polymer solutions)



flat lamellae



pyramidal lamellae

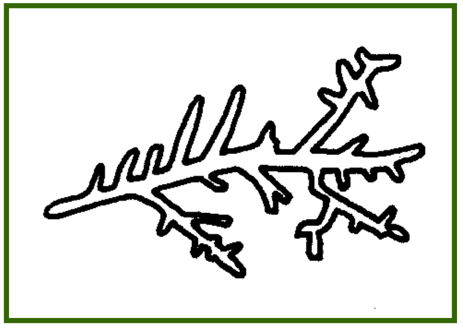
Extended Polymer chain

~ 10^3 Å

Folded chain model

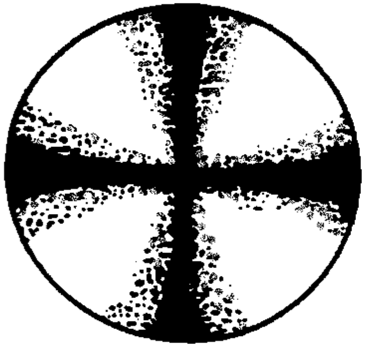
Polymer crystallization from melt or concentrated solutions

Dendrit



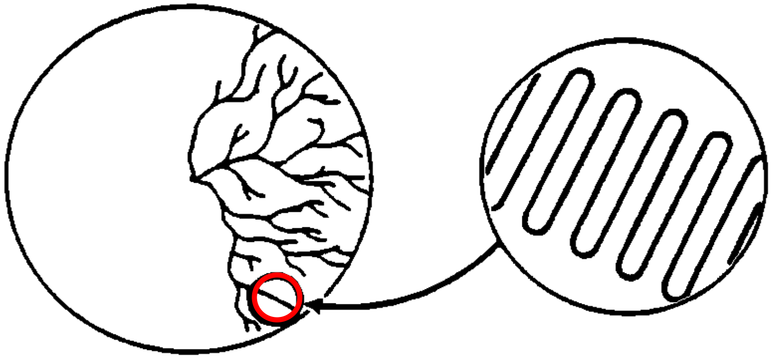
Irregular crystallite growth from edges/corners

Spherulite



View in polarization microscope

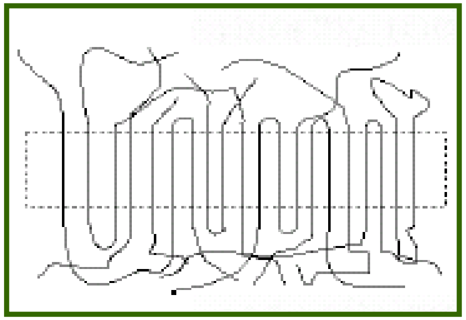
Maltesian cross



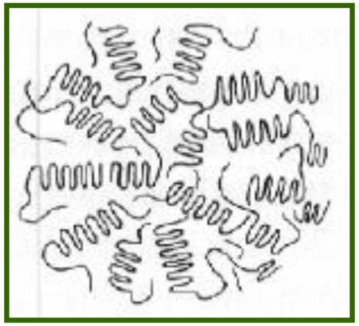
lamellae branching

Chains orientation in lamellea

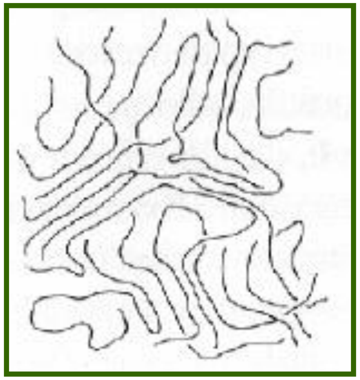
Morphology



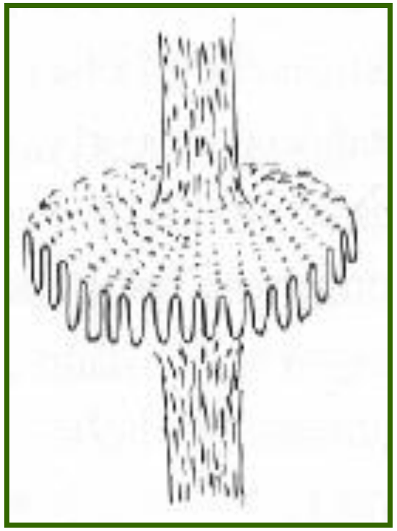
Chain folding



spherulite

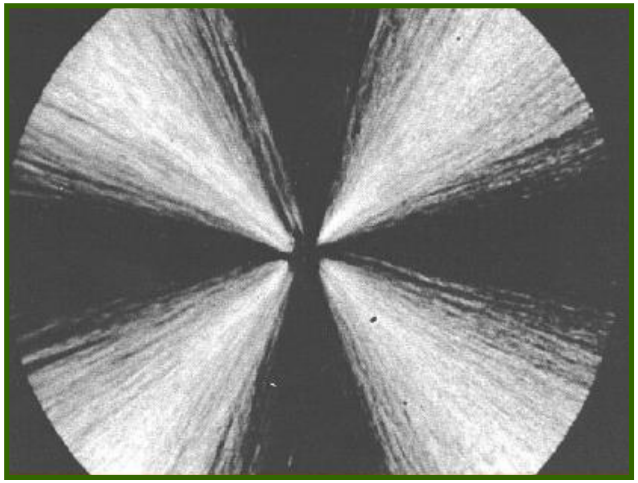


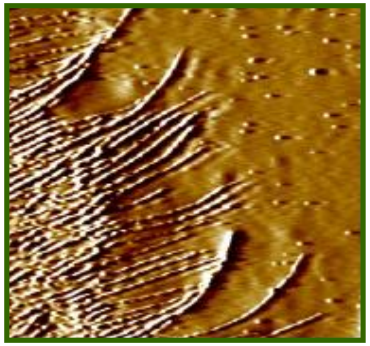
Fringed micelles model



Shish-kebab

(crystallization under stress)





Effect of crystallinity on:

•**Mechanical properties (LDPE vs. HDPE):**
tensile modulus
tensile strength
Hardness

•**Thermal properties (PE):**
Melting temperature

•**Optical properties (PS vs. PE): transparency- opacity**
•**(fillers, two amorphous phases - HI PS, foamed PS)**

Thermal behaviour of polymers

Thermal motions of macromolecules or their segments:

1. **Translational motion of entire molecules-flow**
2. **Motion of macromolecule segment-elasticity**
3. **Motion of few atoms in main chain or in side groups**
4. **Equilibrium vibrations of atoms**

Glass transition temperature-T_g

glassy-rubbery state

Change of polymer properties (mechanical, refractive index, specific volume)

Determines the application of polymer

Motions 1. and 2. are frozen below T_g

Thermal behavior of polymers- Limit temperatures

Amorphous polymer

glass transition temperature T_g

flow temperature T_f

Crystalline polymer (hypothetically 100%)

melting temperature T_m

Semi-crystalline polymer

glass transition temperature

flow temperature

melting temperature

Factors influencing T_g

1.Free volume of the polymer: v_f
The higher v_f the lower T_g

2. Attractive forces between macromolecules

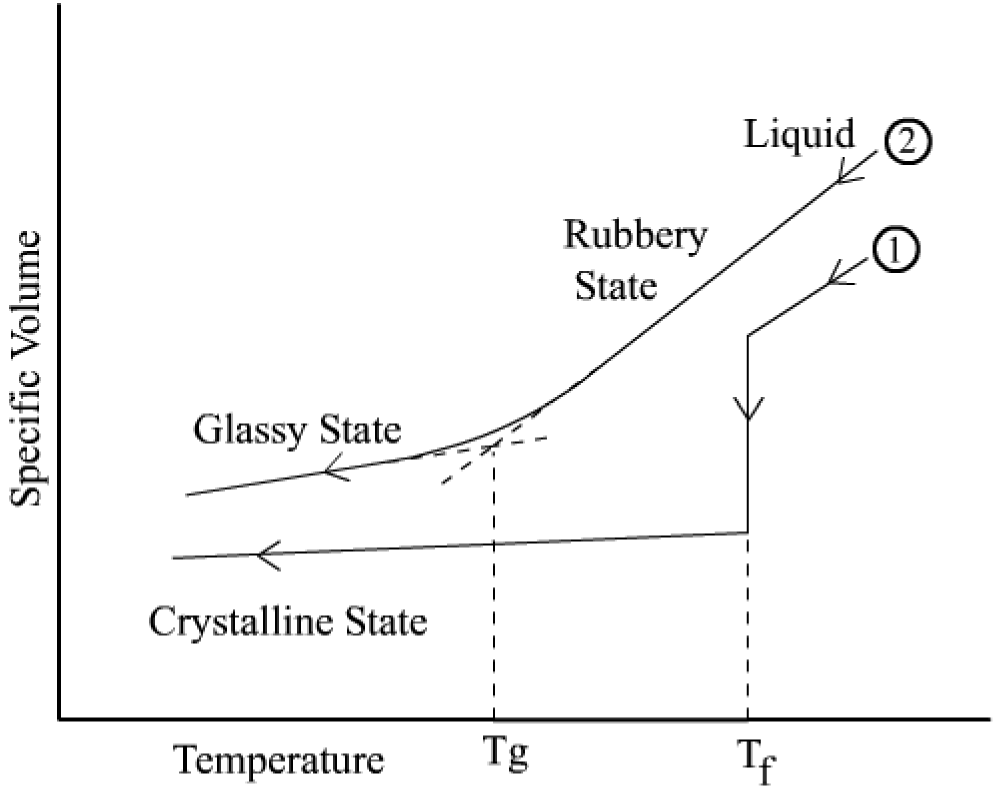
3. Internal mobility of polymer chains - stifness of the chain

4. Molar mass

Determination of T_g

Temperature dependece of thermodynamic property

e.g. specific volume vs. T



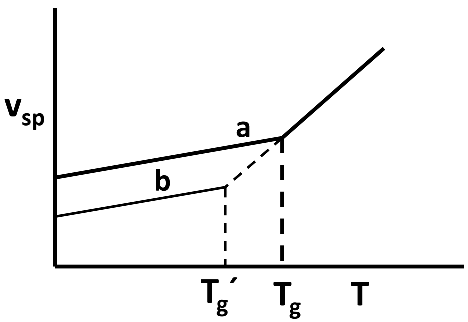
T_g change in slope, dv/dT vs. T –discontinuous-second order tdn. transition
T_m-discontinuous, first order tdn. transition

Plasticizers

Thermal behavior of amorphous polymers

Polymer behavior below T_g

„frozen“ segment movement, polymer is in glassy state

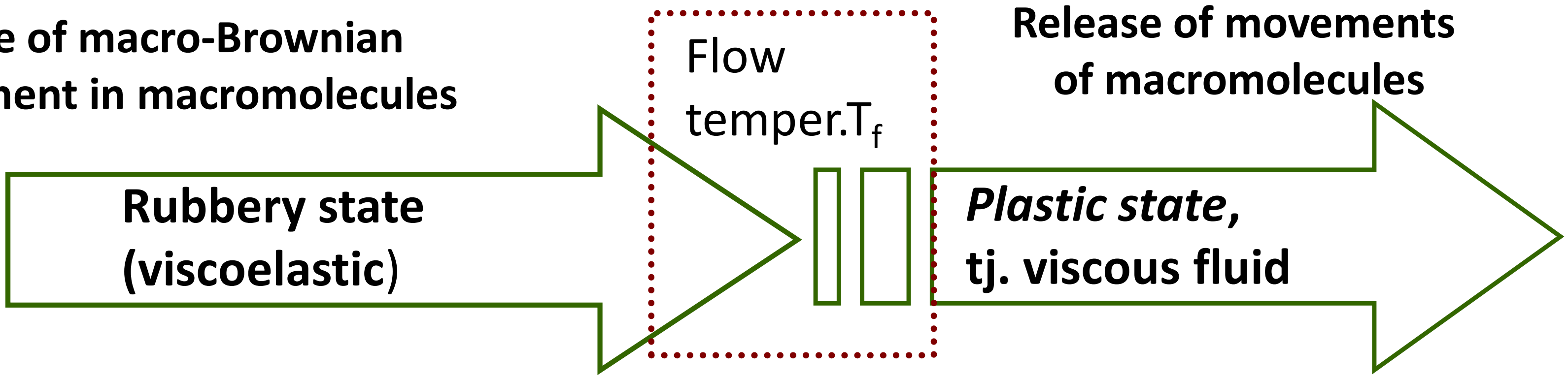


Dependence of specific volume of amorphous polymer on temperature and reaching glass transition temperature during fast (a) and slow (b) cooling of polymer sample

Polymer behavior above T_g

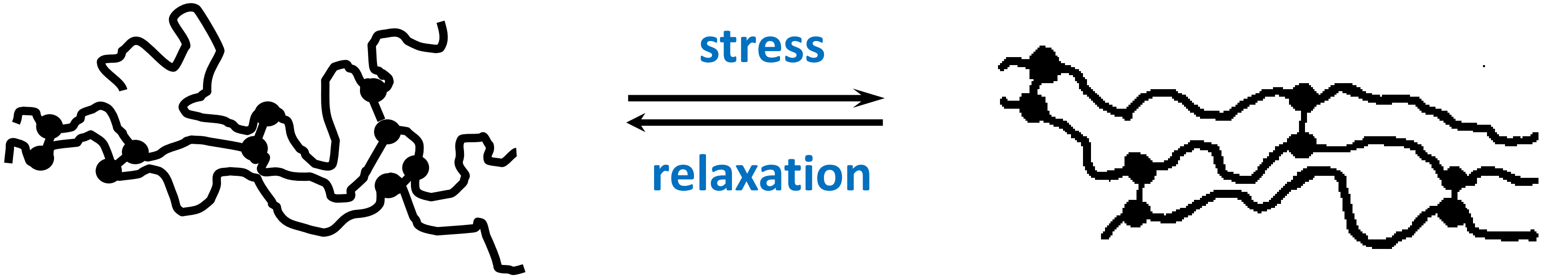
Release of macro-Brownian movement in macromolecules

Release of movements of macromolecules

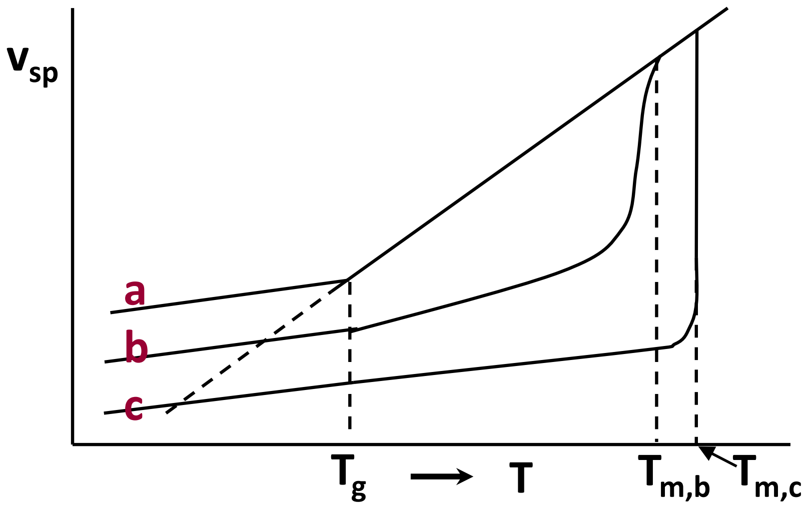


Principle of rubbery elasticity

Polymer above T_g
Suffcient DP-physical interactions-entenglements
Entropic elasticity



Thermal behavior of crystalline polymers



a – totally amorphous

b – partially crystalline

c - hypotetical 100 % crystalline

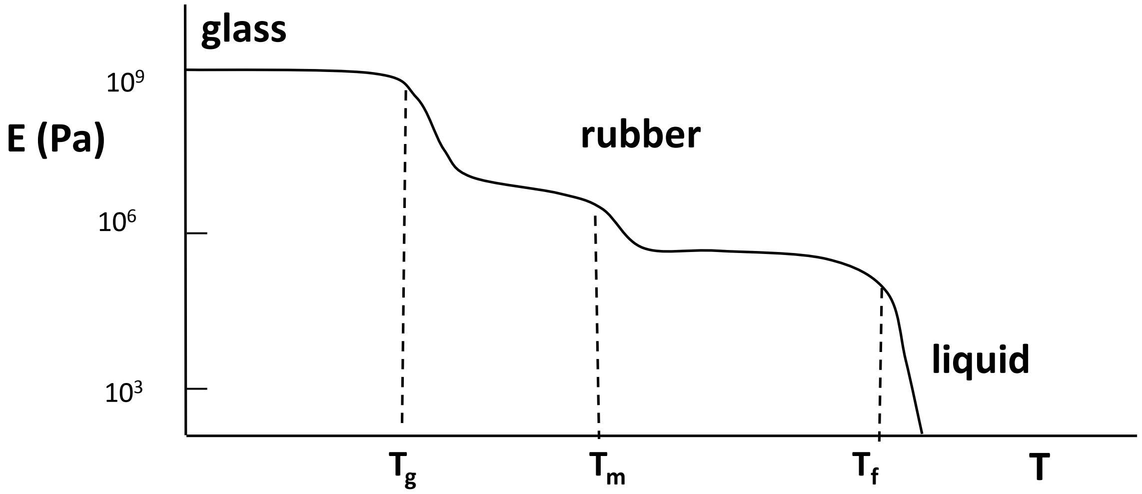
Thermodynamics of melting

$dG_m=dH_m-TdS_m$

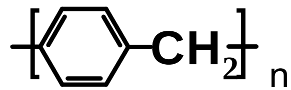
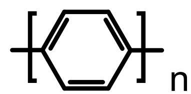
$T_m=dH_m/dS_m$

H_m ~ intermolecular interactions
dS_m~ stiffness of the chain, molar mass

Temperature dependence of flexural module of partially crystalline polymer



Melting temperatures of selected polymers

		T_m [°C]	
Polyethylene (HDPE)	$-[CH_2-CH_2]_n-$	135	
Poly(p-xylylene)		308	
Poly(p-phenylene)		> 500	
Poly(vinylidenchloride	$-[CH_2-CCl_2]_n-$	190	
Poly(vinylcohol)	$-[CH(OH)-CH_2]_n-$	265	syndiotactic

O

Clasification of polymers according to properties and applications

plastics
elastomers
fibers

thermoplastics
reactoplastics

polymer dispersions
varnish/paints
glue

thermoplastic elastomers

Conditions of monomers polymerizability

•**Chemical**- functionality >2 (fct. groups, multiple bonds, cycles)

•**Kinetic**-monomer activation:
bond polarization+resonance stabilization of product

$R_p > R_t$ (R_{tr})

•**Thermodynamic** aspects

$$\text{monomer (m)} \underset{k_{dp}}{\overset{k_p}{\rightleftarrows}} \text{polymer (p)}$$

Thermodynamic aspects

$$P_n^* + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} P_{n+1}^*$$

Termination + transfer neglected

$K=1/[M_e]$

$dG_{mp}=-RT \ln K$

$dG_{mp}=dH_{mp}-TdS_{mp}$

$T_c=dH_{mp}/dS_{mp}$

Ceiling temperature

No depolymerization of terminated chains

dS_{mp} = -100 to -120 $JK^{-1}mol^{-1}$

Independent on monomer structure

dH_{mp}:

- Differences in resonance stabilization of monomer and polymer
- Difference in steric tension in monomer and polymer
- Difference in non-bonding interaction in monomer and polymer

Polymerization enthalpy at 25°C

Monomer	$-\Delta H_{mp}$ (kJ/mol)
ethylene	101,5
vinylchloride	111,5
vinylacetate	89,5
propylene	85,9
methylacrylate	84,5
acrylonitrile	77,5
vinylidenechloride	75,5
butadiene	73,0
styrene	70,0
methylmethacrylate	57,5
izobutylene	53,0
α-methylstyrene	34,5

$$\Delta G_{mp} < 0$$

$$\Delta G_{mp} = \Delta H_{mp} - T\Delta S_{mp}$$

Ceiling temperature of polymn T_c – above no polymer formation

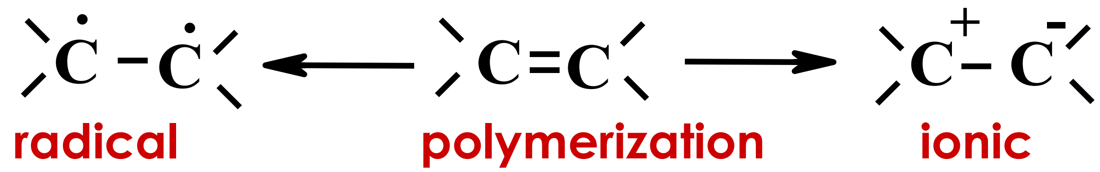
$$\Delta G_{mp} = \Delta H_{mp} - T_c\Delta S_{mp} = 0$$

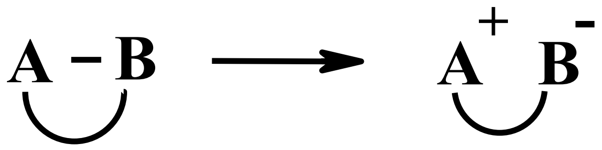
Rate of polymn. = rate of depolymerization

!!!! All, chemical, kinetic and thermodynamic; conditions must be fulfilled !!!!

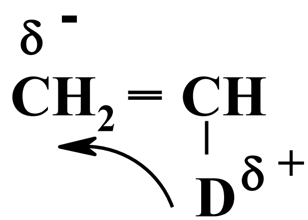
Monomers suitable for chain polyreactions:

- multiple bond between C atoms in molecule
- multiple bond between C and heteroatom in molecule
- (hetero)cyclic molecules

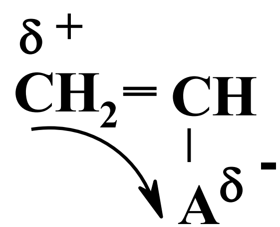


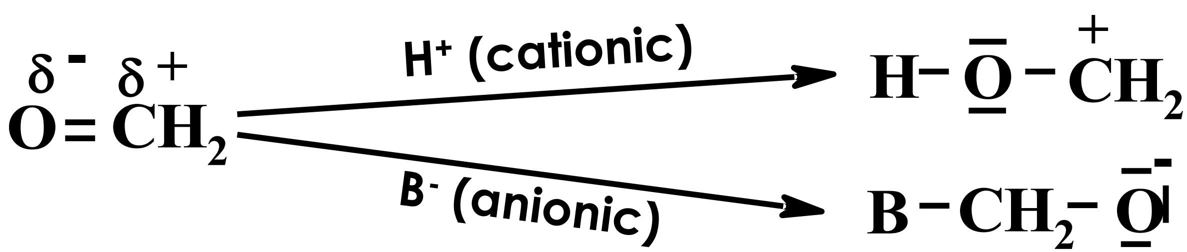


Cationic polymerization



Anionic polymerization





Thermodynamical conditions of polymerizability

	ΔH_{mp}	ΔS_{mp}	ΔG_{mp}	
1.	< 0	< 0	< 0	at $T < T_c$
2.	< 0	> 0	< 0 always	not known
3.	> 0	< 0	> 0 always	
4.	> 0	> 0	< 0	above T_f

Enthalpy and entropy of polymn. for selected monomers at 25 °C *

Monomer	**-ΔH ($kJ\ mol^{-1}$)**	**-ΔS ($J\ K^{-1}\ mol^{-1}$)**
Ethene	93	155
Propene	84	116
But-1-ene	83,5	113
2-Methylpropene	48	121
Buta-1,3-diene	73	89
Isoprene	75	101
Styrene	73	104
α-Methylstyrene	35	110
Vinylchloride	72	-
Vinylidenchloride	73	89
Tetrafluoroethene	163	112
Acrylic acid	67	-
Akrylonitrile	76,5	109
Maleinanhydride	59	-
Vinyl-acetate	88	110
Methyl-acrylate	78	-
Methyl-methacrylate	56	117

*** Brandrup J., Immergut E.H. (Eds), Polymer Handbook, Wiley-Interscience, New York 1989. Sawada H., Thermodynamics of Polymerization, Marcel Dekker 1976**

Means of polymerization

Phase state

Monomer	Polymer	index for molar termodynam. quantity
gas	condensed (amorph.)	gc
gas	condensed (crystal.)	gc´
Liquid	condensed (amorph.)	lc
Liquid	condensed (crystal.)	lc´
Liquid	solution of polymer in monomer	ls
solution m.	solution of polymer	ss
solution m.	condensed	sc

Ceiling temperature T_c of selected monomers

Monomer	T_c (°C)
Styrene	310
Methylmethakrylate	220
a-Methylstyrene	61

Dependence of T_c on pressure

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \qquad \frac{dT_c}{T_c} = \frac{\Delta V}{\Delta H_{mp}} dp$$

$$\ln(T_c)_p = \ln(T_c)_{101,3\ kPa} + \frac{\Delta V}{\Delta H_{mp}} p$$

Bond Energy between atoms capable of chain formation

Bond	kJ/mol	Bond	kJ/mol
C – C	347,8	C – B	372,9
B – B	289,1	C – O	331,0
S – S	264,0	C – N	305,9
P – P	222,1	C – Al	258,1
Se – Se	209,5	C – S	257,6
Te – Te	205,3	C – Si	241,3
Si – Si	186,6	Al – O	578,2
Sn – Sn	197,0	B – O	475,6
Sb – Sb	176,0	Si – O	444,1
Bi – Bi	167,6	B – N	437,0
Ge - Ge	164,2	P - O	342,3

Capability to form isochain

Periode	Group			
	III.	IV.	V.	VI.
2	~5 B	∞ C	N	O
3	Al	45 Si	>4 P	30 000 S
4	Sc	Ti		Cr
	Ga	6 Ge	5 As	? Se
5	Y	Zr	Nb	Mo
	In	5 Sn	3 Sb	? Te
6	La	Hf	Ta	W
	Tl	Pb	? Bi	Po