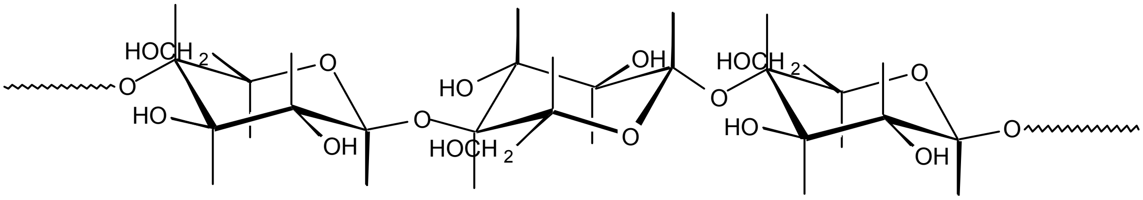
1. Historic Perspective

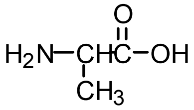
1.1. First Polymers

1.1.1. “Prehistoric” Polymers

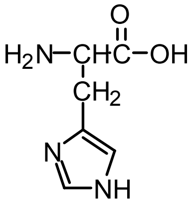
- **Cellulose (Polysaccharide / Glucose)**

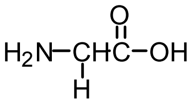


cellulose chain segment

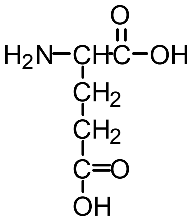


$H_2N-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$

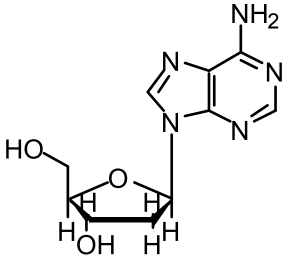




$H_2N-\underset{H}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$



$H_2N-\underset{\underset{\underset{\underset{\underset{OH}{|}}{C=O}}{|}}{CH_2}}{\underset{|}{\underset{CH_2}{\underset{|}{CH}}}}-\overset{O}{\overset{\|}{C}}-OH$



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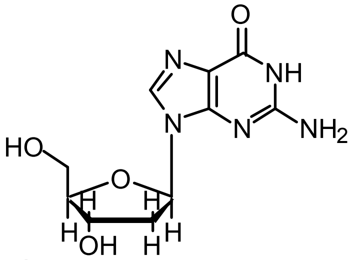

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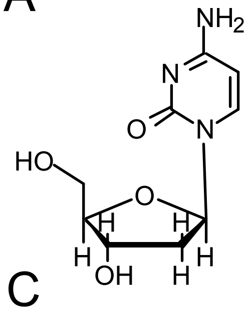

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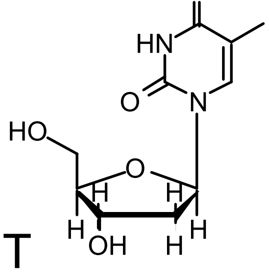

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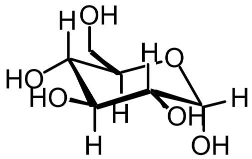
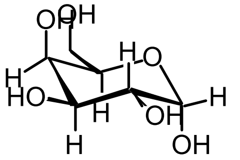
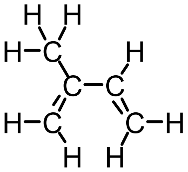


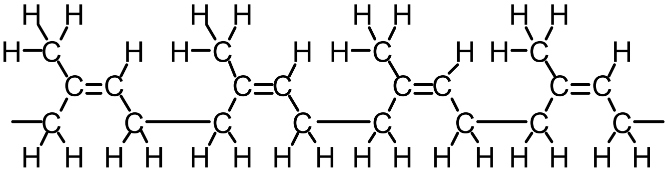


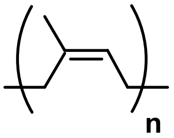
1.1.2. Synthetic Polymers

1770	• Priestly wrote: "I have seen a substance excellently adapted to the purpose of wiping from paper the marks of black pencil (referring to "india rubber").	• cis-isoprene
1805	• Description of rubber elasticity by Gough. Stretching creates heat.	• crosslinking
1823	• MacIntosh patented a process in which rubber was used to bond two layers of fabric for the production of a waterproof sheet	• polymer interphase
1826	• Faraday working on the analysis of rubber.	
1832	• Berzelius uses the term "polymeric"	
1839	• C. Goodyear discovered the process of rubber vulcanisation	• crosslinking / sulphur
1845	• Blyth and Hofmann observed that "metastyrol" was formed when styrene was exposed to sunlight, while it remained unchanged in the dark. This is probably the first report of photopolymerisation.	• styrene • polystyrene • photopolymerisation
1872	• The acid catalysed condensation of phenol with methylal into Bakelite was reported by Baeyer	• phenol resins • condensation • crosslinking
1879	• Bouchardat, exposing isoprene to concentrated hydrochloric acid, obtained as one of the product a solid which "has the composition of isoprene". This product subjected to dry distillation yields the same product as rubber.	• polymer characterisation • identification of repeat unit
1900	• Bamberger and Tschirner found another route to polyethylene using diazomethane (instead of acid catalysis) • Kondakov demonstrated the polymerisation of 2,3-dimethyl butadiene.	• radical addition polymerisation
1906	• E. Fischer coined the term polypeptide. He embarked on the laborious step-by-step synthesis in order to obtain chain molecules.	• polypeptide • stepwise synthesis • dendrimers
1907	• Fischer had synthesised an octadeca peptide. • Baekeland patented his "heat and pressure" process (Bakelite)	
1917	• In a lecture to the Swiss Chemical Society, Staudinger speculated for the first time that "high molecular compounds" consist of covalently bonded long-chain molecules.	• polymers are hold together by covalent bonds
1927	• Hengstenberg provided the first unambiguous proof on crystallographic grounds that a synthetic polymer (polyoxymethylene) consists of long chain molecules. • Accidental discivery of "plexiglass" in an attempt to prepare a sheet of PMMA.	• polymer characterisation • x-ray crystallography • polyformaldehyde
1930	• Carothers and Hill succeeded in the preparation of the first synthetic fibre by high vacuum technique and cold drawing.	• Nylon • polymer fibres • polycondensation
1939	• High pressure process for the production of polyethylene patented by ICI.	• polyethylene
1951	• Discovery of coordination polymerisation by Ziegler and coworkers. • Discovery of interfacial polymerisation (nylon rope trick).	• polyethylene • polypropylene • tacticity • interfacial polymerisation

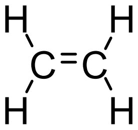
Rubber (cis polyisoprene)

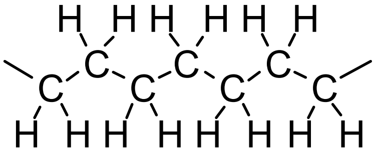


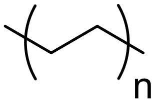




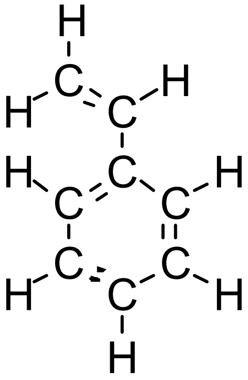
Polyethylene (polythene)

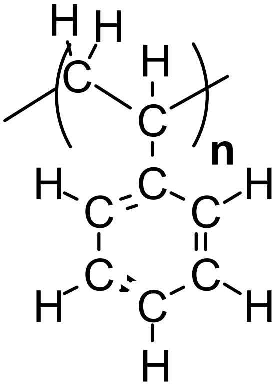


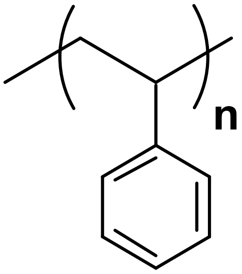




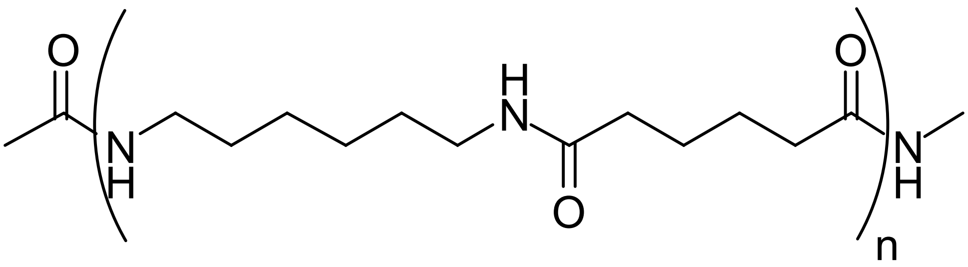
Polystyrene

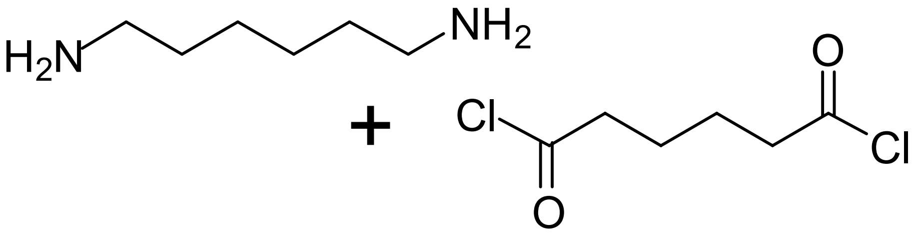




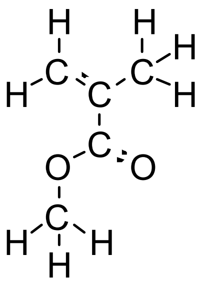


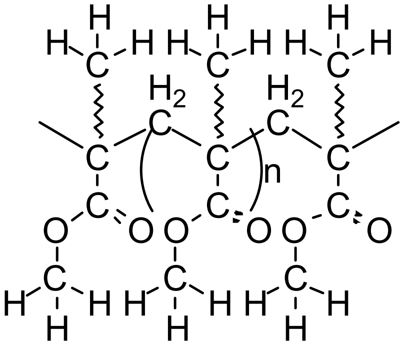
Nylon 6,6

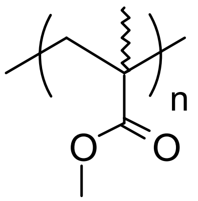




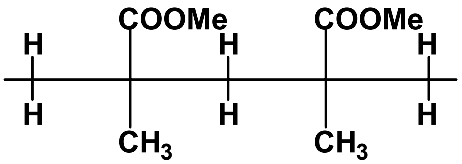
Poly(methyl methacrylate)



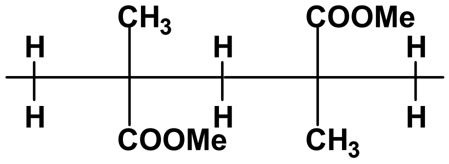




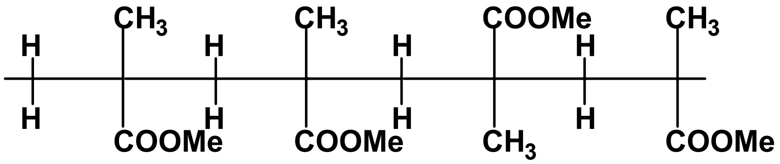
1.1.3. Tacticity / Property



isotactic



syndiotactic



atactic

Polymer	**Tg (°C)**		
	syndiotactic	atactic	isotactic
poly(methyl methacrylate)	145	105	45
poly(ethyl methacrylate)	65	65	12
poly(propylene)	~ 40-60	-6	-18 (Tm= 165°C

1.2. What Makes Polymers Special?

- **Chain Entanglement**
- **Summation of Intermolecular Forces**
- **Time Scale of Motion**

Polymers exhibit a number of properties that sets them apart from small molecules.

- **Mechanical Strength**
- **Elasticity**
- **Plasticity**
- **Thermal Stability**
- **Tuning of Properties**
- **Conductivity**
- **Insulation**
- **Chemical Inertness**
- **Usually Lightweight**

2. Polymerisation

Initiation

Here a reactive species is generated that reacts with the monomer to yield an activated chain end ready to react with another monomer subsequently.

Propagation

A reactive polymer chain end adds on more monomers.

Termination

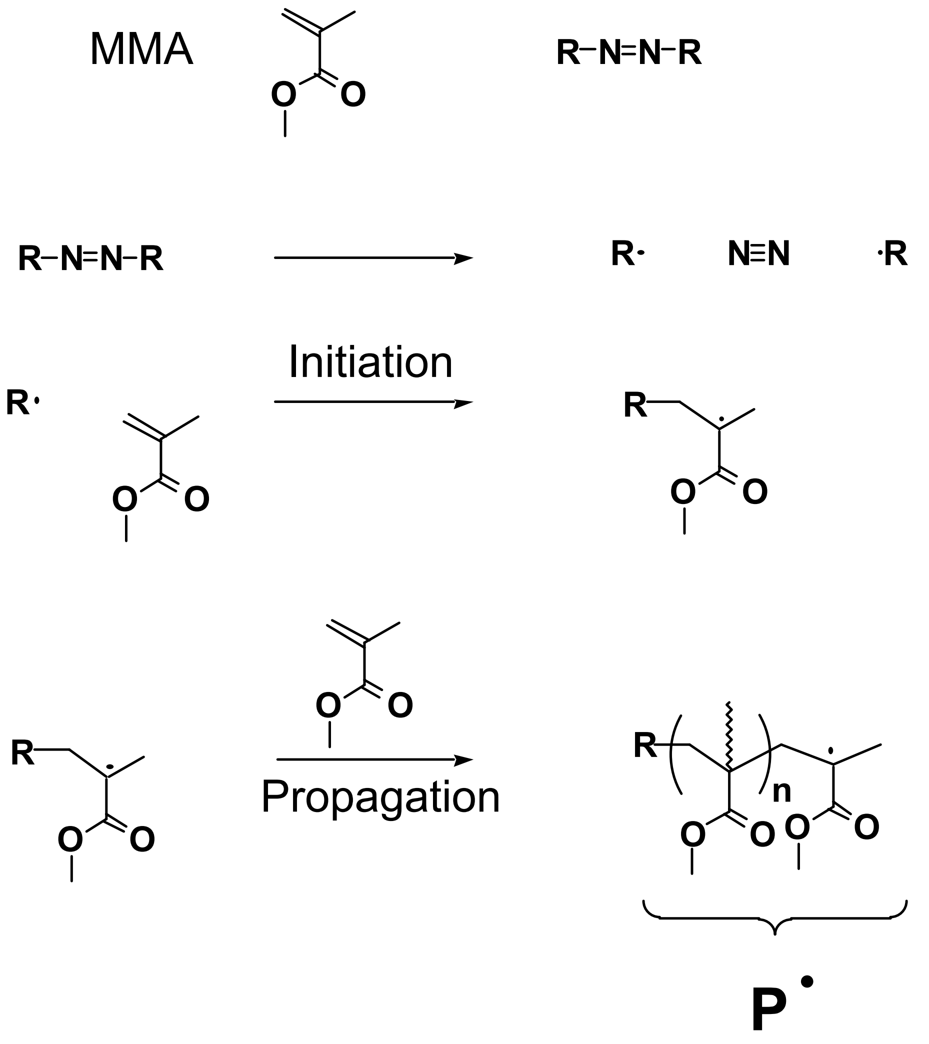
Further addition of monomers to a growing polymer chain is inhibited through deactivation (side reaction) of the propagating chain end.

Chain Transfer

This is essentially a side reaction that leads to the termination of one polymer chain but as a chemical consequence of the termination chemistry, a new polymer chain is initiated. The overall result is a decrease in molecular weight.

2.1. Two Examples - A

Initiation, propagation and termination in the polymerisation of methyl methacrylate.



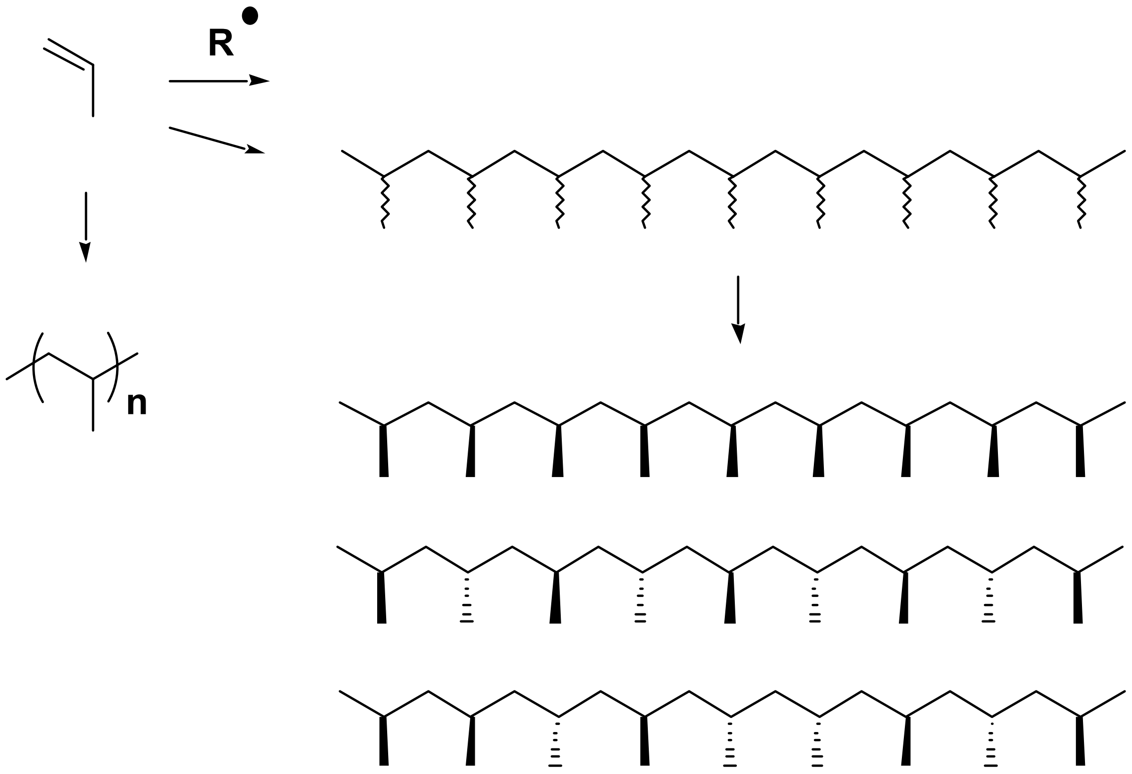
$$P_n^{\bullet} + P_m^{\bullet} \longrightarrow P_{n+m}$$

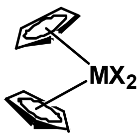
Comproportionation
or
Recombination

$$P_n^{\bullet} + P_m^{\bullet} \longrightarrow P_n + P_m$$

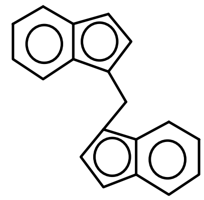
Disproportionation

2.1. Two Examples - B

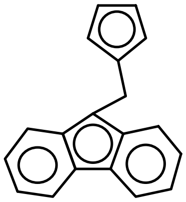




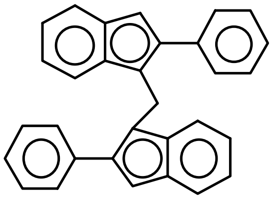
atactic PP



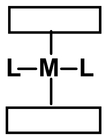
isotactic PP

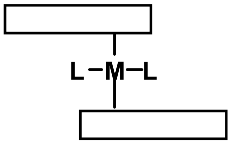


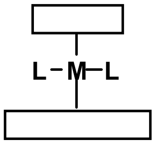
syndiotactic PP

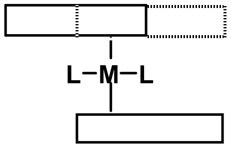


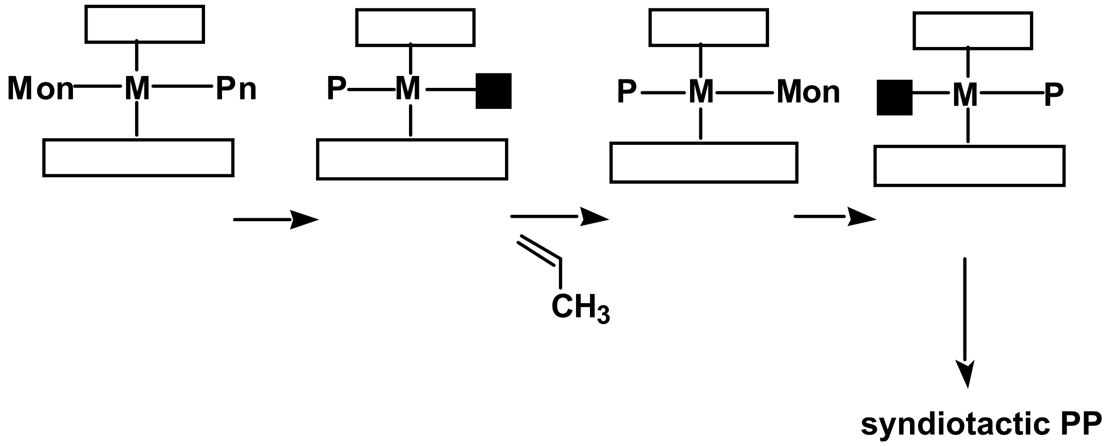
atactic-isotactic PP

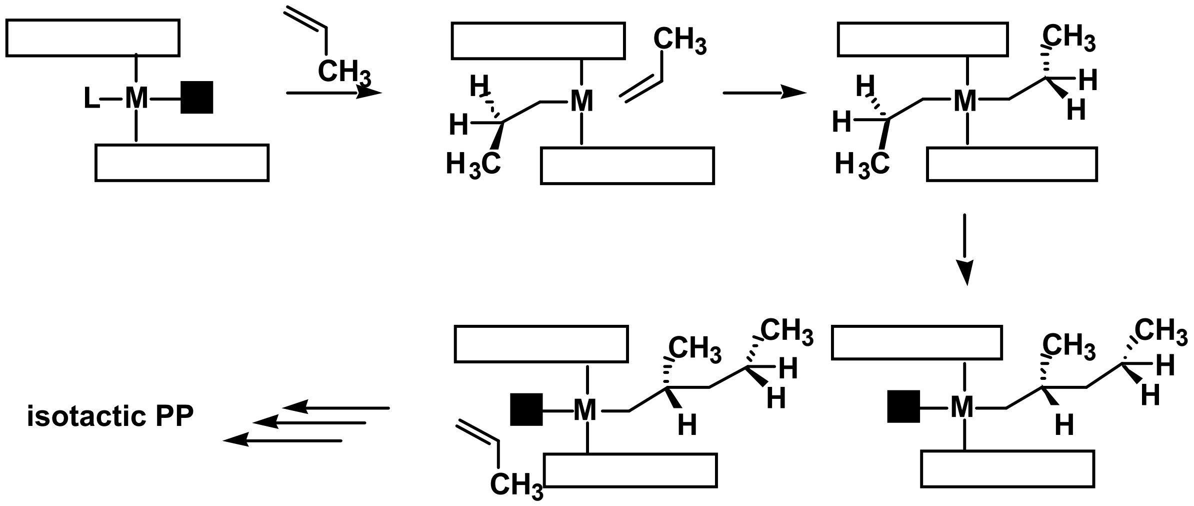


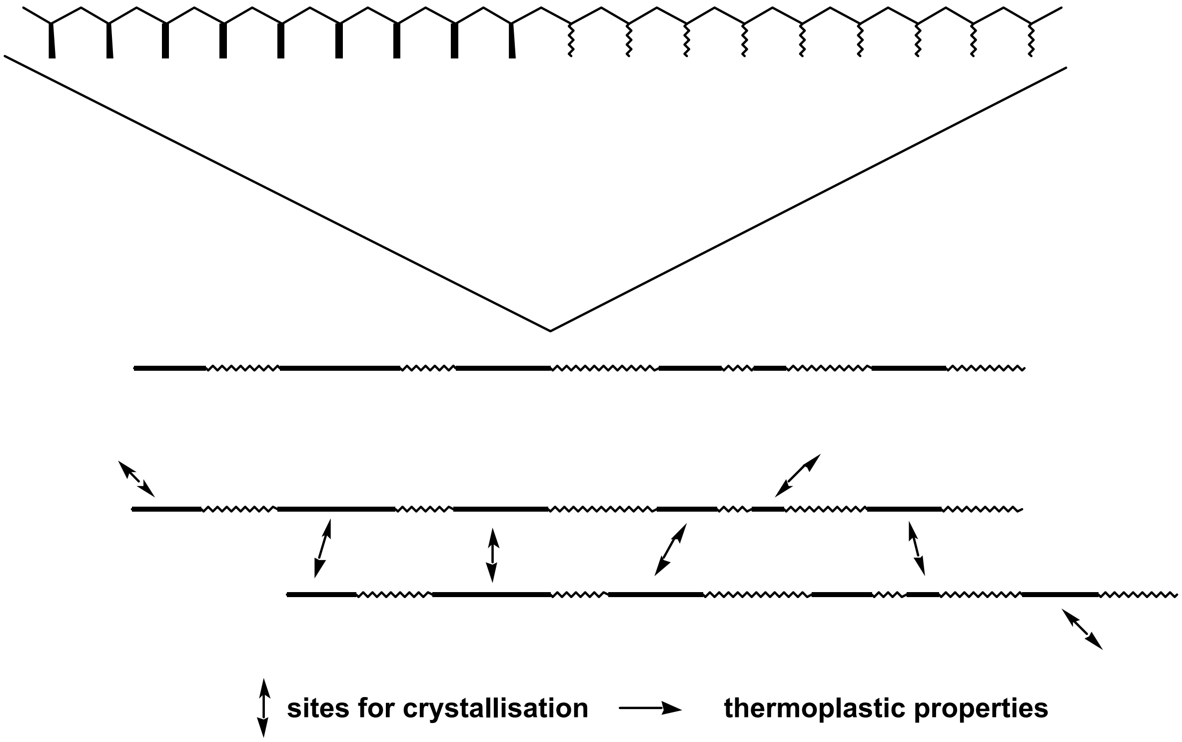


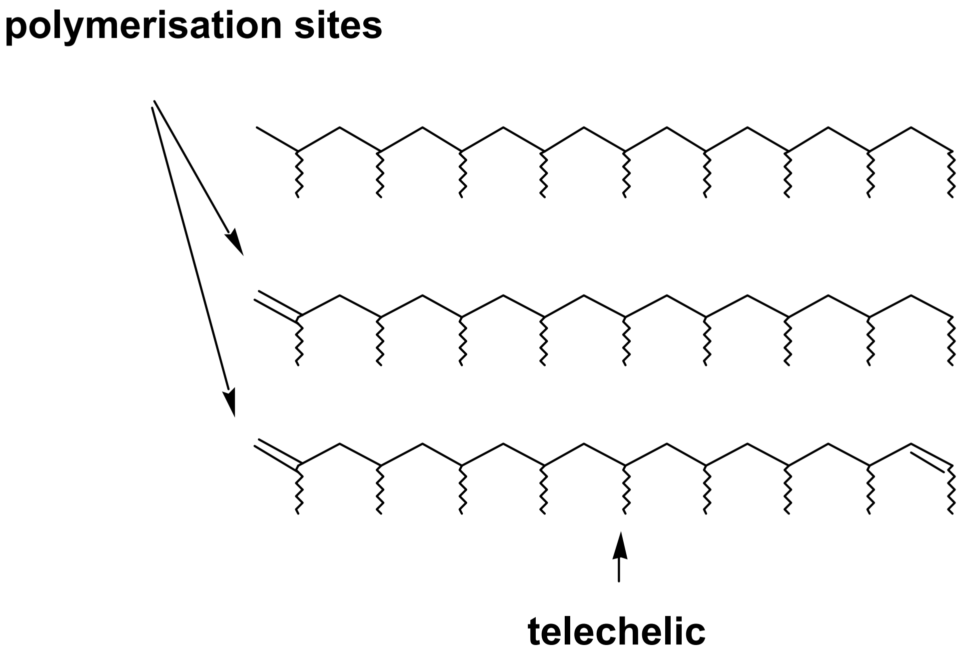




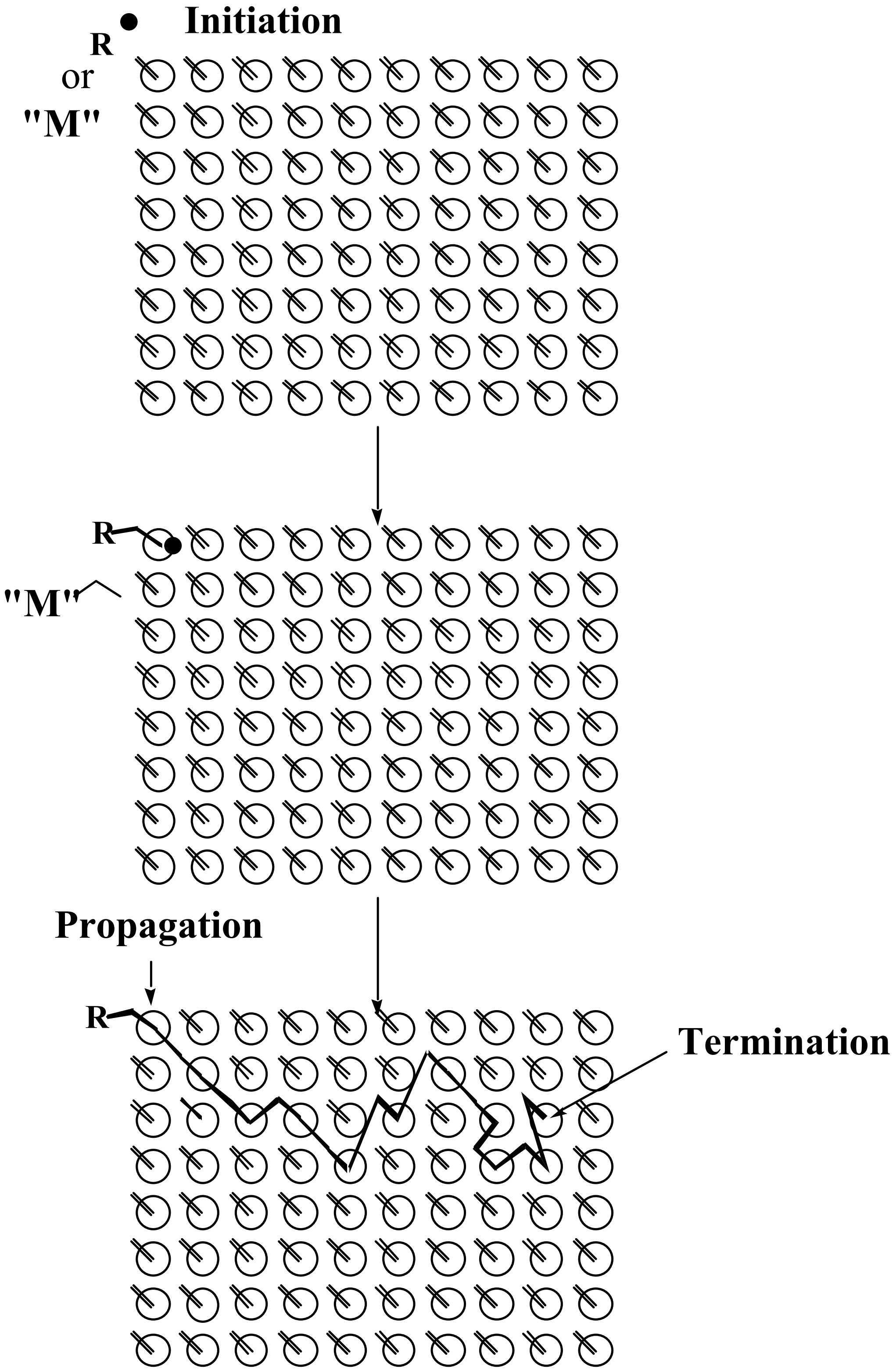

Mon
M
Pn
P
M
CH3
P
M
Mon
M
P
syndiotactic PP


L
M
CH3
H
H
H3C
CH3
M
H
H
H3C
M
CH3
H
H
CH3
CH3
H
H
H
M
CH3
isotactic PP


sites for crystallisation
thermoplastic properties

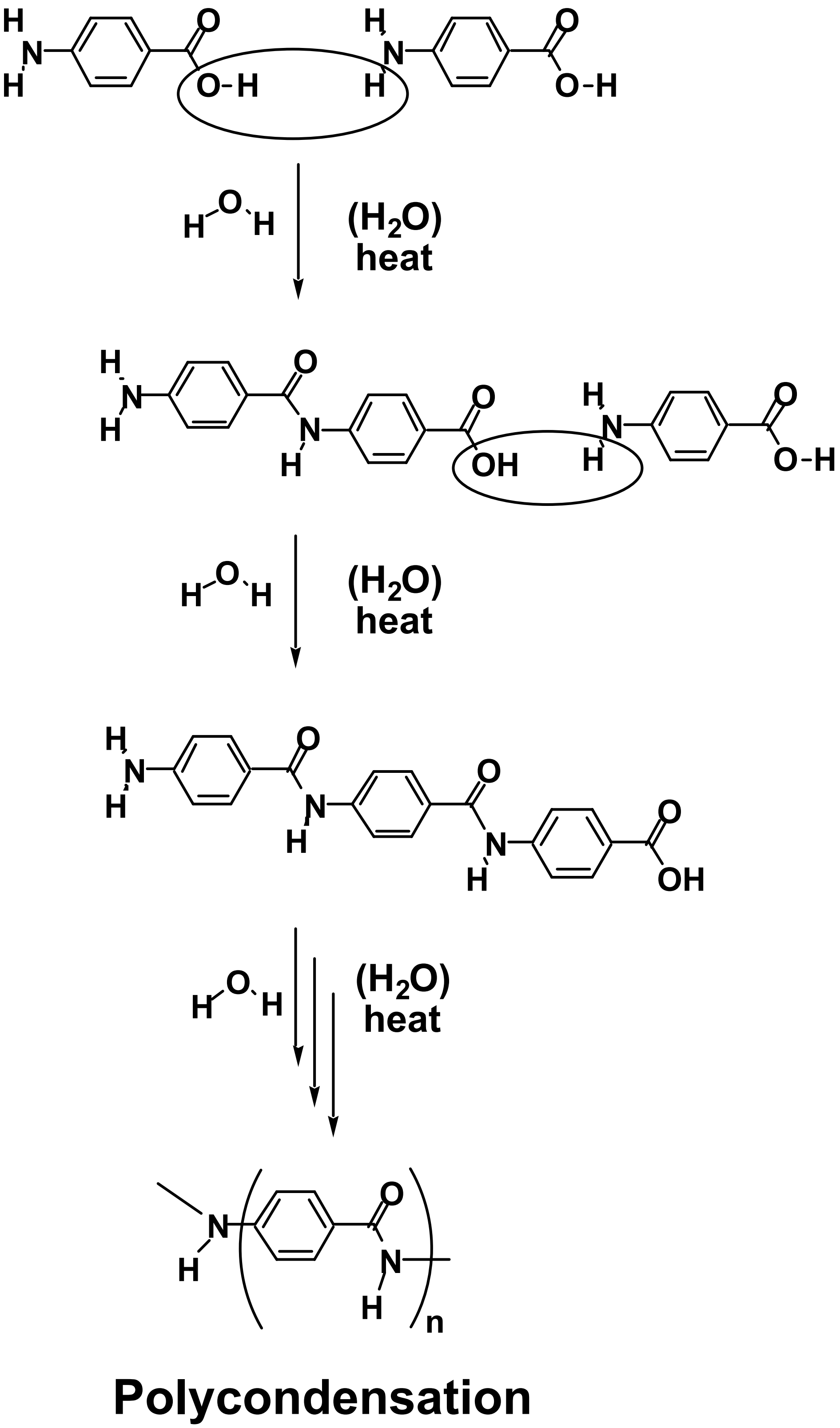

polymerisation sites
telechelic

2.1.1. Kinetics of Chain Growth Polymerisation



2.2. Step-Growth Polymerisation

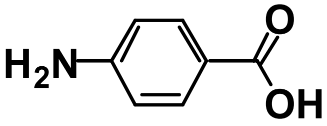
2.2.1. Linear Polymers

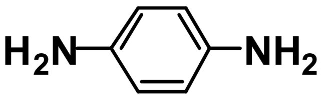


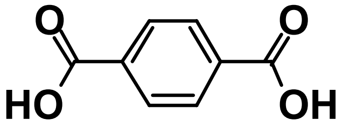
Polycondensation

2.2.1.1. Carother’s Equation

Crucial for a successful synthesis of high molecular weight polymers is the purity of the starting materials. The correct 1:1 (equimolar) ratio of starting materials becomes paramount if the step polymerisation is carried out using two or more monomers at the same time.







The degree of polymerisation (average number of monomer units per polymer chain) in step polymerisation can be calculated by using Carother's equation.

p = probability of finding a reacted functional group A
= conversion or extent of reaction of A groups
1-p = probability of finding an unreacted functional group

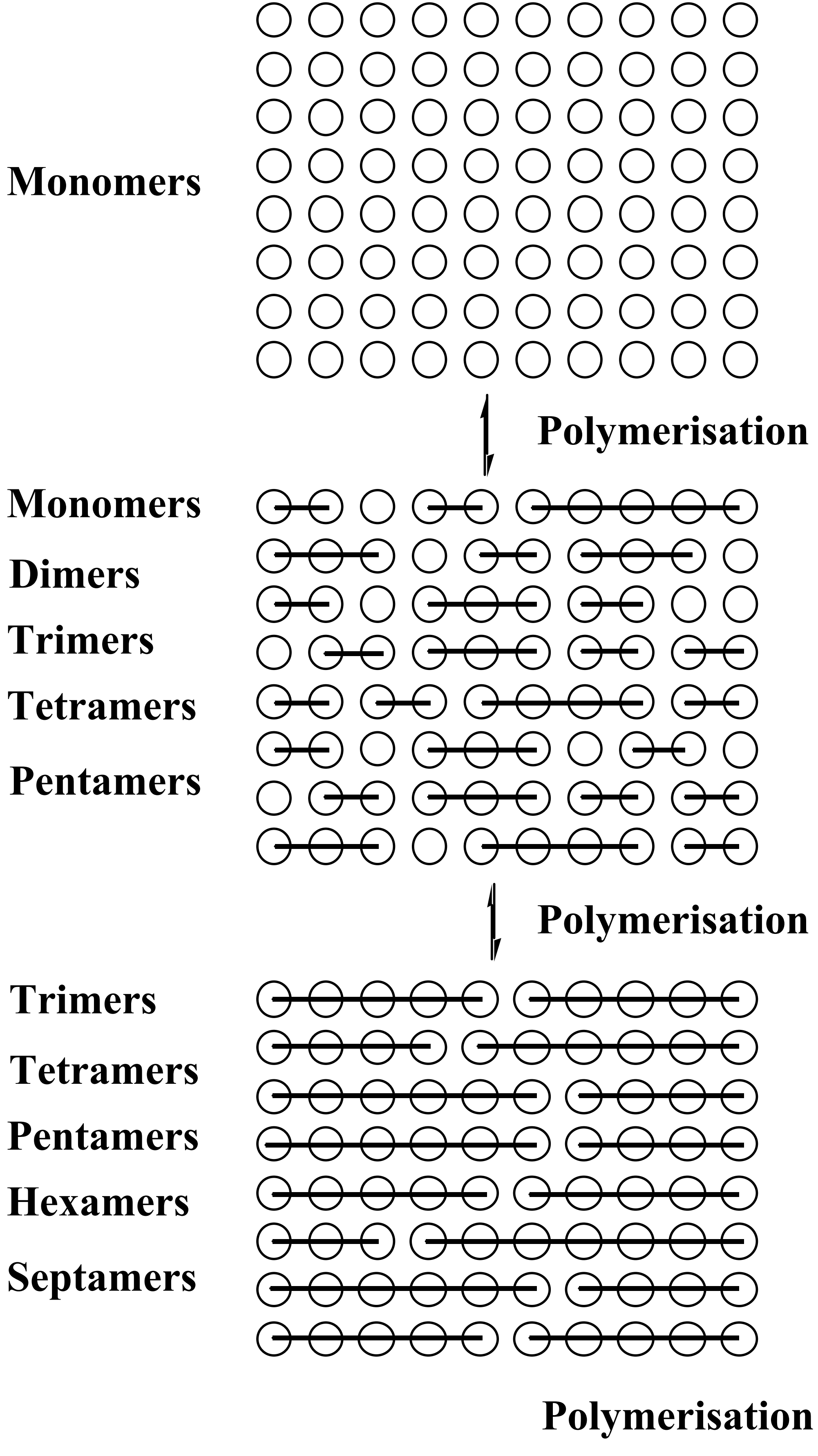
$$\overline{X}_n = \frac{1}{1 - p}$$

(Carother's equation)

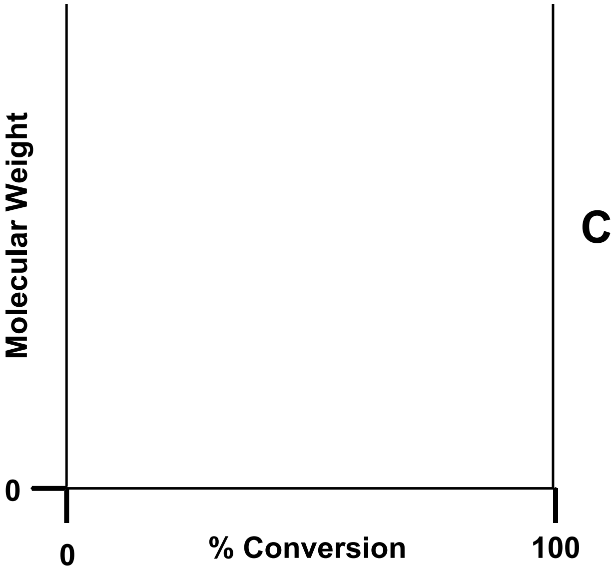
$\overline{X}_n$ = degree of polymerisation

p	X_n
0.900	10
0.990	100
0.998	500

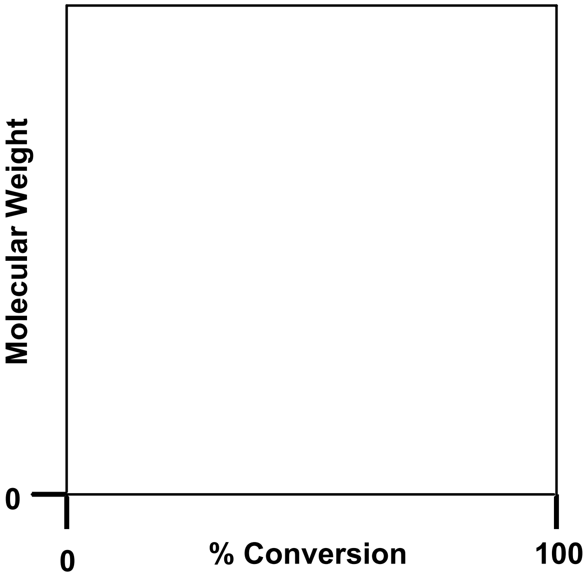
2.2.1.2. Kinetics of Polycondensation



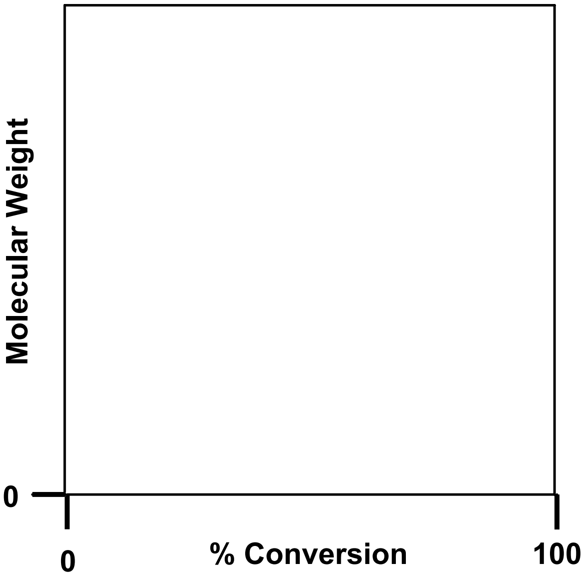
2.2.1.3. Molecular Weight vs Conversion



Chain-Growth Polymerisation



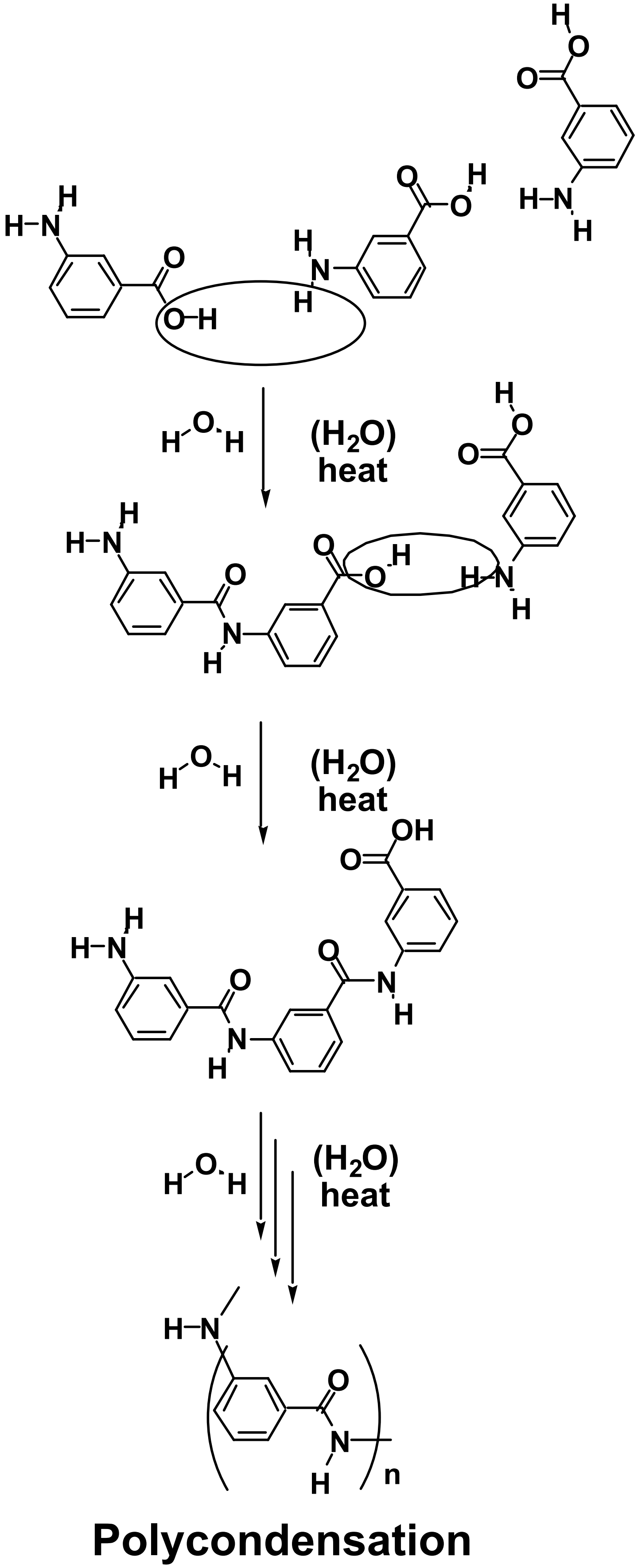
Step-Growth Polymerisation



Polypeptide Formation

"Living" Polymerisation

2.2.1.4. Influence of Monomer Structure



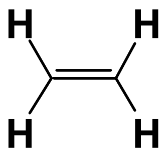
Polycondensation

3. Polymer Structure

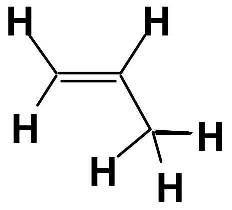
3.1. Monomers

3.1.1. Synthetic Monomers

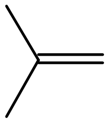
ethylene



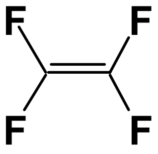
propylene



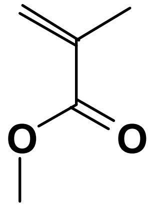
isobutylene



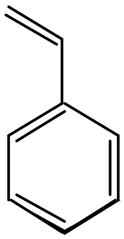
tetrafluoroethylene



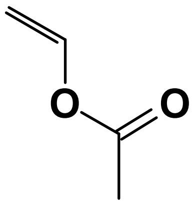
methyl methacrylate



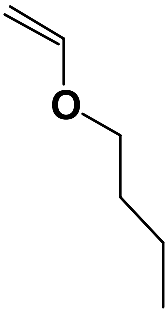
styrene



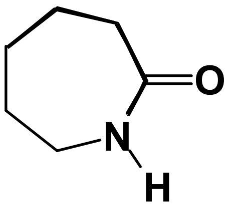
vinyl acetate



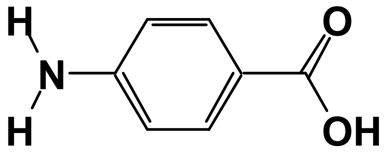
butyl vinylether



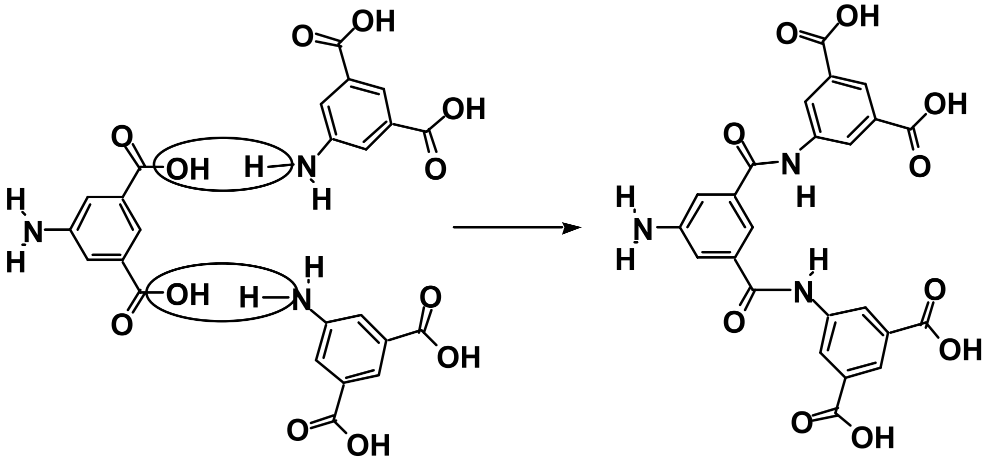
epsilon-caprolactam

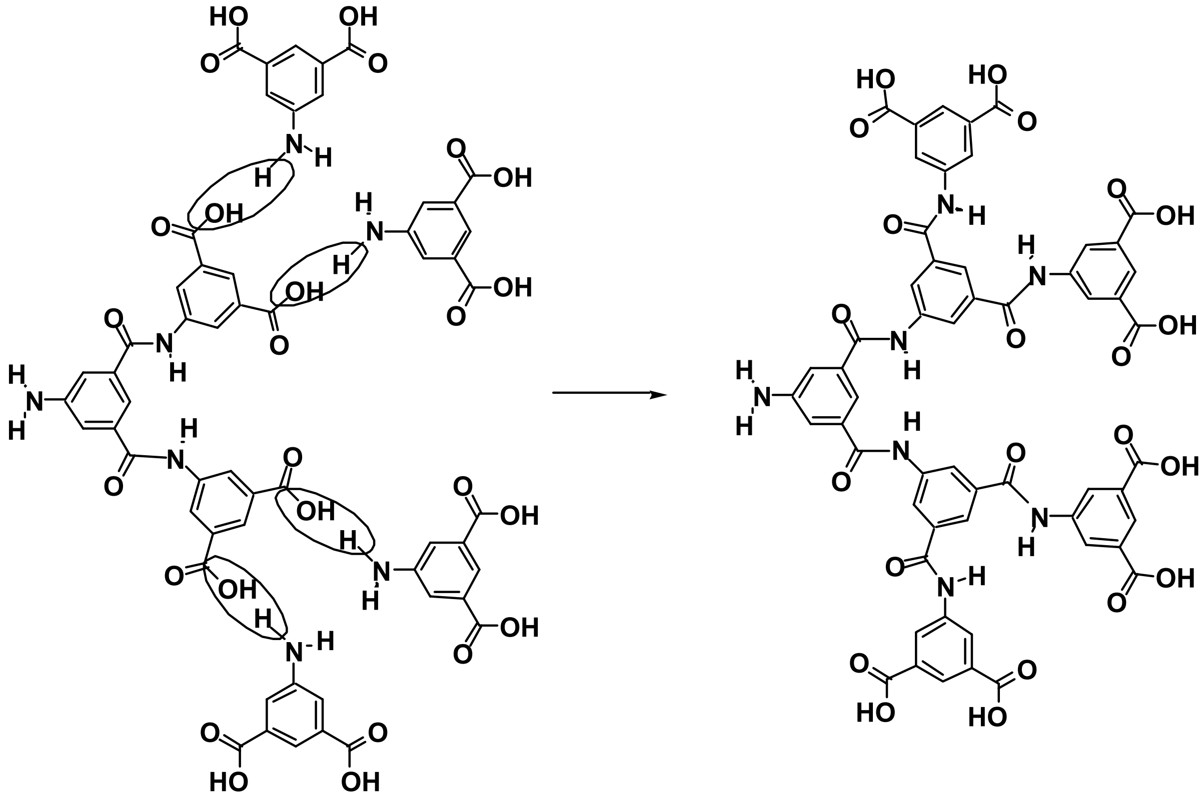


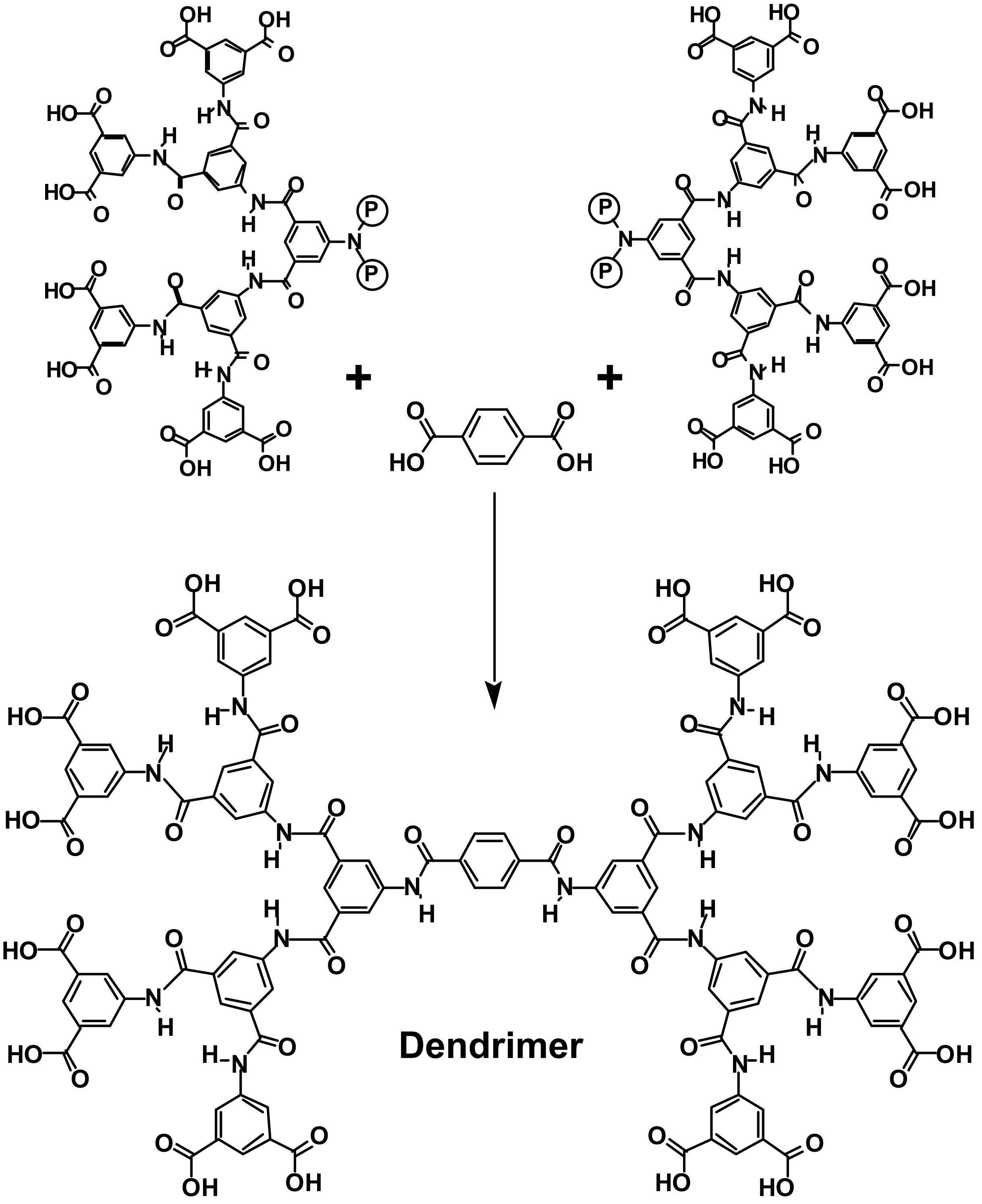
p-aminobenzoic acid



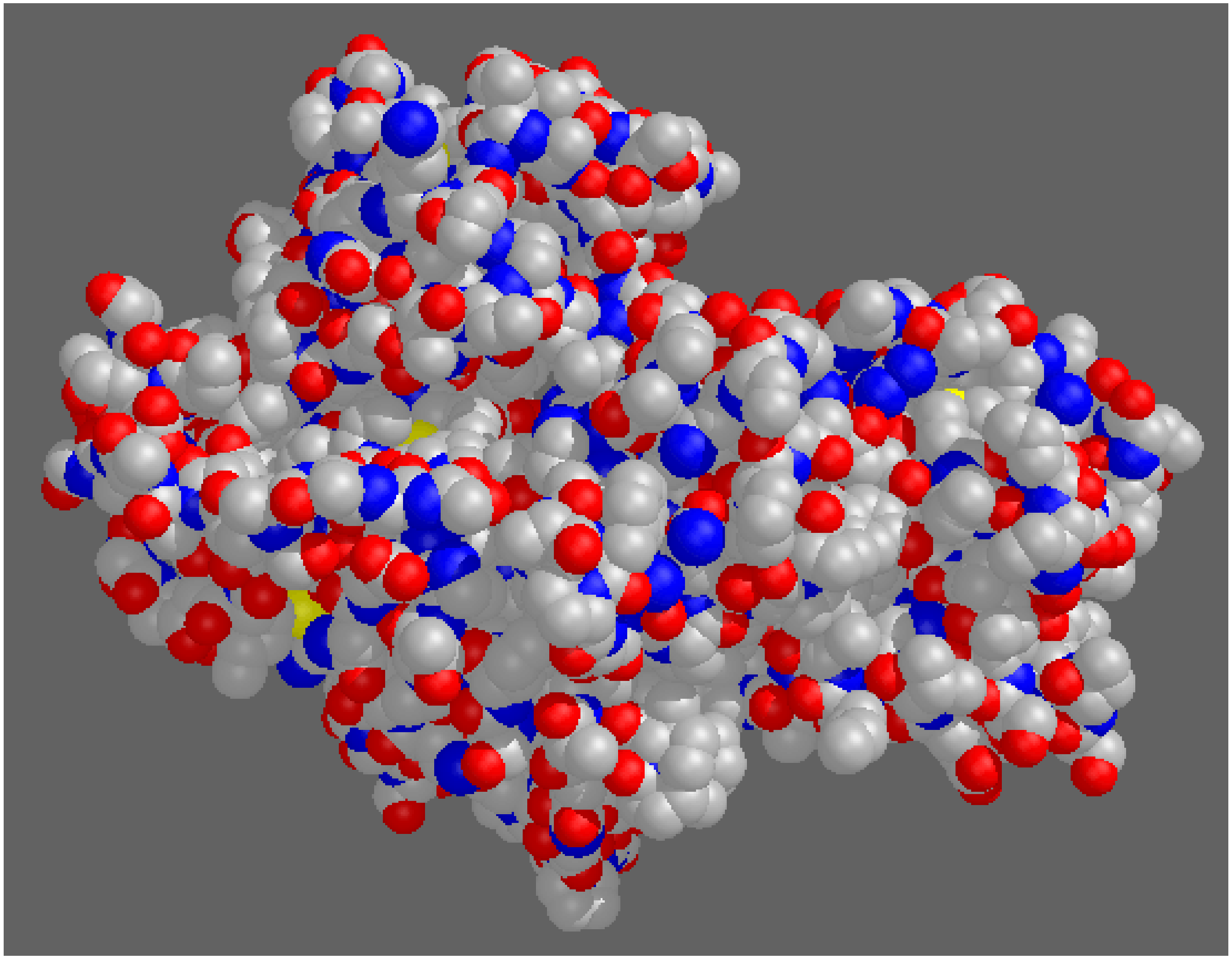
3.2. Branched Homopolymers



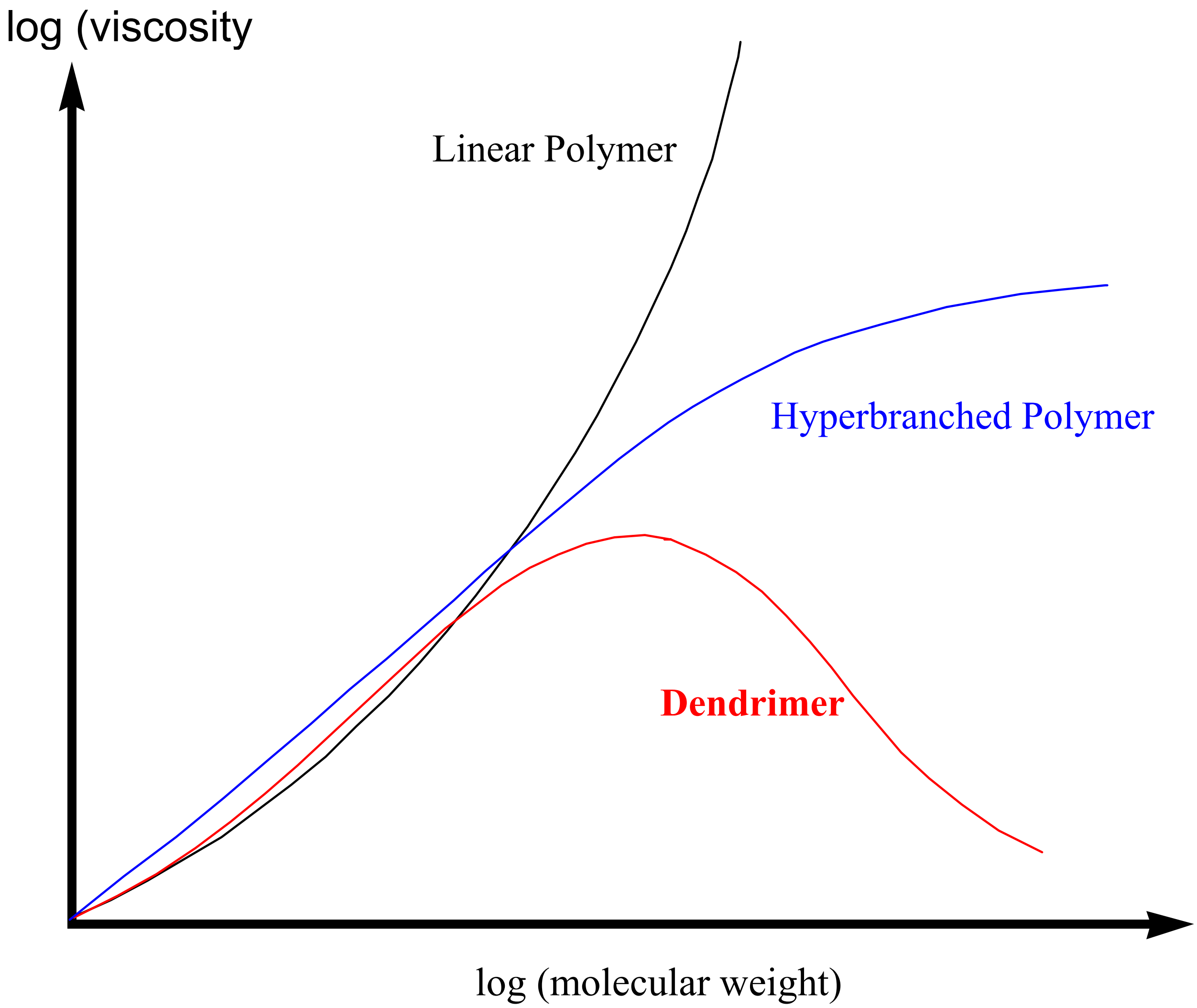




Dendrimer



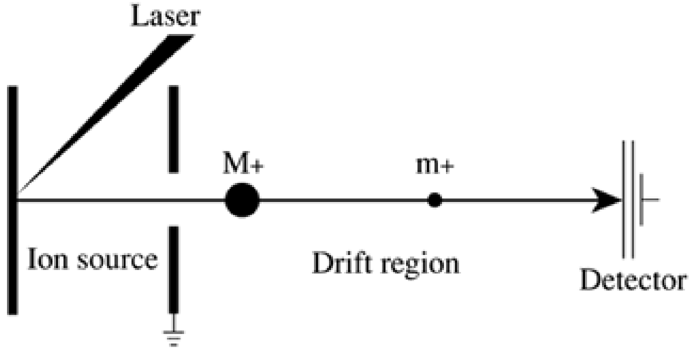
3.2.1. Viscosity versus Polymer Architecture



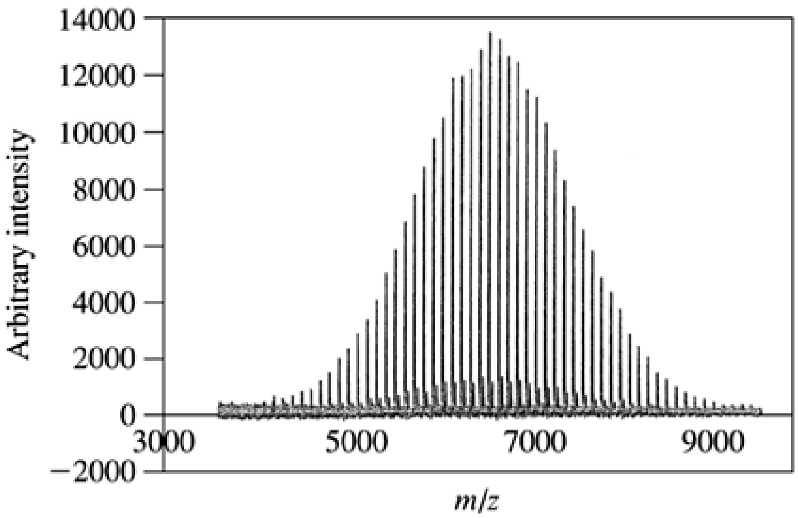
3.3. Characterisation

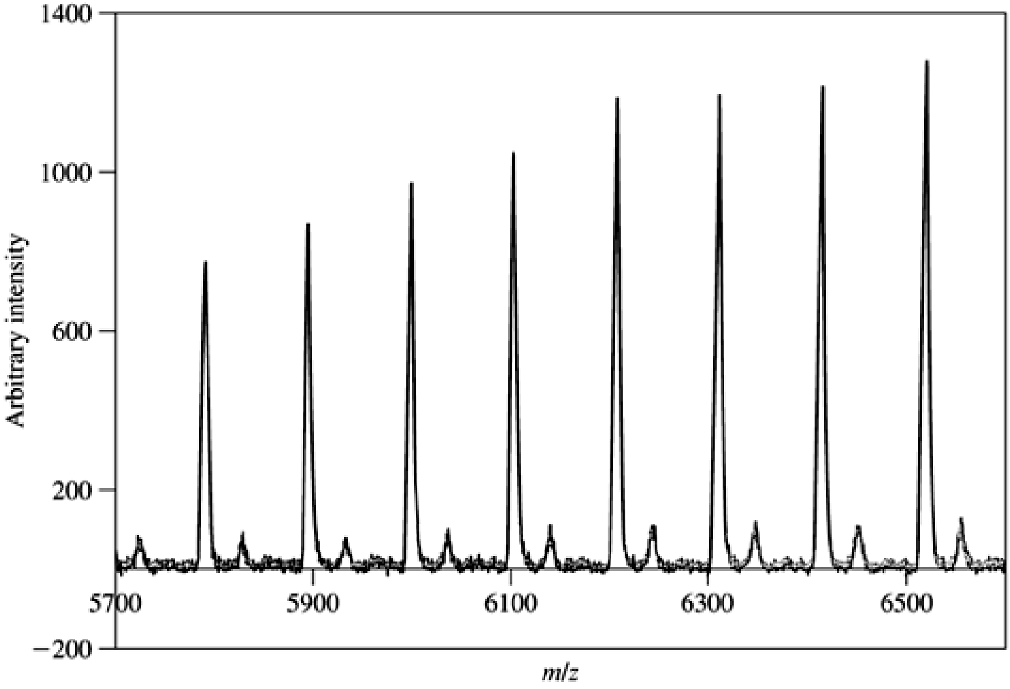
- **NMR spectroscopy**
- **IR spectroscopy**
- **UV spectroscopy**
- **Mass spectrometry**
- **Chromatography**
- **Elemental analysis**

MALDI-tof

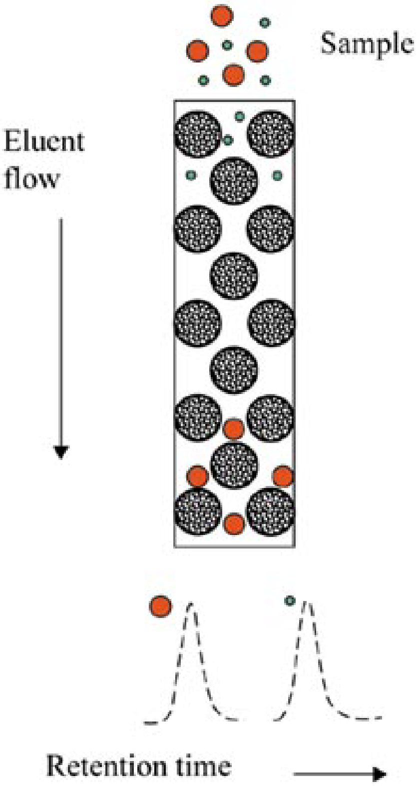


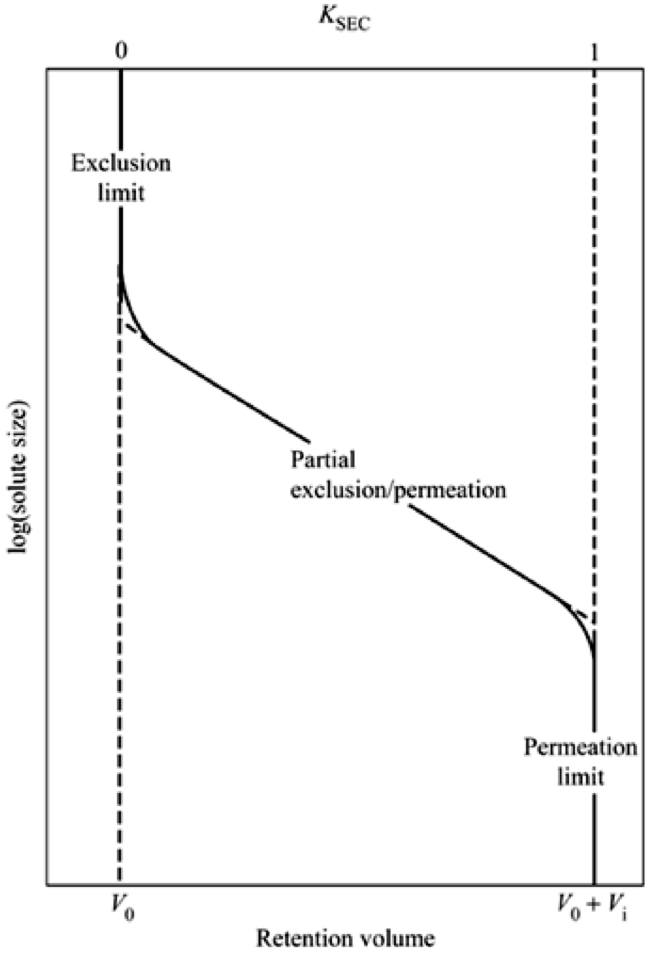
MALDI-tof-ms of polystyrene around 7000 molecular mass. This maldi spectrum was generated using dithranol as the matrix and AgTFA as the salt. The polystyrene, dithranol, and salt were dissolved in tetrahydrofuran. The solution was then electrosprayed onto the sample plate. The polymer analysed in reflectron mode with an extraction voltage of about 25 keV.



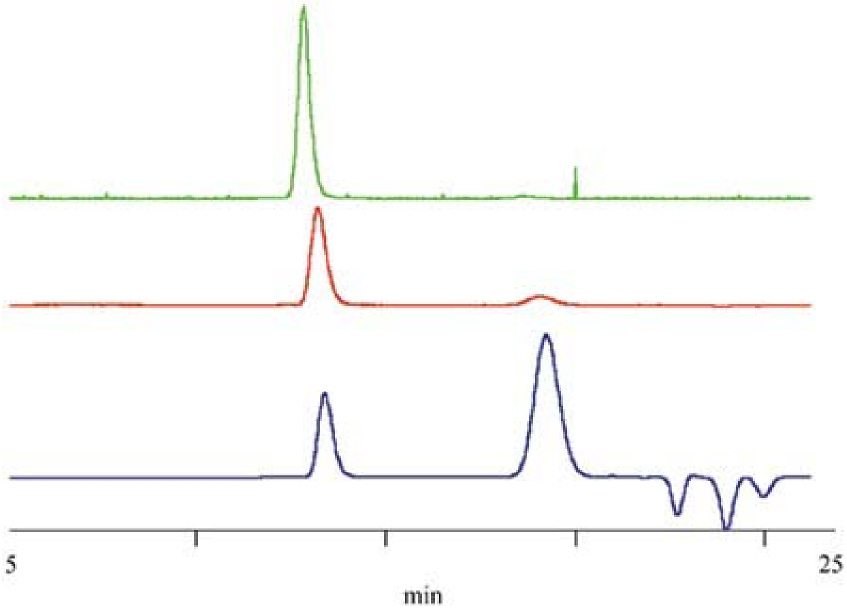


Gel Permeation Chromatography - GPC
(Size Exclusion Chromatography - SEC)

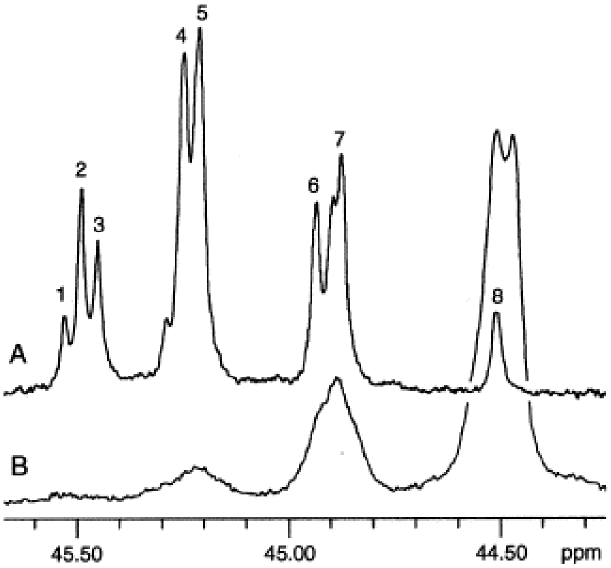




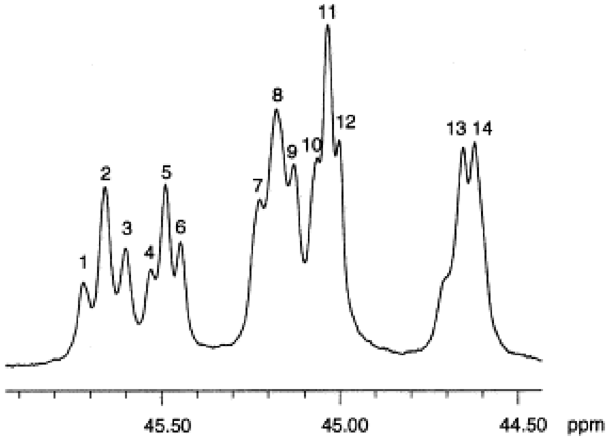
Comparison of detector sensitivity for DRI (bottom), viscosity (middle), and light scattering (top) for two narrow PS standards (M_{peak} 186,000 and 1260). Columns: 2 × PLgel 5 µm MIXED-C 300 × 7.5 mm, eluent: THF, flow rate: 1 mL/min, temperature: 40°C.



NMR spectroscopy



^{13}C NMR spectra of methylene carbon of poly(vinyl alcohol)s measured in DMSO-d_6: (A) S-PVA; (B) I-PVA.

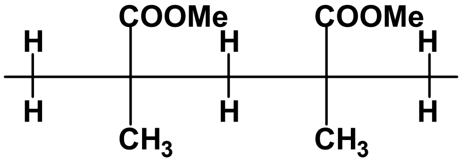


^{13}C NMR spectra of methylene carbon of atactic poly(vinyl alcohol) measured in D_2O.

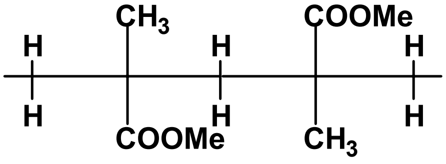
Assignment of methylene carbon spectra of atactic poly(vinyl alcohol) in D_2O at 100°C

Peak no.	Chemical shift (ppm)	Assignment	A-PVA ($r = 0.54$)	
			Observed	Calculated[a]
1	45.72	mrrrm	0.038	0.033
2	45.66	mrrrr	0.070	0.078
3	45.60	rrrrr	0.041	0.046
4	45.53	mrmrm	0.029	0.028
5	45.49	mrmrr + rrmrm	0.059	0.065
6	45.45	rrmrr	0.051	0.038
7	45.23	mmrrm	0.075	0.057
8	45.18	mmrrr + rmrrm	0.118	0.133
9	45.13	rmrrr	0.066	0.076
10	45.07	mmmrm	0.058	0.050
11	45.04	rmmrm + mmmrr	0.107	0.115
12	45.01	rmmrr	0.079	0.066
13	44.56	mmrmm + mmrmr + mmmmm	0.101	0.104
14	44.53	rmrmr + mmmmr + rmmmr	0.109	0.111

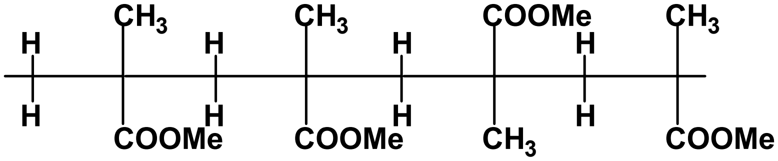
[a] Assuming Bernoullian statistics for P_m=0.46.



isotactic

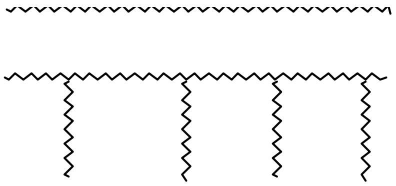


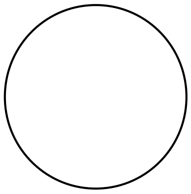
syndiotactic

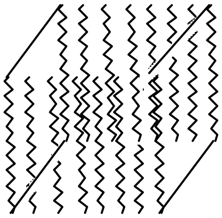


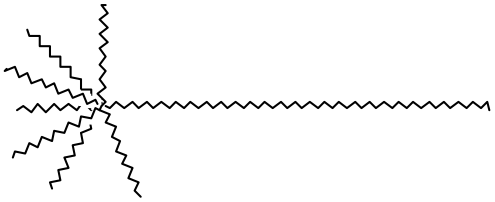
atactic

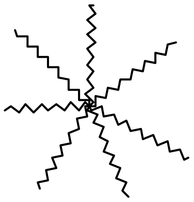
3.4. Homopolymer Architectures

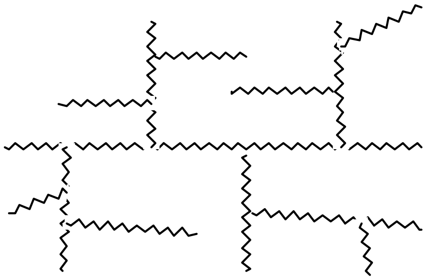


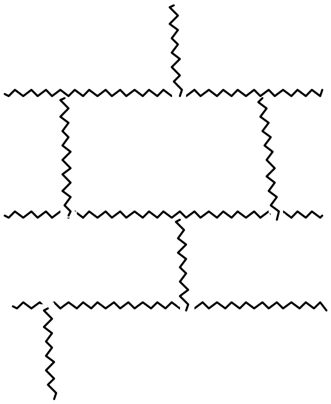


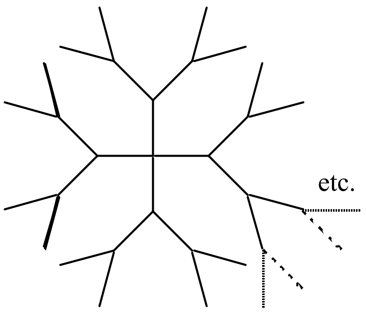




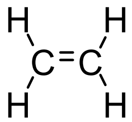


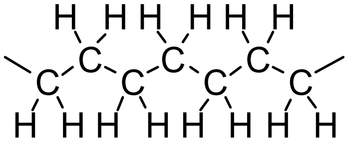


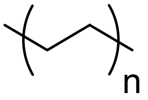


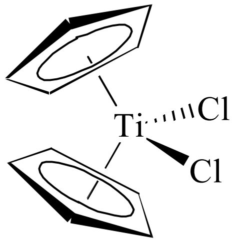


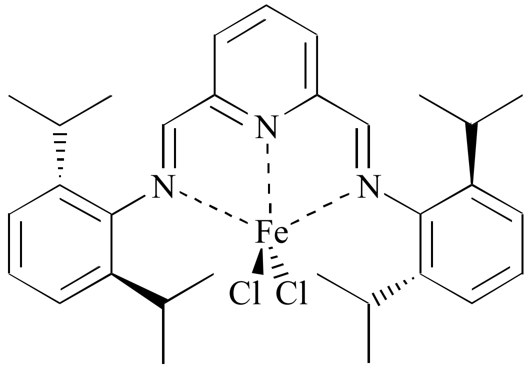
3.5. Ziegler-Natta / Metallocene / Schiff Base Catalysts

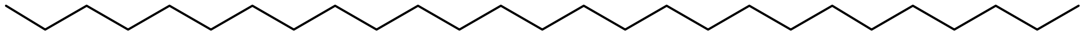


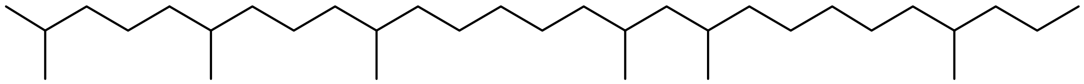


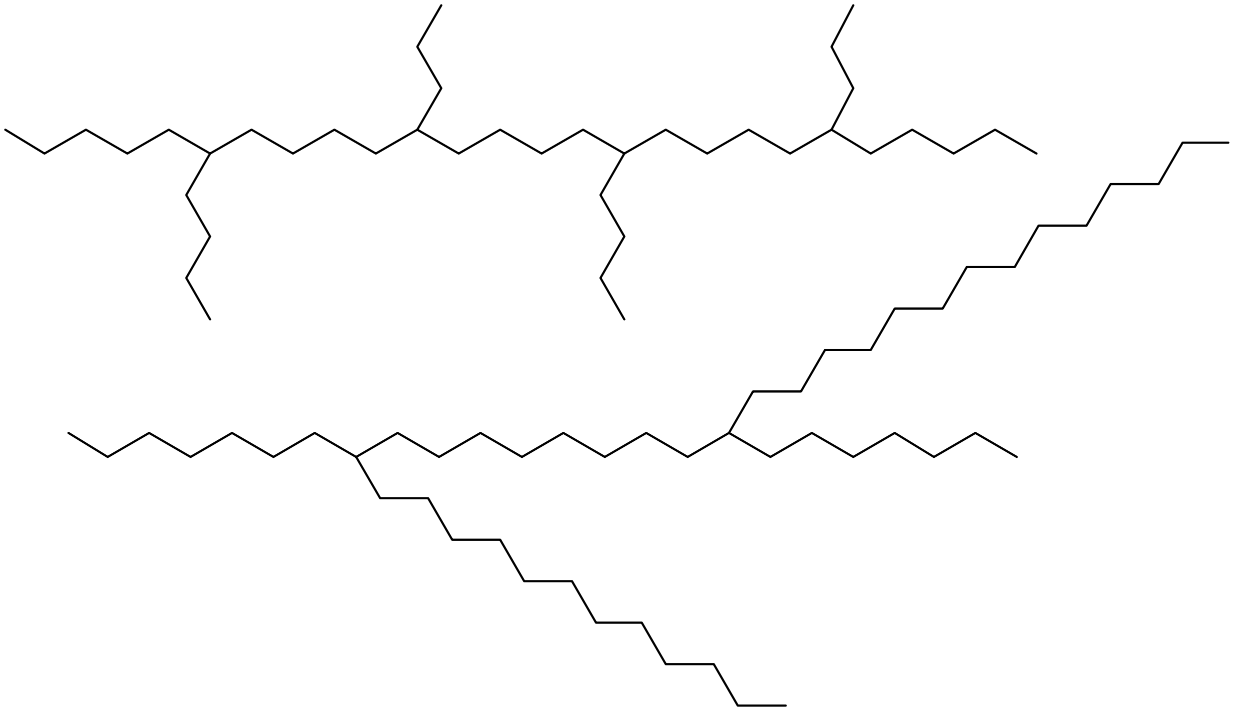












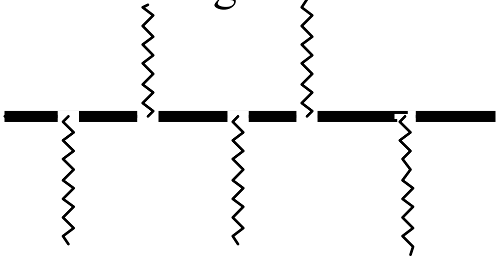
3.6. Copolymer Architectures

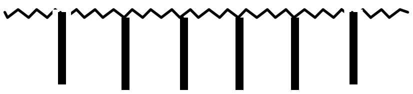
linear

di block

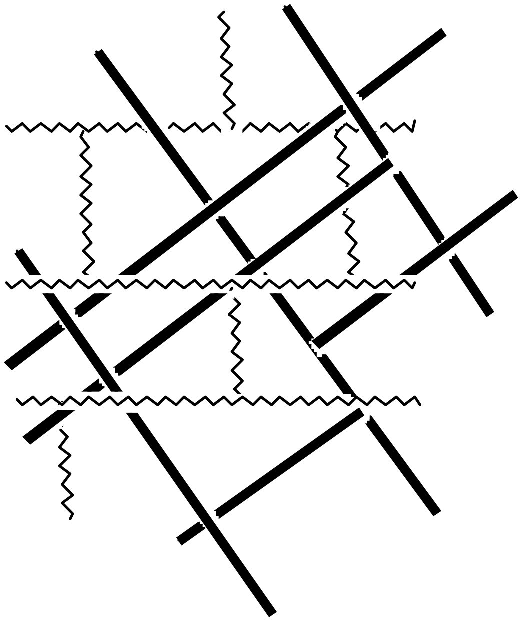
multi block

linear A-graft - linear B



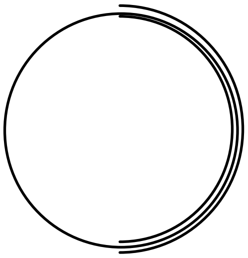


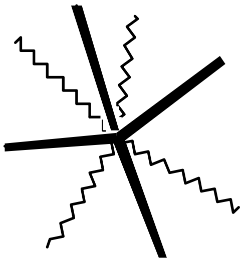
linear B - graft - linear A



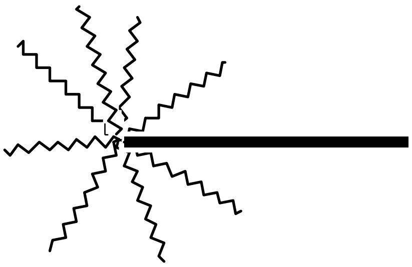
interpenetrating network
of A and B

cyclic di-block

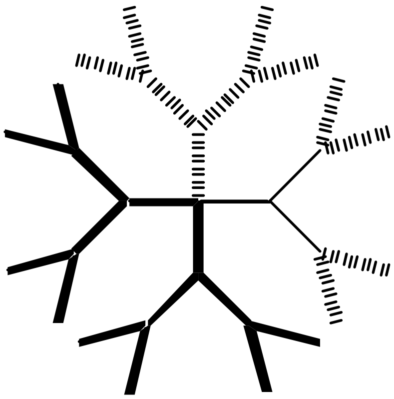




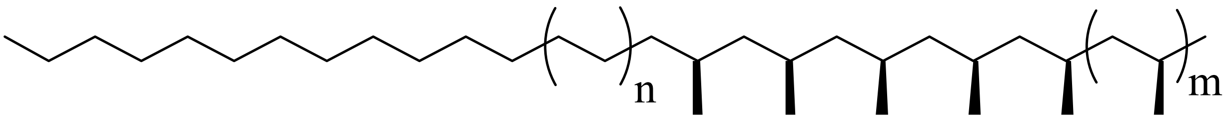
star "di-block"



star B - block- linear A



mixed A + B dendrimer



PE-block-isoPP

4. Polymerisation Techniques

- **Bulk**
- **Solution**
- **Suspension**
- **Emulsion**