Step Polymerization - Outline

1. Understanding kinetics of step polymerization
   - Reactivity of functional groups
   - Polymerization mechanism

2. Controlling molecular weight and polydispersity
   - Stoichiometric imbalance
   - Chain termination („chain stoppers")

3. Copolymerization

4. Industrial step polymerization

Step Polymerization

Condensation Polymers

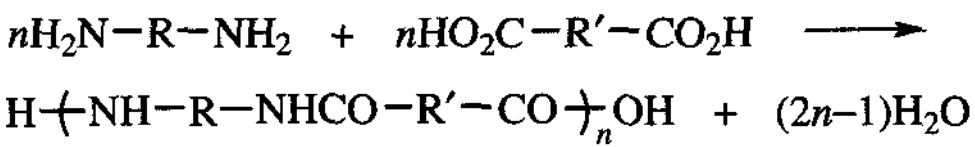
Ring-opening polymerization

Step polymerization

Chemistry : esterification, amidation, urethane formation, aromatic substitution etc.

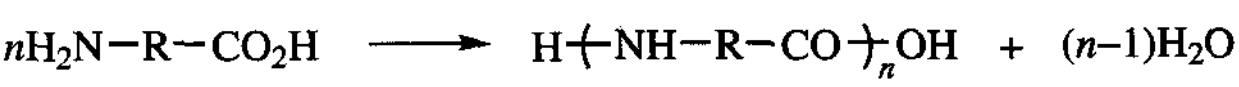
Two strategies:

1. Reaction of two different bifunctional/polyfunctional monomers:



or, more general: n A-A + n B-B → -(-A-AB-B-)$_n$-

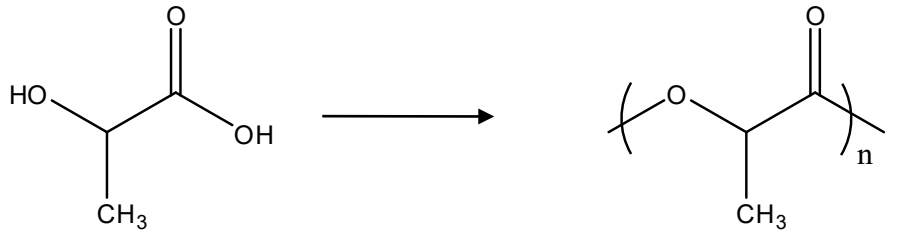
2. Polymerization of a single monomer:



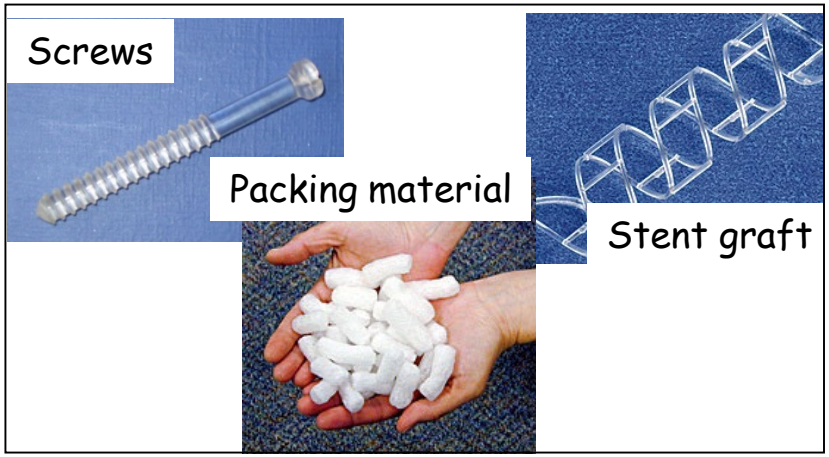
general: n A-B → -(-AB-)$_n$-

Example: Synthesis of Poly(Lactic acid)

High molecular weight poly(lactic acid) (PLA) can be synthesized by step polymerization of lactic acid. PLA has good mechanical properties and can be processed into products such as cups, films and fibers, which can be used as compostable materials. PLA is also widely used for biomaterials applications



Further, recommended reading:
M. Ajioka, K. Enomoto, K. Suzuki, A. Yamaguchi, *J. Environm. Polym. Degrad.* **1995**, *3*, 225



An understanding of the polymerization mechanism and kinetics is important to control the properties of PLA

How does the polymer molecular weight change with the reaction time ?

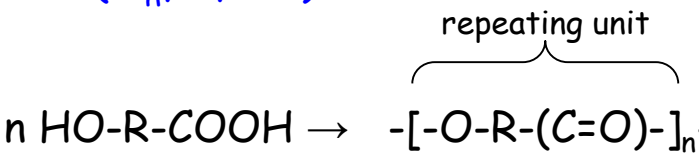
Some Definitions

- **Conversion (p)** The conversion is defined as: $p = \frac{[M]_0 - [M]}{[M]_0}$

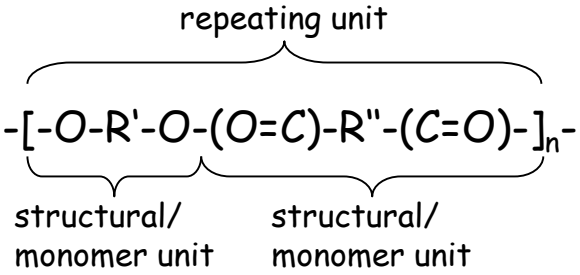
$[M]$, $[M]_0$: concentration of reacting groups, i.e. the concentration of OH or COOH groups during polyester synthesis

- **Number-average degree of polymerization ($\overline{X}_n$, $\overline{P}$, $\overline{DP}$)**

1. The AB case:



2. The AA + BB case:



$\overline{X}_n$, $\overline{P}$, $\overline{DP}$ =
Total number of molecules initially present/total number of molecules present at time t = Average number of repeat units per chain (AB polymerization) or the average number of structural units per chain (AA + BB polymerization):

$$\overline{X}_n = \frac{N_0}{N} = \frac{[M]_0}{[M]}$$

$$[M] = [M]_0 - [M]_0 p = [M]_0(1-p)$$

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

Carothers equation

Assumption: equimolar quantities of reacting groups A and B

- Number-average molecular weight (M_n):
  Total weight of a polymer sample/the total number of moles in it:

$$\overline{M}_n = M_o\overline{X}_n + M_{eg} = \frac{M_o}{(1-p)} + M_{eg}$$

M_0 = molecular weight of the repeat unit (AB) or mean molecular weight of the structural units (AA + BB)

M_{eg} = end group molecular weight

Example:

$HO_2C(CH_2)_4CO_2H + HOCH_2CH_2OH \rightarrow -(-OCH_2CH_2OCO(CH_2)_4CO-)_n-$

M = 146 M = 62 M_0 = 86, M_{eg} = 18

$$\left[M_0 = \frac{146 + 62}{2} - 18 = 86 \right]$$

Already at modest molecular weights, i.e. reasonable conversion, the contribution of M_{eg} becomes neglible and

$$\overline{M}_n = M_o\overline{X}_n = \frac{M_o}{(1-p)}$$

Step Polymerization Kinetics

Reactivity of Functional Groups

- SP proceeds by a slow increase in MW
- Monomer disappears early in the reaction, far before the production of any high MW polymer
- The rate of a SP is the sum of the rates of reaction between molecules of different sizes

monomer + monomer	→	dimer
dimer + monomer	→	trimer
dimer + dimer	→	tetramer
trimer + monomer	→	tetramer
trimer + dimer	→	pentamer
trimer + trimer	→	hexamer
in general terms:		
n-mer + *m*-mer	→	(*n* + *m*)-mer

To simplify kinetic analysis, assume that:

a) the reactivities of both functional groups of a bifunctional monomer are the same
b) the reactivity of one functional group of a bifunctional reactant is the same irrespective of whether the other functional group has reacted
c) the reactivity of a functional group is independent of the size of the molecule to which it is attached (i.e. independent of *n* and *m*)

Concept of equal reactivity of functional groups

Are these Assumptions Valid?

Generally, yes!

TABLE 2-1 Rate Constants for Esterification (25°C) in Homologous Compounds[a,b]

Molecular Size (x)	$k \times 10^4$ for $H(CH_2)_xCO_2H$	$k \times 10^4$ for $(CH_2)_x(CO_2H)_2$
1	22.1	
2	15.3	6.0
3	7.5	8.7
4	7.5	8.4
5	7.4	7.8
6		7.3
8	7.5	
9	7.4	
11	7.6	
13	7.5	
15	7.7	
17	7.7	

[a] Rate constants are in units of L mol^{-1} s^{-1}.
[b] Data from Bhide and Sudborough [1925].

(alcohol = ethanol)

TABLE 2-2 Rate Constants for Polyesterification (26.9°C) of Sebacoyl Chloride with α,ω-Alkane Diols in Dioxane[a,b]

Molecular Size (x)	$k \times 10^3$ for $HO(CH_2)_xOH$
5	0.60
6	0.63
7	0.65
8	0.62
9	0.65
10	0.62

[a] Rate constants are in units of L mol^{-1} s^{-1}.
[b] Data from Ueberreiter and Engel [1977].

Sebacoyl chloride:

$ClCO(CH_2)_8COCl$

Does this make Sense?

Yes!

The observed reactivity of a functional group depends on the collision frequency of that group and not on the diffusion rate of the whole molecule.

A terminal functional group attached to a growing polymer chain has a much greater mobility than would be expected from the mobility of the polymer molecule as a whole. The collision rate of such a functional group will be about the same as for small molecules.

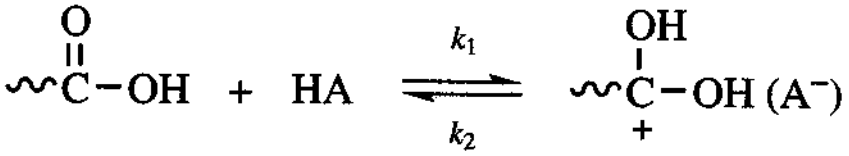
Reaction in step polymerization only occurs 1 out of ~ 10^{13} collisions, and this time interval is usually sufficient to maintain the equilibrium concentration of collision pairs of functional groups.

Exceptions can occur when the reactivities of the groups are very high and/or the molecular weights of the polymers are very high. In this case, the polymerization becomes diffusion-controlled because mobility is too low to allow maintenance of the equilibrium concentration of reactive pairs and of their collision frequencies.

Kinetics of Step Polymerization

Polyesterification:

Mechanism:



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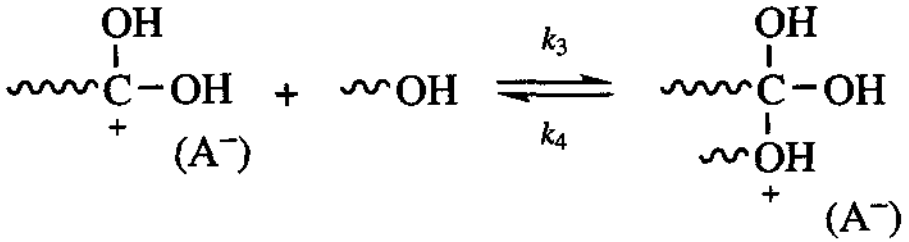
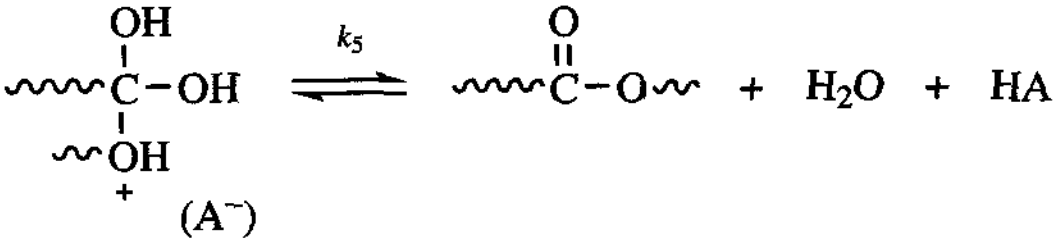


II



To obtain high molecular weight polymer, reactions are carried out to shift the equilibrium towards polymer formation; removal of water from the reaction mixture

Under the usual conditions, k_4 is vanishing small and k_1, k_2, and $k_5 > k_3$ and the rate of polymerization (R) is given by:

$$R = \frac{-d[\mathrm{COOH}]}{dt} = k_3[\overset{+}{\mathrm{C}}(\mathrm{OH})_2][\mathrm{OH}]$$

$$K = \frac{k_1}{k_2} = \frac{[\overset{+}{\mathrm{C}}(\mathrm{OH})_2]}{[\mathrm{COOH}][\mathrm{HA}]}$$

$$\frac{-d[\mathrm{COOH}]}{dt} = k_3 K[\mathrm{COOH}][\mathrm{OH}][\mathrm{HA}]$$

Polyesterification can be carried out both with and without the addition of an acid catalyst, which leads to two different kinetic situations.

I. Self-Catalyzed Polymerization

- The diacid acts as its own catalyst and [*HA*] is replaced by [*COOH*]

$$\frac{-d[\mathrm{COOH}]}{dt} = k_3 K[\mathrm{COOH}][\mathrm{OH}][\mathrm{HA}] \longrightarrow \frac{-d[\mathrm{COOH}]}{dt} = k[\mathrm{COOH}]^2[\mathrm{OH}] \qquad \text{with } k = k_3 K$$

- Most polymerizations are carried out under stoichiometric conditions, with [*COOH*] = [*HA*] = [M]

$$\frac{-d[\mathrm{M}]}{dt} = k[\mathrm{M}]^3 \qquad \frac{-d[\mathrm{M}]}{[\mathrm{M}]^3} = k\,dt$$

- Integration from t = 0 to t yields:

$$2kt = \frac{1}{[\mathrm{M}]^2} - \frac{1}{[\mathrm{M}]_0^2}$$

- The extent, or fraction of reaction, or extent or fraction of conversion p is defined as:

$$[\mathrm{M}] = [\mathrm{M}]_0 - [\mathrm{M}]_0 p = [\mathrm{M}]_0(1-p)$$

- Combination with the previous equation:

$$\frac{1}{(1-p)^2} = 2[\mathrm{M}]_0^2 kt + 1$$

Experimental Observations

$$\frac{1}{(1-p)^2} = 2[\mathrm{M}]_0^2 kt + 1$$

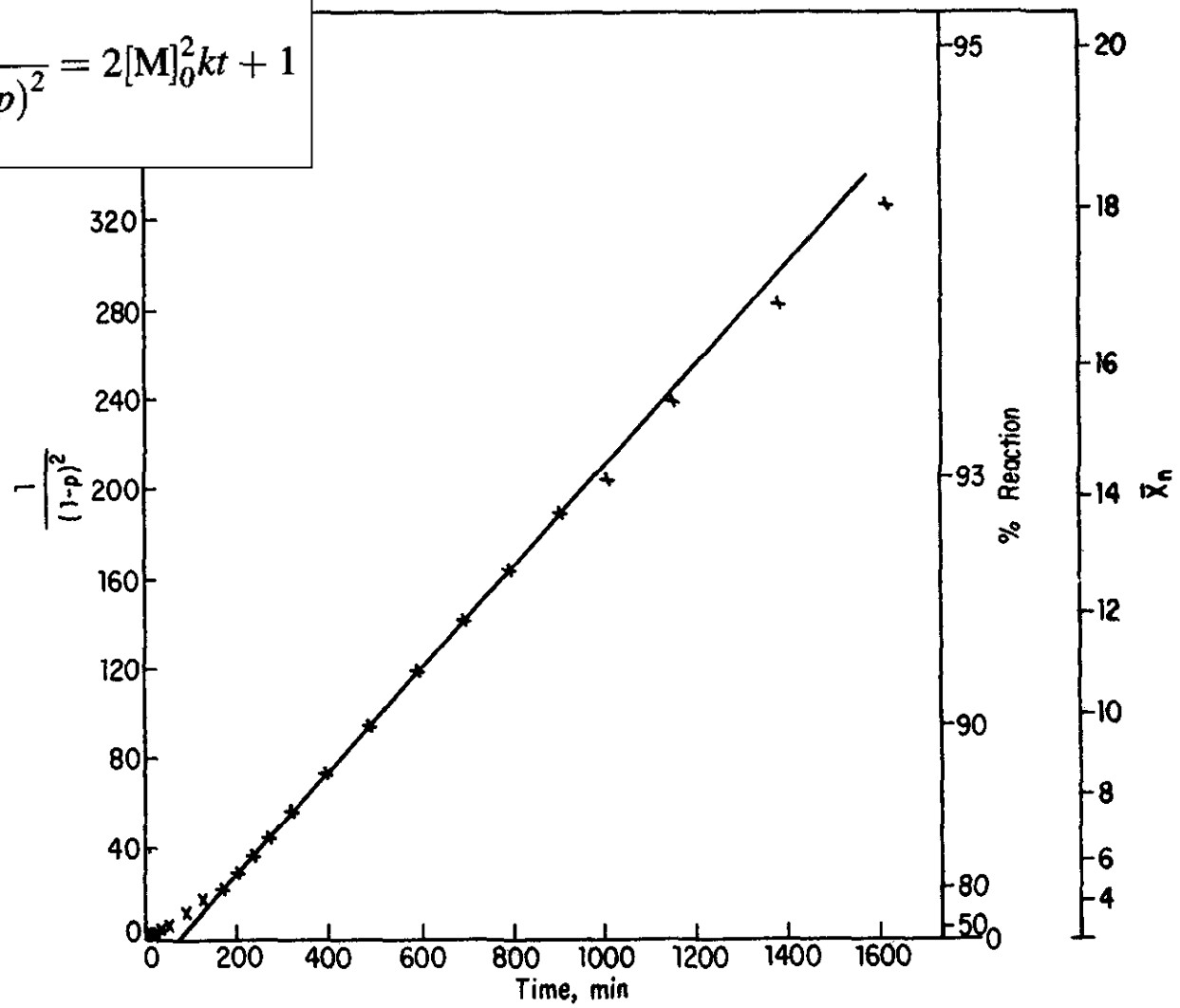


Fig. 2-1 Third-order plot of the self-catalyzed polyesterification of adipic acid with diethylene glycol at 166°C. After Solomon [1967] by permission of Marcel Dekker, New York) from the data of Flory [1939] (by permission of American Chemical Society, Washington, DC).

Evolution of Degree of Polymerization

Number-average degree of polymerization ($\overline{X}_n$, $\overline{P}$, $\overline{DP}$):

$$\overline{X}_n = \frac{N_0}{N} = \frac{[M]_0}{[M]}$$

$$[M] = [M]_0 - [M]_0 p = [M]_0(1-p)$$

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

Carothers equation

See slide 5

For a self-catalyzed step polymerization, this becomes:

$$\frac{1}{(1-p)^2} = 2[M]_0^2 kt + 1$$

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

$$\overline{X}_n^2 = 1 + 2[M]_0^2 kt$$

$\Rightarrow$ Slow increase in degree of polymerization with reaction time

II. External Catalyzed Polymerization

$$\frac{-d[\mathrm{COOH}]}{dt} = k_3 K[\mathrm{COOH}][\mathrm{OH}][\mathrm{HA}]$$

- With external added acid (e.g. sulfuric acid or p-toluene sulfonic acid), [HA] is the concentration of the catalyst, which remains constant throughout the reaction
- Stoichiometric amounts of diol and diacid

$$\frac{-d[\mathrm{M}]}{dt} = k'[\mathrm{M}]^2 \qquad \text{with } k' = k_3 K[\mathrm{HA}]$$

Integration yields:

$$k't = \frac{1}{[\mathrm{M}]} - \frac{1}{[\mathrm{M}]_0} \quad \Rightarrow \quad [\mathrm{M}]_0 k't = \frac{1}{(1-p)} - 1 \quad \text{and} \quad \overline{X}_n = 1 + [\mathrm{M}]_0 k't$$

- Much greater increase in X_n with time compared to uncatalyzed process!
- Polymerization versus small molecule reactions: importance of high conversion!

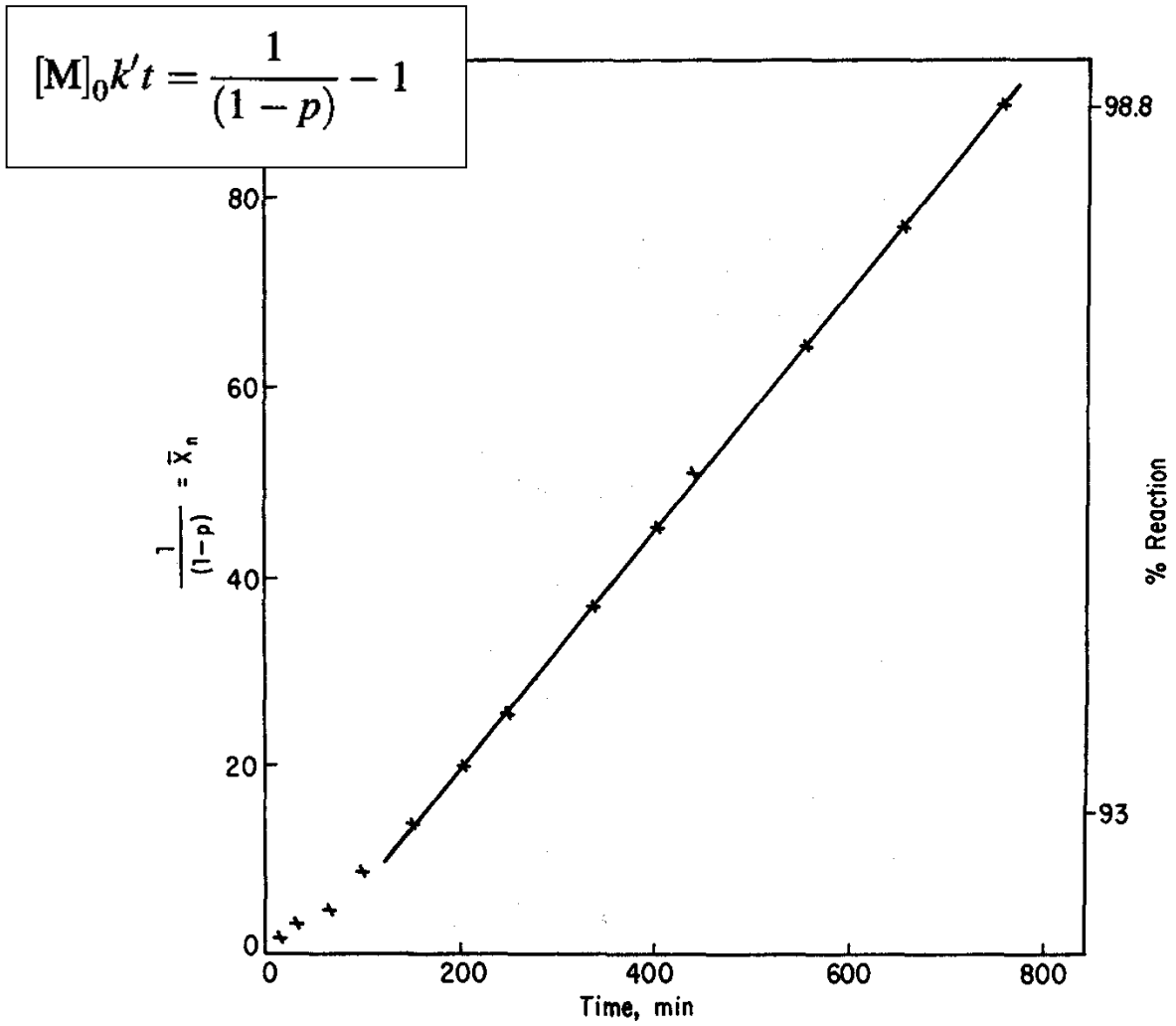


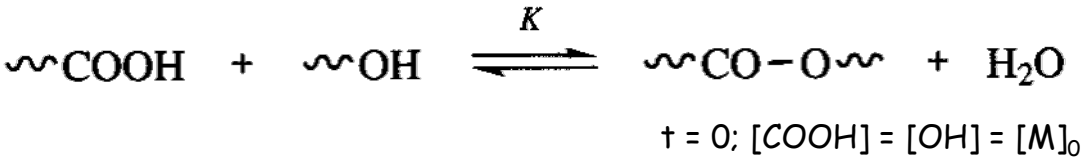
Fig. 2-2 Polyesterification of adipic acid with diethylene glycol at 109°C catalyzed by 0.4 mol% *p*-toluenesulfonic acid. After Solomon [1967] (by permission of Marcel Dekker, New York) from the data of Flory [1939] (by permission of American Chemical Society, Washington, DC).

Equilibrium Considerations

Most step polymerizations involve equilibrium reactions

Case I.: Closed system: none of the products of the forward reaction are removed

External catalyzed polyesterification:



t = 0; [COOH] = [OH] = $[M]_0$

$$K = \frac{[COO][H_2O]}{[COOH][OH]} = \frac{(p_e[M]_0)^2}{([M]_0 - p_e[M]_0)^2} = \frac{p_e^2}{(1-p_e)^2} \Rightarrow p_e = \frac{K^{1/2}}{1+K^{1/2}}$$

$$\bar{X}_n = \frac{1}{(1-p)}$$

$$\bar{X}_n = 1 + K^{1/2}$$

TABLE 2-5 Effect of Equilibrium Constant on Extent of Reaction and Degree of Polymerization in Closed System

Equilibrium Constant (K)	p	$\bar{X}_n$
0.001	0.0099	1.01
0.01	0.0909	1.10
1	0.500	2
16	0.800	5
81	0.900	10
361	0.950	20
2,401	0.980	50
9,801	0.990	100
39,601	0.995	200
249,001	0.998	500

Typical values for K:

- Polyesterification; K = 1 – 10
- Transesterification; K = 0.1 – 1
- Polyamidation; $K = 10^2 - 10^3$

Case II.: Open, driven system: at least one of the products of the forward reaction is removed to drive the equilibrium to high molecular weights

TABLE 2-6 Effect of Water Concentration on Degree of Polymerization in Open, Driven System

K	$\bar{X}_n$	$[H_2O]^a$ (mol L^{-1})
0.1	1.32[b]	1.18[b]
	20	1.32×10^{-3}
	50	2.04×10^{-4}
	100	5.05×10^{-5}
	200	1.26×10^{-5}
	500	2.00×10^{-6}
1	2[b]	2.50[b]
	20	1.32×10^{-2}
	50	2.04×10^{-3}
	100	5.05×10^{-4}
	200	1.26×10^{-4}
	500	2.01×10^{-5}
16	5[b]	4.00[b]
	20	0.211
	50	3.27×10^{-2}
	100	8.10×10^{-3}
	200	2.01×10^{-3}
	500	3.21×10^{-4}
81	10[b]	4.50[b]
	20	1.07
	50	0.166
	100	4.09×10^{-2}
	200	1.02×10^{-2}
	500	1.63×10^{-3}
361	20[b]	4.75[b]
	50	0.735
	100	0.183
	200	4.54×10^{-2}
	500	7.25×10^{-3}

[a] $[H_2O]$ values are for $[M]_0 = 5$.
[b] These values are for a closed reaction system at equilibrium.

$$K = \frac{[COO][H_2O]}{[COOH][OH]} = \frac{p_e\,[M]_0\,[H_2O]}{([M]_0 - p_e[M]_0)^2}$$

$$K = \frac{p[H_2O]}{[M]_0(1-p)^2}$$

$$\bar{X}_n = \frac{1}{(1-p)}$$

$$K = \frac{p[H_2O]\bar{X}_n^2}{[M]_0}$$

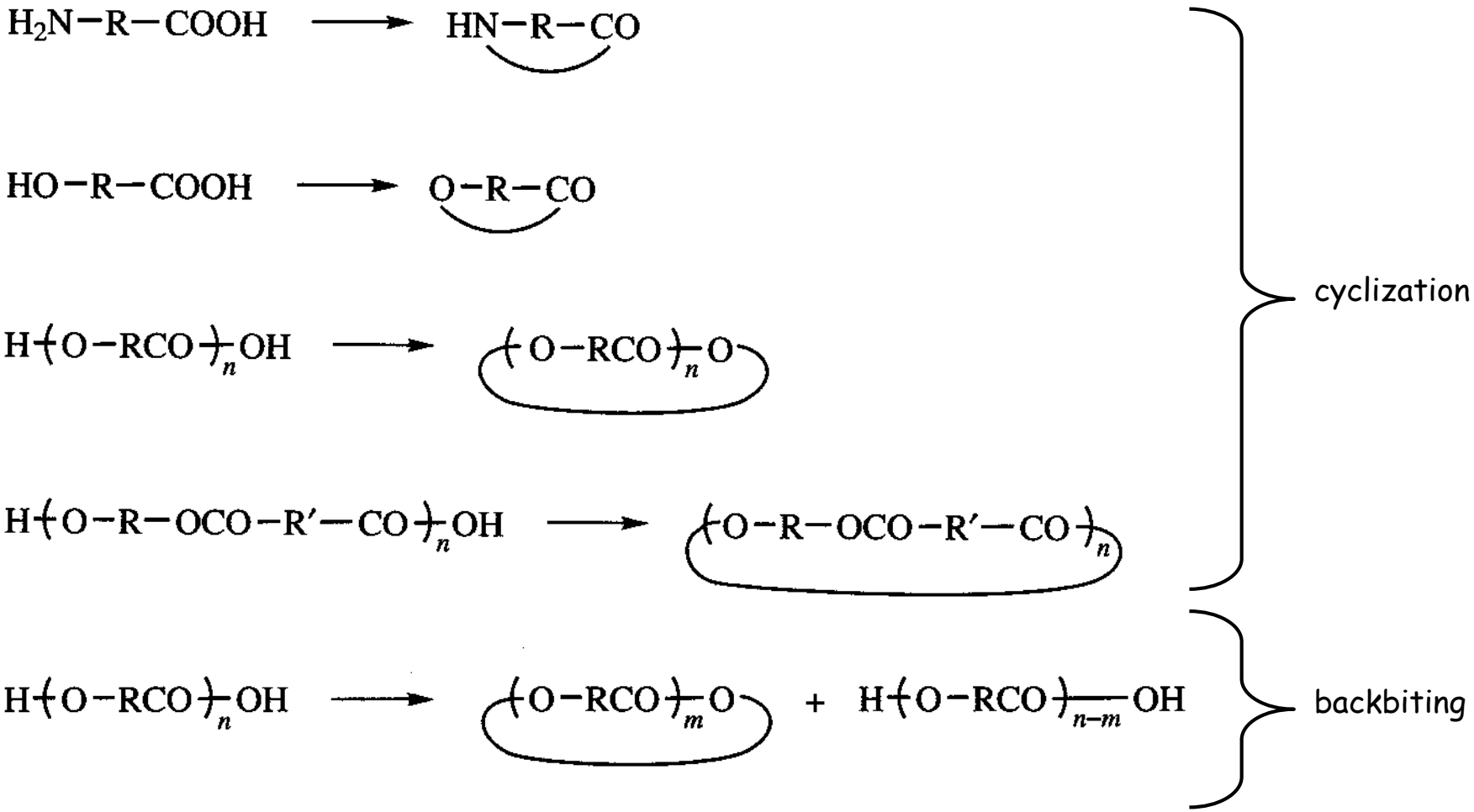
$$\bar{X}_n = \frac{1}{(1-p)}$$

$$[H_2O] = \frac{K[M]_0}{\bar{X}_n(\bar{X}_n - 1)}$$

The ultimate goal in a polyesterification is not necessarily to remove as much H_2O as possible, but to control $[H_2O]$ in order to obtain the desired degree of polymerization!!

Cyclization versus Linear Polymerization

Cyclization competes with polymerization



Cyclization: Thermodynamic stability of rings

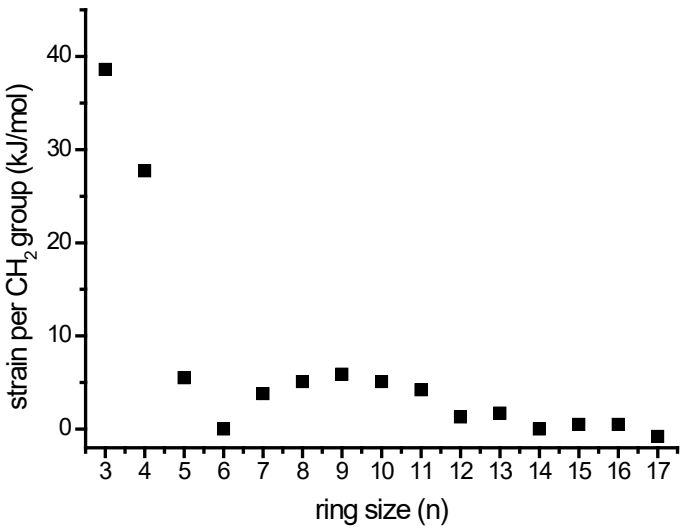
Thermodynamic stability of cycloalkanes

n = 3, 4 << 5,7 – 13 < 6, 14 and larger

TABLE 2-7 Heats of Combustion and Strains of Cycloalkanes per Methylene Group[a]

$(CH_2)_n$	Heat of Combustion per Methylene Group (kJ mol^{-1})	Strain per Methylene Group[b] (kJ mol^{-1})
3	697.6	38.6
4	686.7	27.7
5	664.5	5.5
6	659.0	0.0
7	662.8	3.8
8	664.1	5.1
9	664.9	5.9
10	664.1	5.1
11	663.2	4.2
12	660.3	1.3
13	660.7	1.7
14	659.0	0.0
15	659.5	0.5
16	659.5	0.5
17	658.2	−0.8
n-Alkane	659.0	0.0

[a] Data from Eliel [1962].
[b] Calculated as the heat of combustion per methylene group minus the value (659.0) for the *n*-alkane methylene group.



Ring strain:

1) Angle strain (n < 5): bond angle distortion
2) Conformational strain:
   (a) torsional strain (n = 5, 7): eclipsed conformations
   (b) transannular strain (n ≥ 8)

Eclipsed Conformations and Gauche Interactions

Conformational analysis of ethane

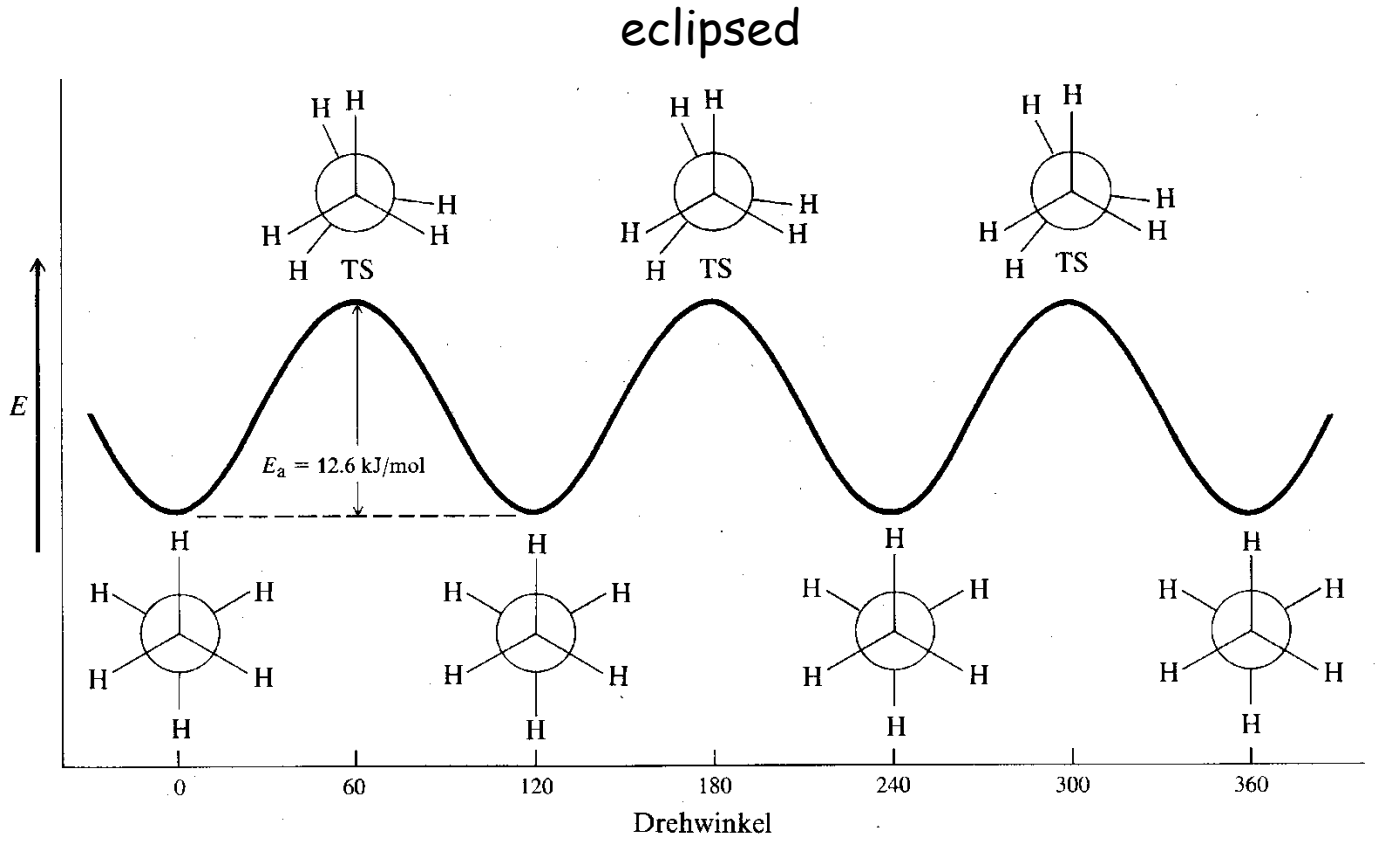


Abb. 2-8 Diagramm der potentiellen Energie der Rotationsisomere des Ethans; TS = Übergangszustand (engl. *transition state*).

Conformational analysis of butane

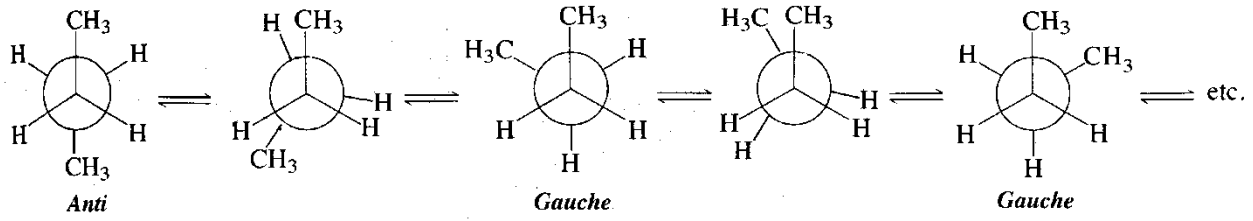


Abb. 2-11 Verschiedene Newman-Projektionen des Butans. Der hintere Kohlenstoff der C-2—C-3-Bindung wird beim Übergang von einer Projektion zur nächsten im Uhrzeigersinn gedreht.

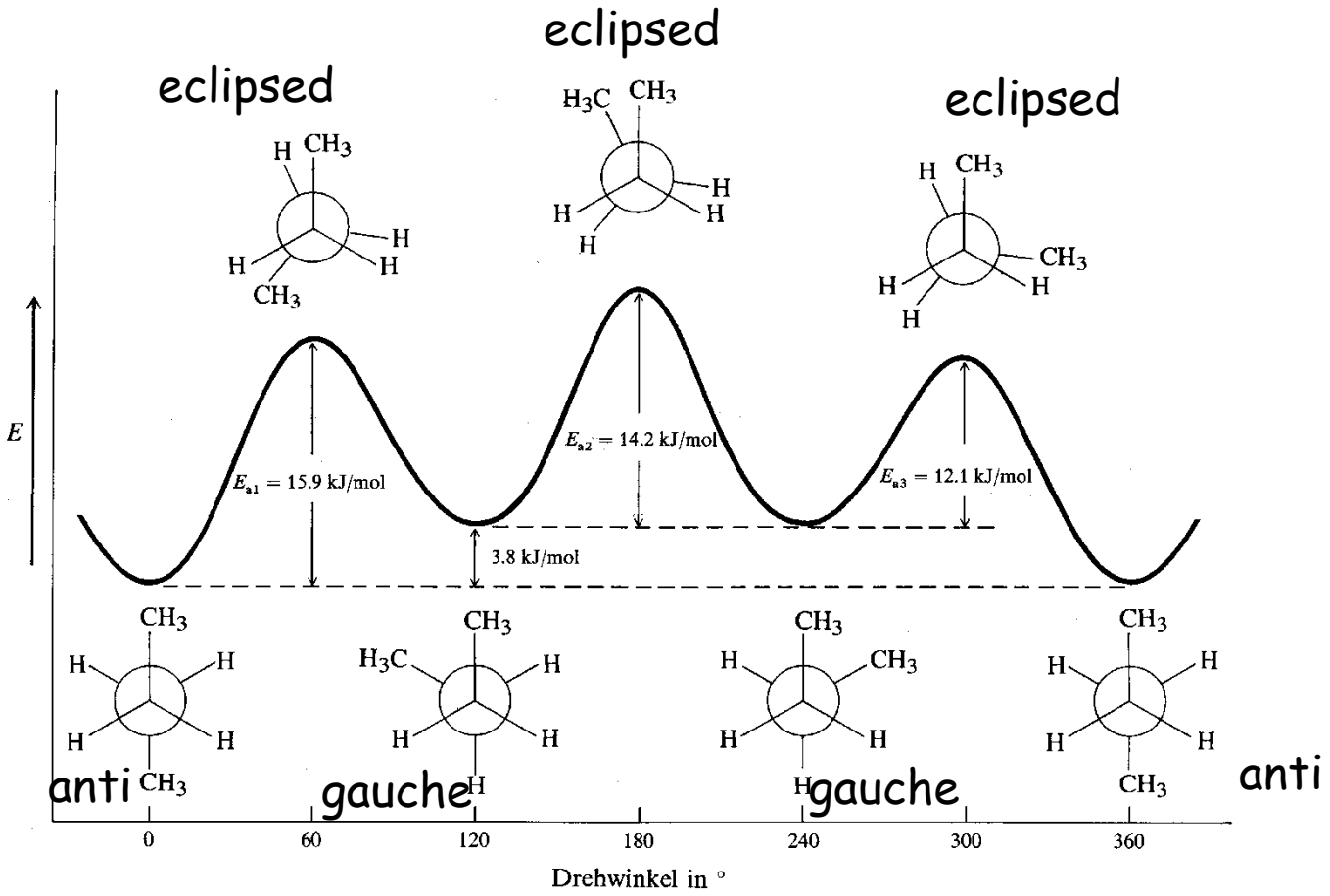
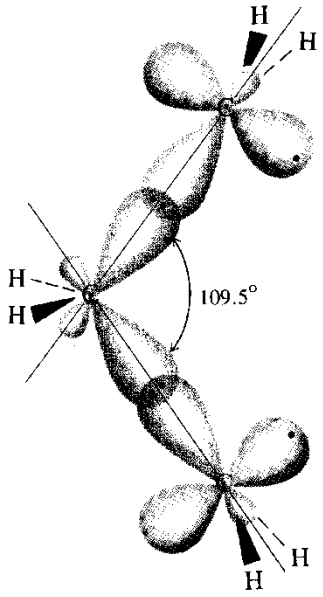


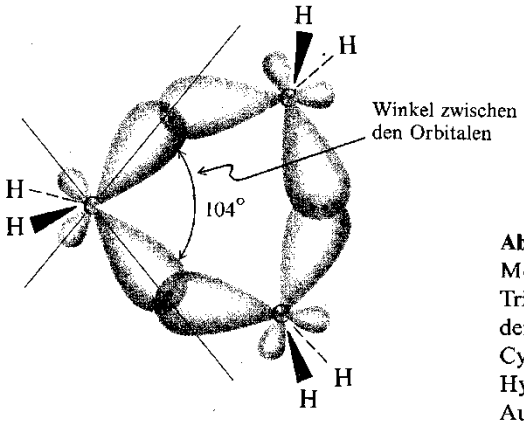
Abb. 2-12 Diagramm der potentiellen Energie im Butan während der Drehung um die C-2—C-3-Bindung. Es gibt drei Prozesse: die *anti* ⟶ *gauche*-Umlagerung (E_{a1} = 15.9 kJ/mol), die *gauche* ⟶ *gauche*-Umlagerung (E_{a2} = 15.1 kJ/mol) und die *gauche* ⟶ *anti*-Umlagerung (E_{a3} = 12.1 kJ/mol).

Cyclopropane

Angle strain

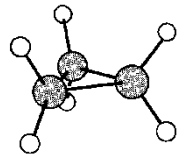


A



B

Abb. 4-2 Darstellung der Molekülorbitale (A) des Trimethylen-Diradikals und (B) der gebogenen Bindungen im Cyclopropan. Es sind nur die Hybridorbitale, die an der Ausbildung von C–C-Bindungen beteiligt sind, eingezeichnet. Beachten Sie den Winkel von 104° zwischen den Orbitalen des Cyclopropans.



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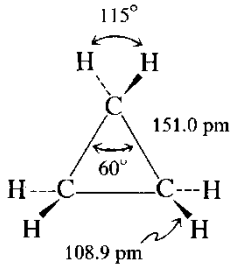
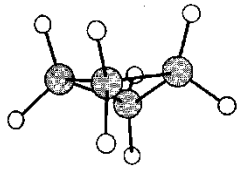


B

Abb. 4-1 Cyclopropan:
(A) Molekülmodell;
(B) Bindungslängen und -winkel.

Cyclobutane



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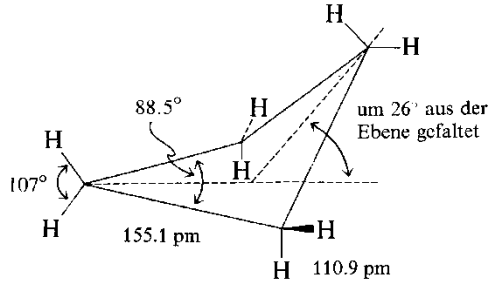
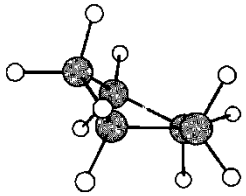
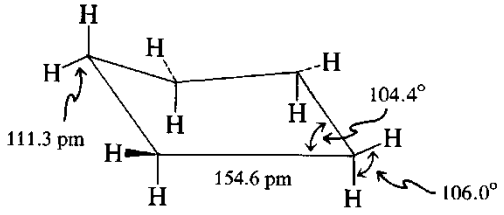


B

Cyclopentane



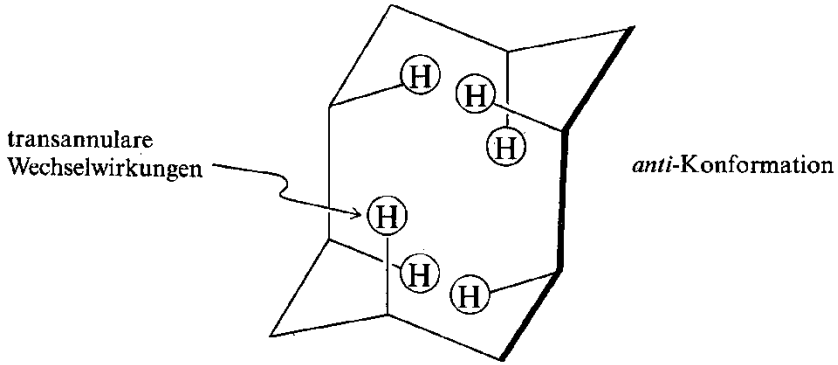
A



B

Conformation is a compromise between angle strain and eclipsed interactions

Cyclododecane



Cyclodecan

Cyclization: Kinetic feasibility

The probability of two functional endgroups of the reactant molecules to approach each other decreases with increasing ring size

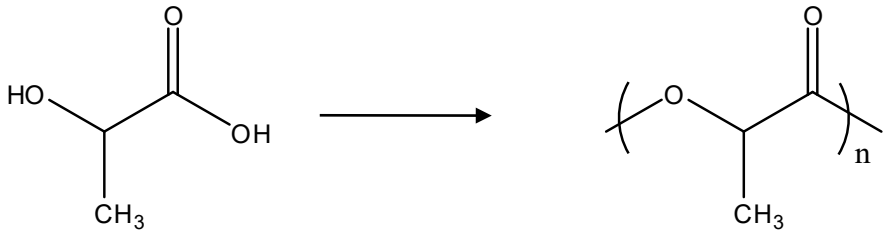
Cyclization is governed by:

(1) The continuous decrease in kinetic feasibility with increasing ring size
(2) The thermodynamic stability of the rings

Cyclization is especially a problem when 6-membered rings can be formed

Influence of Molecular Weight on Polymer Properties

The molecular weight of a polymer such as poly(lactic acid) affects its mechanical properties, kinetics of biodegradation, etc..



How can we control the molecular weight of a polymer prepared by step polymerization ?

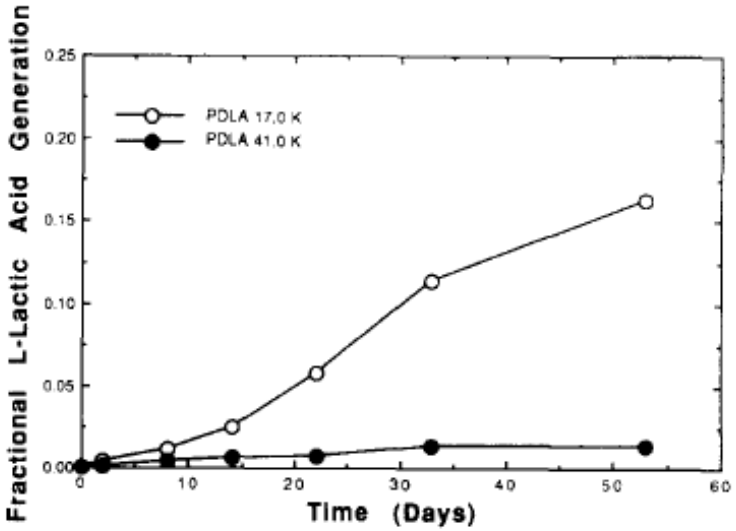


Fig. 5. L-Lactic acid concentration in the releasing medium as a function of time.

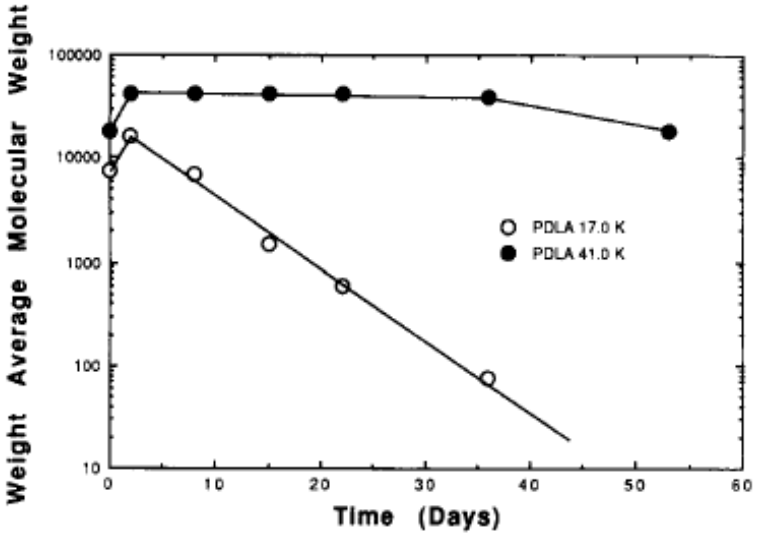
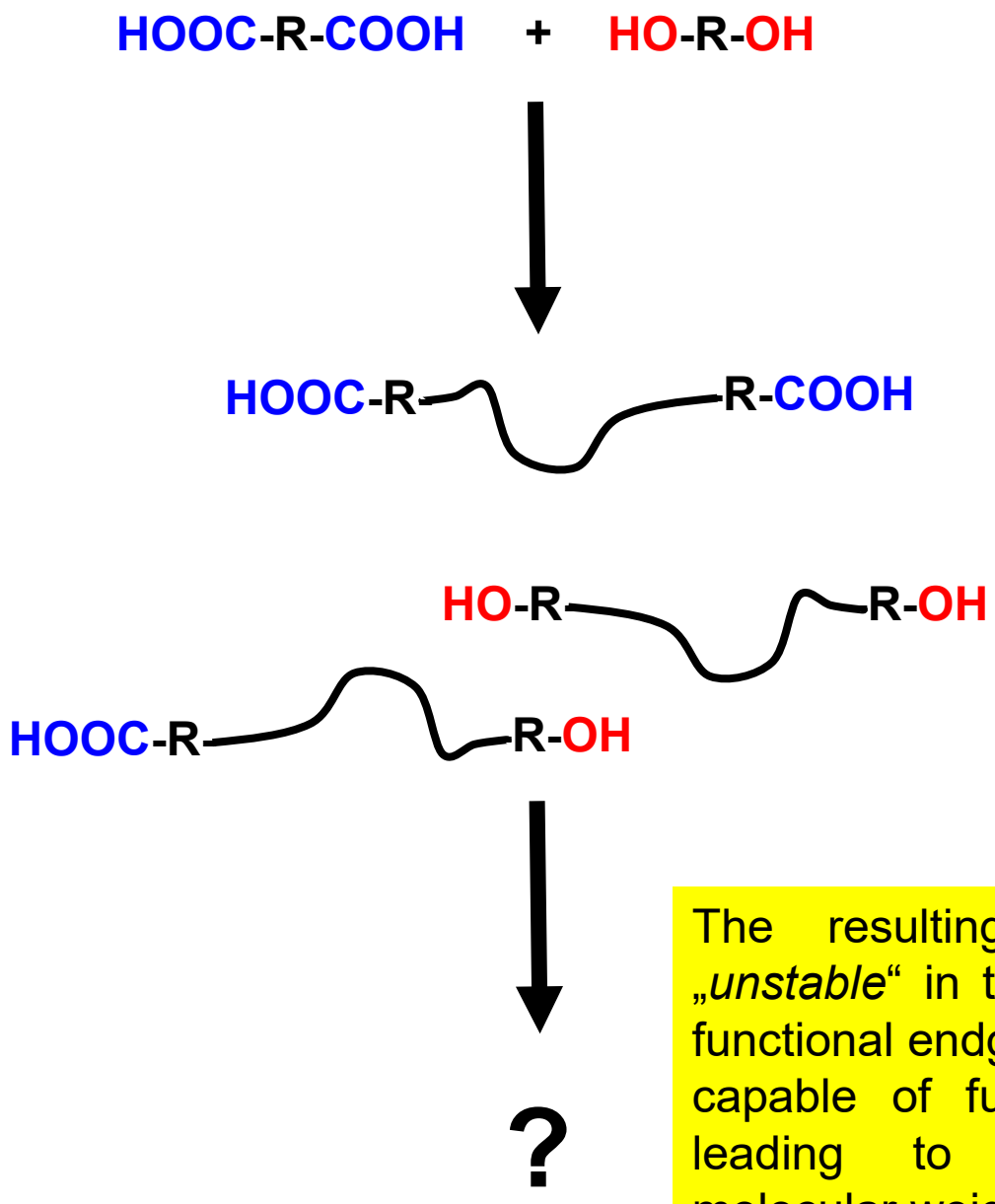


Fig. 7. Plot of weight average molecular weight vs. incubation time.

J. Control. Rel. **1994** *30*, 161-173

Controlling Polymer Molecular Weight

Polymerization of an equimolar mixture of a diacid and diol monomer



What is the nature of the end groups of the polymers that are produced ?

What happens if the final product is heated again ?

The resulting product is „*unstable*“ in that it contains functional endgroups that are capable of further reacting leading to changes in molecular weight

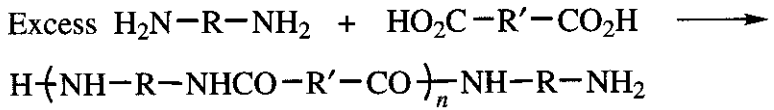
Molecular Weight Control in Linear Polymerization

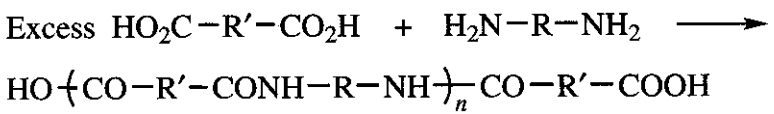
Control of molecular weight:

(1) Control of $[H_2O]$(*)
(2) Control of reaction time; quenching the polymerization, e.g. by decreasing temperature(*)

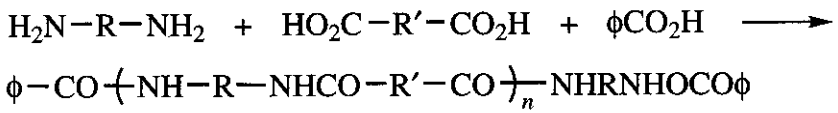
(*) The resulting product is „unstable" in that it contains functional endgroups that are capable of further reacting leading to changes in molecular weight

(3) Nonstoichiometry





(4) Addition of a monofunctional monomer (chain stopper)



Effect of Stoichiometric Imbalance on Molecular Weight

CASE I: Polymerization of bifunctional monomers (A-A, B-B) with excess B-B

- $N_A = N_B$ = number of functional groups A, resp., B (2 x the number of the corresponding monomers)
- $r = N_A/N_B$ = stoichiometric ratio/imbalance ($r \leq 1$)
- p = extent of reaction = fraction of limiting groups that has reacted

$$\overline{X}_n = \frac{N_A(1 + 1/r)/2}{[N_A(1 - p) + N_B(1 - rp)]/2} = \frac{1 + r}{1 + r - 2rp}$$

$$\overline{X}_n = \frac{N_A(1+1/r)/2}{[N_A(1-p)+N_B(1-rp)]/2} = \frac{1+r}{1+r-2rp}$$

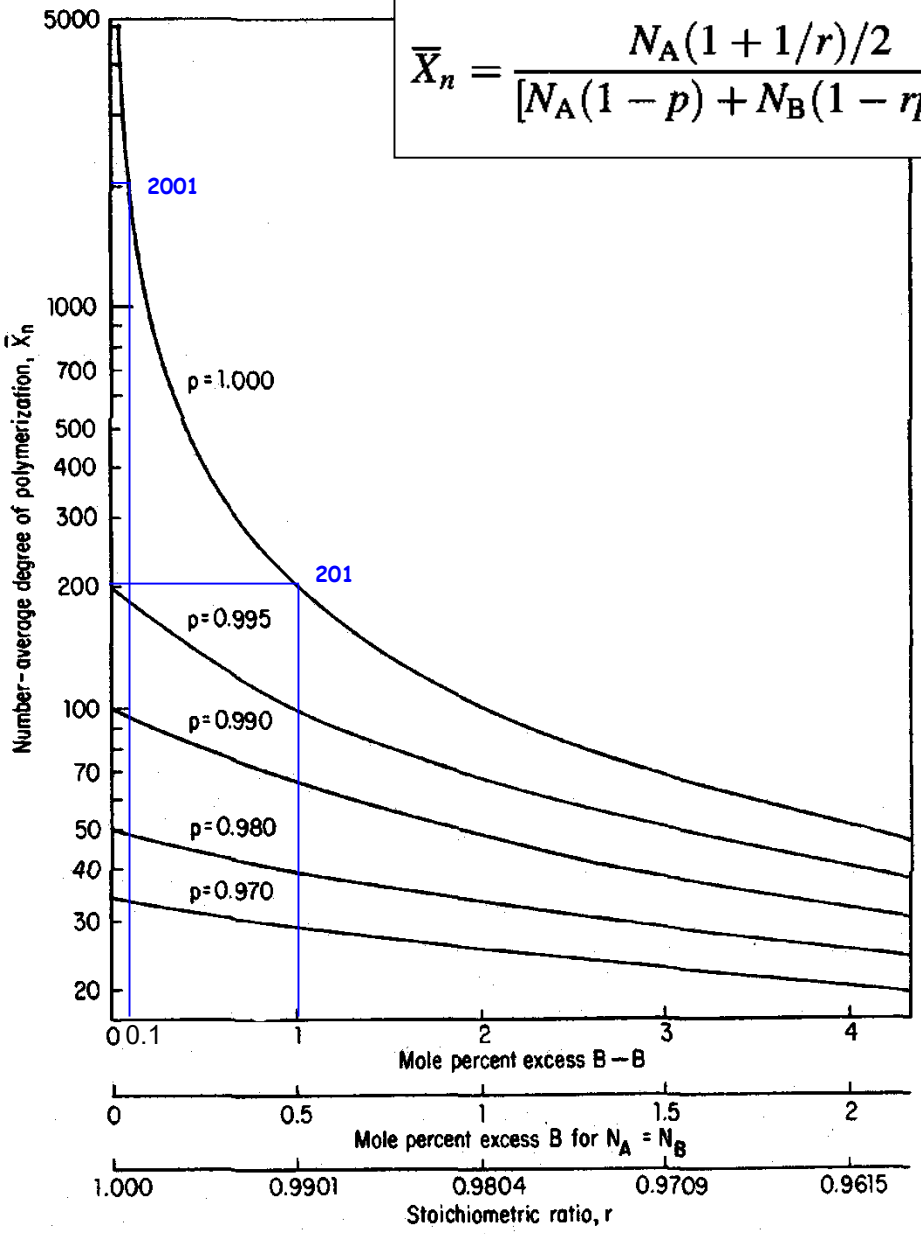


Fig. 2-8 Dependence of the number-average degree of polymerization $\overline{X}_n$ on the stoichiometric ratio r for different extents of reaction p in the polymerization of A—A with B—B.

CASE II: Polymerization of equimolar amounts of A-A and B-B in the presence of a monofunctional reactant B

Here:

$$r = \frac{N_A}{N_B + 2N_{B'}}$$

$N_{B'}$ is the number of molecules B and $N_A = N_B$

the monofunctional reagent has the same effect on X_n as a bifunctional molecule with 2 B groups and therefore is doubly effective

and

$$\overline{X}_n = \frac{N_A(1 + 1/r)/2}{[N_A(1 - p) + N_B(1 - rp)]/2} = \frac{1 + r}{1 + r - 2rp}$$

CASE III: Polymerization of A-B monomers in the presence of a monofunctional reactant B

Here:

$$r = \frac{N_A}{N_B + 2N_{B'}}$$

$N_{B'}$ is the number of molecules B and
$N_A = N_B$ = the number of A-B molecules

and

$$\overline{X}_n = \frac{N_A(1 + 1/r)/2}{[N_A(1 - p) + N_B(1 - rp)]/2} = \frac{1 + r}{1 + r - 2rp}$$

Molecular Weight Distribution in Linear Polymerization

Size Distributions

- A-B polymerization and stoichiometric A-A and B-B polymerization
- Equal reactivity of functional groups

„most probable" / „Flory" / „Flory-Schulz Distributions"

Number-distribution function

$$N_x = p^{x-1}(1-p)$$

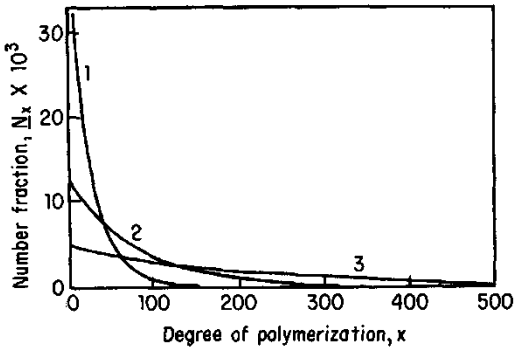


Fig. 2-9 Number-fraction distribution curve for linear polymerization. Plot 1, $p = 0.9600$; plot 2, $p = 0.9875$; plot 3, $p = 0.9950$. After Howard [1961] (by permission of Iliffe Books, London and Elsevier, Oxford).

Weight-distribution function

$$w_x = x(1-p)^2 p^{x-1}$$

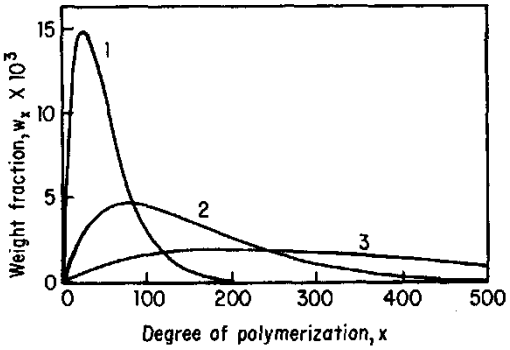


Fig. 2-10 Weight fraction distribution plot for linear polymerization. Plot 1, $p = 0.9600$; plot 2, $p = 0.9875$; plot 3, $p = 0.9950$. After Howard [1961] (by permission of Iliffe Books, London and Elsevier, Oxford).

Breadth of the Molecular Weight Distribution

$$\overline{X}_n = \frac{1}{(1-p)} \qquad \overline{X}_w = \frac{(1+p)}{(1-p)} \qquad \frac{\overline{X}_w}{\overline{X}_n} = (1+p)$$

X_w/X_n synonymous with M_w/M_n = polydispersity index (PDI)

Step Copolymerization

Pure homopolymers (one type of repeat unit) sometimes do not have the desired properties. For example, lactic acid can be copolymerized with glycolic acid to control the rate of degradation.

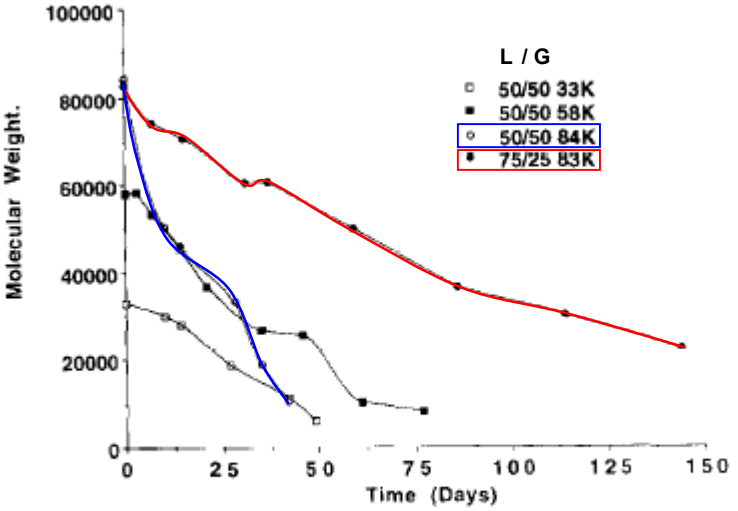


Fig. 3. The reduction in the molecular mass of different polymers with time as a result of polymer degradation.

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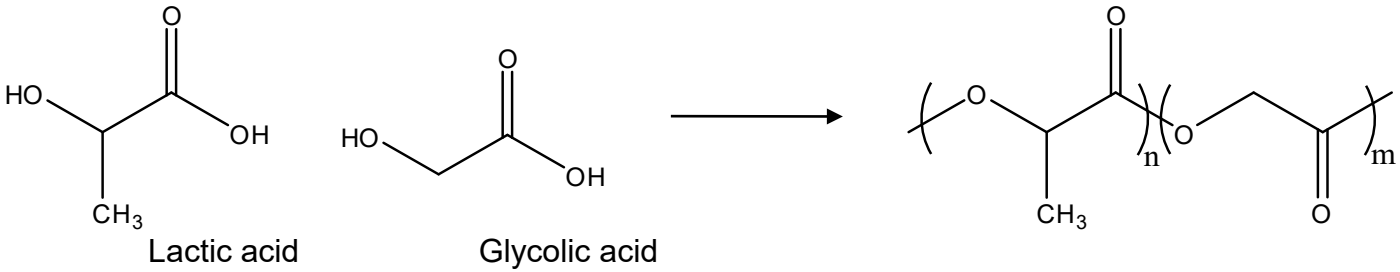
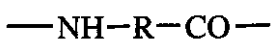


How can we synthesize such polymers?
How can we control the architecture of such polymers?

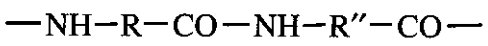
Copolymer Structures

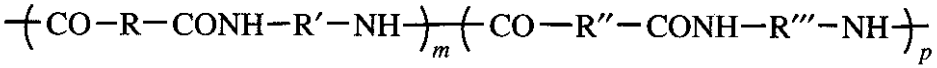
homopolymers



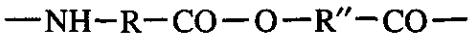
Copolymers (from 2 diacid and 2 diamine building blocks)

alternating copolymer





block copolymer

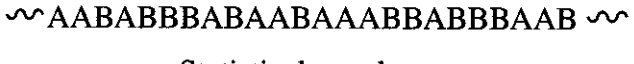


amide-ester copolymer

Copolymer Structures

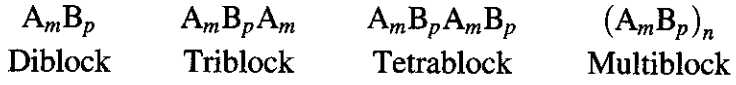
Alternating copolymer

Alternating copolymer:
Poly(*A*-*alt*-B)

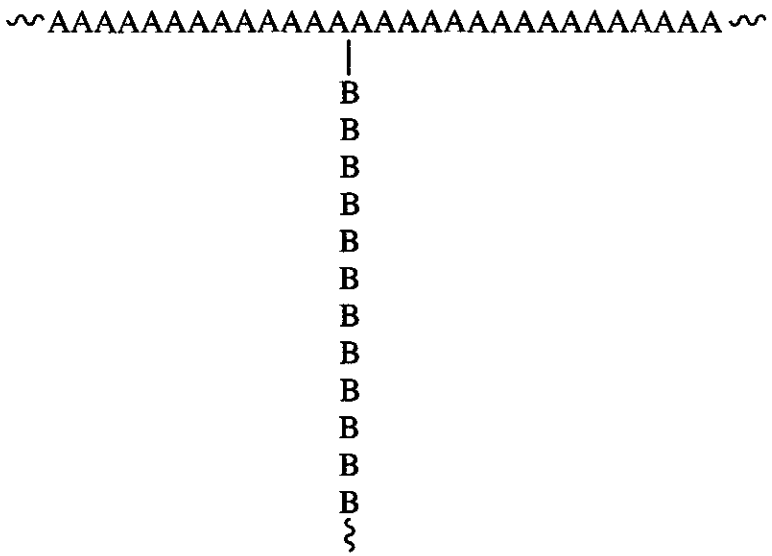


Statistical copolymer

Random copolymer:
Poly(*A*-*ran*-B) (Bernoullian statistics)
Statistical copolymer:
Poly(*A*-*stat*-B)



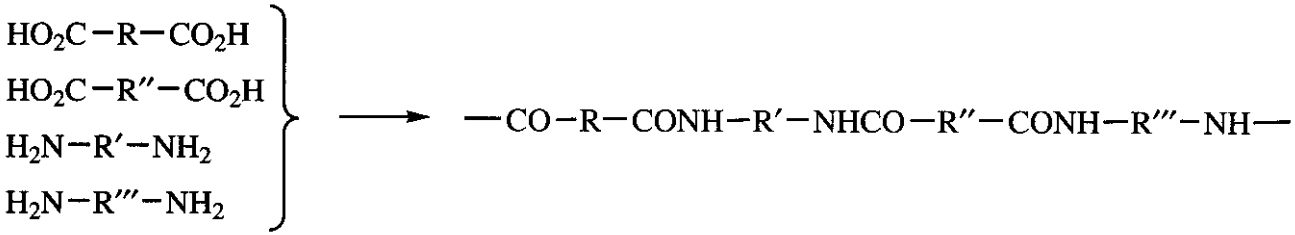
Block copolymer:
Poly*A*-*block*-PolyB
Poly*A*-*block*-PolyB-*block*-Poly*C*



Graft copolymer:
Poly*A*-*graft*-PolyB

Copolymer Synthesis

Statistical copolymers



- Since reactions are carried to ~ 100 % conversion, the composition of the copolymer will be the same as that of the monomer mixture
- A random microstructure results because there are no differences in reactivity and/or since the polymerization proceeds under conditions where there is extensive interchange

Alternating copolymers

Direct synthesis is not possible. Alternative: two-stage process

excess

$$n\mathrm{HO_2C{-}R{-}CO_2H} + n\mathrm{H_2N{-}R'{-}NH_2} \longrightarrow n\mathrm{HO_2C{-}R{-}CONH{-}R'{-}NHCO{-}R{-}CO_2H}$$

$$n\mathrm{HO_2C{-}R{-}CONH{-}R'{-}NHCO{-}R{-}CO_2H} + n\mathrm{H_2N{-}R'''{-}NH_2} \longrightarrow \mathrm{HO}\left(\mathrm{CO{-}R{-}CONH{-}R'{-}NHCO{-}R{-}CONH{-}R'''{-}NH}\right)_n\mathrm{H} + (2n-1)\mathrm{H_2O}$$

Block copolymers *One-prepolymer & two-prepolymer method*

- Two-prepolymer method

(α,ω-dihydroxypolyester macrodiol)

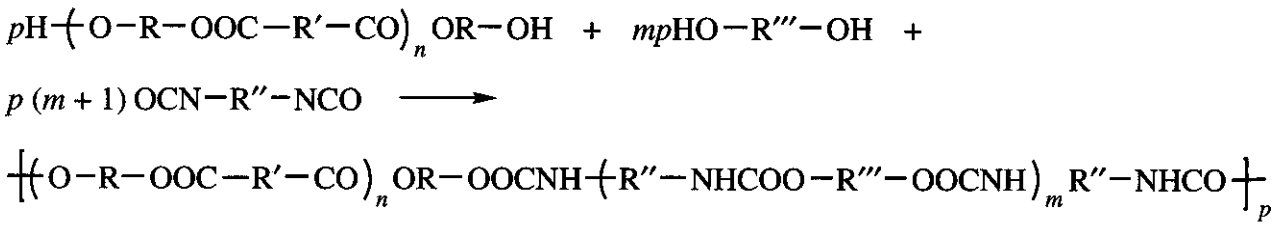
$$p\mathrm{H}\left(\mathrm{O{-}R{-}OOC{-}R'{-}CO}\right)_n\mathrm{OR{-}OH} +$$

$$p\mathrm{OCN}\left(\mathrm{R''{-}NHCOO{-}R'''{-}OOCNH}\right)_m\mathrm{R''{-}NCO} \longrightarrow$$

(α,ω-diisocyanatopolyurethane macrodiisocyanate)

$$\left[\left(\mathrm{O{-}R{-}OOC{-}R'{-}CO}\right)_n\mathrm{OR{-}OOCNH}\right)\left(\mathrm{R''{-}NHCOO{-}R'''{-}OOCNH}\right)_m\mathrm{R''{-}NHCO}\right]_p$$

- One-prepolymer method



Alternative: reacting the macrodiol with excess diisocyanate, followed by chain extension by reaction with a diol

Telechelic polymers contain functional groups that are capable of reacting with other molecules

Step Polymerization: Process Conditions

High molar mass polymers via step polymerization:

- Absence/minimum of side-reactions that could limit high conversions
- Polymerizations carried out at high monomer concentrations to minimize cyclization and maximize the rate of polymerization
- High purity reactants in stoichiometric quantities
- Control of molecular weight: chain stopper or excess of a bifunctional reagent
- Equilibrium considerations: removal of small molecule byproducts

TABLE 2-8 Values of Reaction Parameters in Typical Polymerizations

Reactants	T (°C)	$k \times 10^3$ (L mol^{-1} s^{-1})	E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})
Polyester				
$HO(CH_2)_{10}OH + HOOC(CH_2)_4COOH$	161	7.5×10^{-2}	59.4	
$HO(CH_2)_{10}OH + HOOC(CH_2)_4COOH$[c]	161	1.6		
$HOCH_2CH_2OH$ + *p*-HOOC–ϕ–COOH	150	–		−10.9
$HO(CH_2)_6OH + ClOC(CH_2)_8COCl$	58.8	2.9	41	
p-$HOCH_2CH_2OOC$–ϕ–$COOCH_2CH_2OH$	275	0.5	188	
p-$HOCH_2CH_2OOC$–ϕ–$COOCH_2CH_2OH$[d]	275	10	58.6	
Polyamide				
$H_2N(CH_2)_6NH_2 + HOOC(CH_2)_8COOH$	185	1.0	100.4	
Piperazine + *p*-Cl–CO–ϕ–CO–Cl		$10^7 - 10^8$		
$H_2N(CH_2)_5COOH$	235			−24
Polyurethane				
m-OCN–ϕ–NCO + $HOCH_2CH_2OCO(CH_2)_4COOCH_2CH_2OH$	60	0.40[e]	31.4	
m-OCN–ϕ–NCO + $HOCH_2CH_2OCO(CH_2)_4COOCH_2CH_2OH$	60	0.23[f]	35.0	
Phenol-formaldehyde polymer				
ϕ–OH + H_2CO[c]	75	1.1[g]	77.4	
ϕ–OH + H_2CO[h]	75	0.048[g]	76.6	

[a] Uncatalyzed unless otherwise noted.
[b] 1 cal = 4.184 J.
[c] Acid-catalyzed.
[d] Catalyzed by Sb_2O_3.
[e] k_1 value.
[f] k_2 value.
[g] Average k for all functional groups.
[h] Base-catalyzed.

k = rate constant
E_a = activation energy
Δ H = enthalpy of polymerization

Most step polymerizations are slow, even at high temperatures!

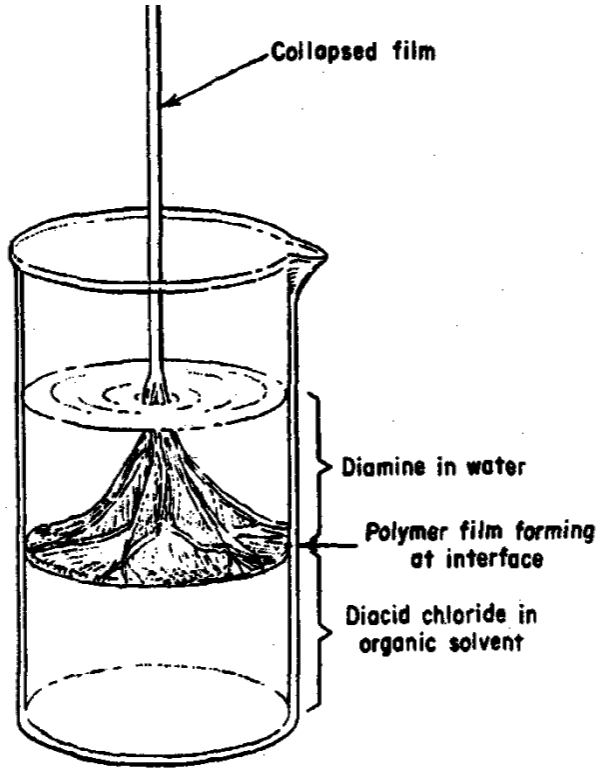
High polymerization temperatures can pose risks, including loss of one of the reactants by degradation or volatilization, or oxidative degradation of the polymer (this can be minimized by working under an inert atmosphere (e.g. N_2))

Interfacial Polymerization

Schotten-Baumann reactions:

$$n\text{ClCO–R–COCl} + n\text{HO–R'–OH} \longrightarrow \text{–(CO–R–COO–R'–O)–}_n + 2n\text{HCl}$$

$$n\text{ClCO–R–COCl} + n\text{H}_2\text{N–R'–NH}_2 \longrightarrow \text{–(CO–R–CONH–R'–NH)–}_n + 2n\text{HCl}$$



Higher rate constants
→ lower polymerization temperature

T = 0 - 50°C

Fig. 2-11 Interfacial polymerization; removal of polymer film from the interface. From Morgan and Kwolek [1959 a,b] (by permission of Division of Chemical Education, American Chemical Society, Washington, DC and Wiley-Interscience, New York); an original photgraph, from which this figure was drawn, was kindly supplied by Dr. P. W. Morgan.

Special features of interfacial polymerization:

- Polymerization rate is usually diffusion controlled
- Monomers that diffuse to the interface will only react with polymer chain ends; there is a higher tendency to form high molecular weight polymer
- Bulk stoichiometry is not required
- Overall conversion can be increased by stirring (i.e. increasing the reaction interface area)

Important considerations:

- Inorganic base needs to be added to the aqueous phase to neutralize the HCl byproduct
- Acid chloride hydrolysis (by diffusion into the aqueous phase): can be a problem for slow polymerization rates (e.g. polyester formation)
- Organic solvent: polymerization occurs on the organic side of the interface. Organic solvent should precipitate the high molar mass product, but not the low molar mass.
- Organic solvent also affects the polymerization rates: the degree of swelling of the precipitated polymer influences reactant diffusion

However:

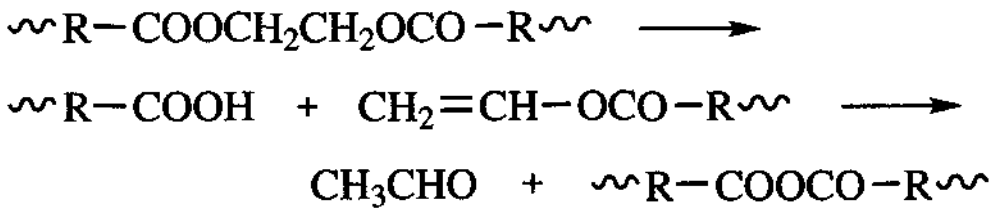
- Interfacial polymerization is expensive: diacid chlorides, large amounts of solvents
- Mainly used for some polycarbonates, aliphatic polysulfides and aromatic polyamides

Polyesters

Carboxylic acid sources: hydroxy acids, diacids, acid anhydrides, diacid dichlorides, dimethylesters

Polyesterification, possible side reactions:

- Dehydration of the diol
- Scission of the polyester
- Dehydration between alcohol endgroups
- Decarboxylation of diacid monomer
- Dehydration between carboxyl endgroups
- Scission and polymerization of alkene endgroups

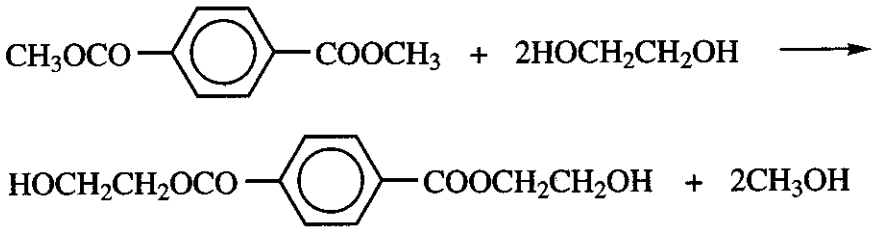


Poly(ethylene terephthalate)

PET, Mylar, Dacron, Terylene

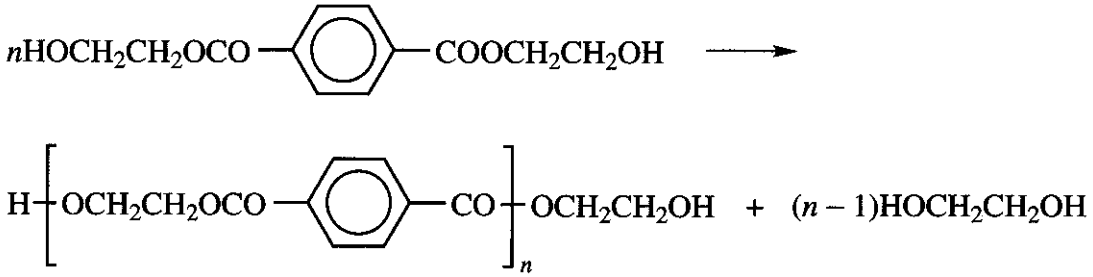
DMT (dimethylterephthalate) process: two-stage ester interchange process

Step I: ester interchange to produce bis(2-hydroxyethylterephthalate)



- Solution process
- T = 150 - 210 °C
- MeOH distilled off
- Cat.: acetates of Mn, Zn, Ca, Co or Mg

Step II:



- Melt polymerization
- T = 270 – 280 °C
- Vacuum to remove ethylene glycol
- Cat.: Antimony(III)oxide

Advantage: no need for stoichiometric balance of reactants at the beginning of the process!!

TA (terephthalic acid) process: similiar to DMT process

The DMT process

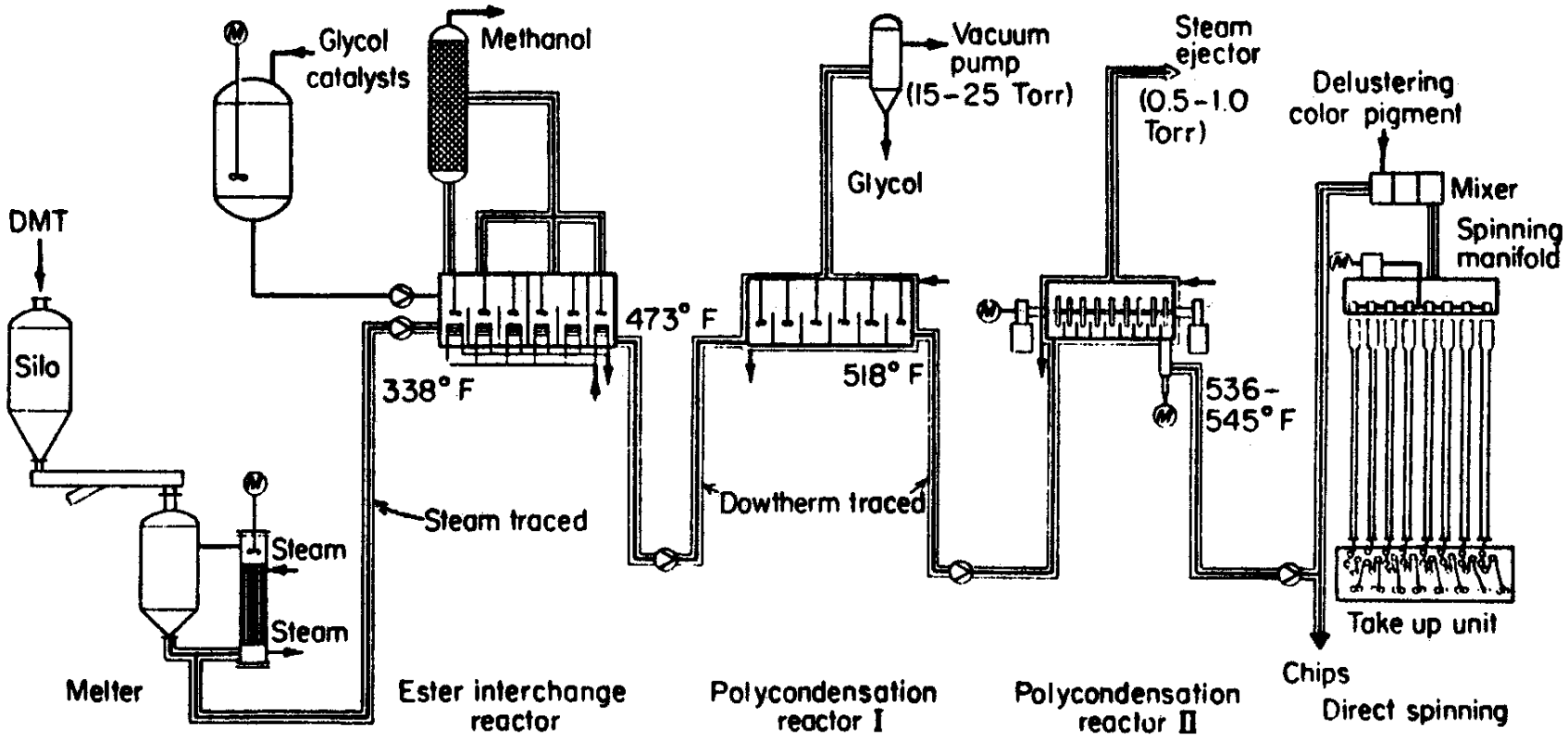


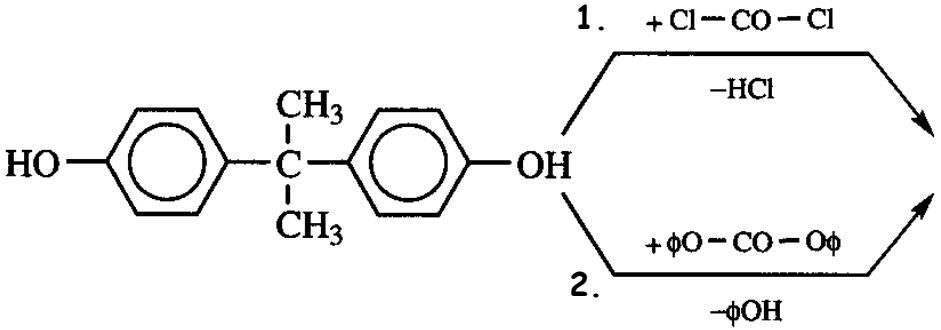
Fig. 2-12 Schematic representation of industrial process for synthesis of poly(ethylene terephthalate). After Ellwood [1967] (by permission of American Chemical Society, Washington, DC).

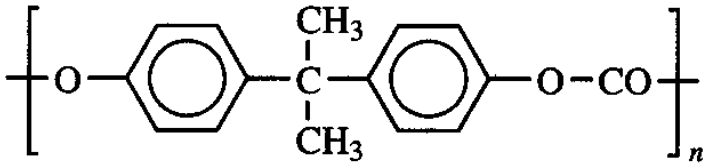
Polycarbonates

Polycarbonates are polyesters of carbonic acid. Mostly based on 2,2'-bis(4-hydroxyphenyl)propane (Bisphenol A)

Synthesis:

1. Reaction of the dihydric phenol with phosgene (stirred interfacial polymerization). Preferred process
2. Ester interchange with diphenyl carbonate (two stage melt polymerization, see PET)





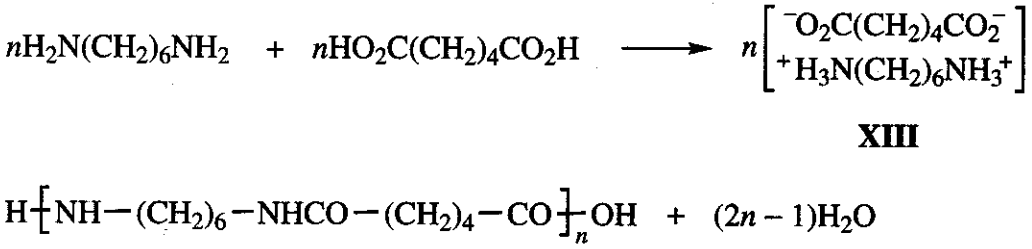
Polyamides

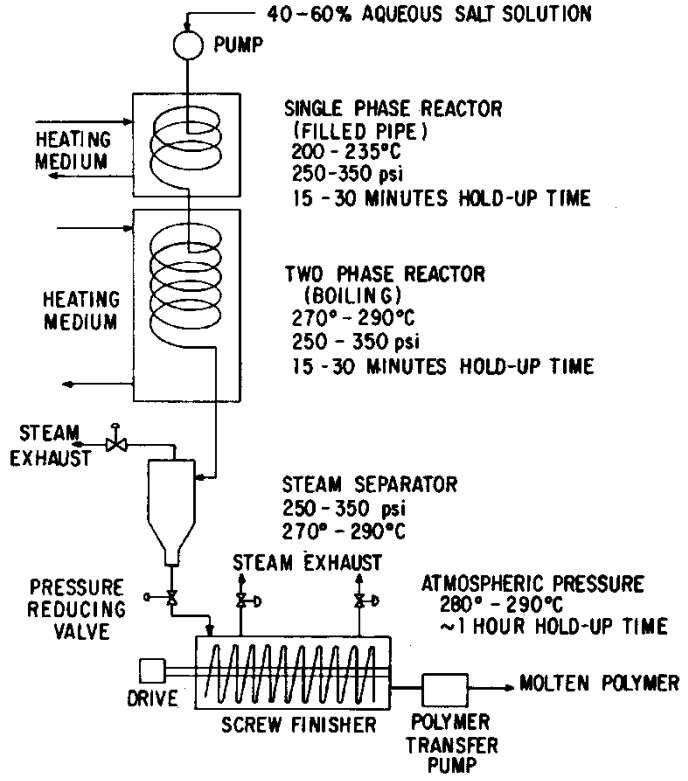
Synthesis:

- Direct amidation of a diacid with a diamine
- Self-amidation of an amino acid (not as useful due to risk of cyclization)
- Ring opening polymerization of lactams

Synthesis of poly(hexamethylene adipamide) (Nylon 6,6)

- Stoichiometry warranted through the formation of a preliminary 1:1 ammonium salt
- No acid catalysts needed

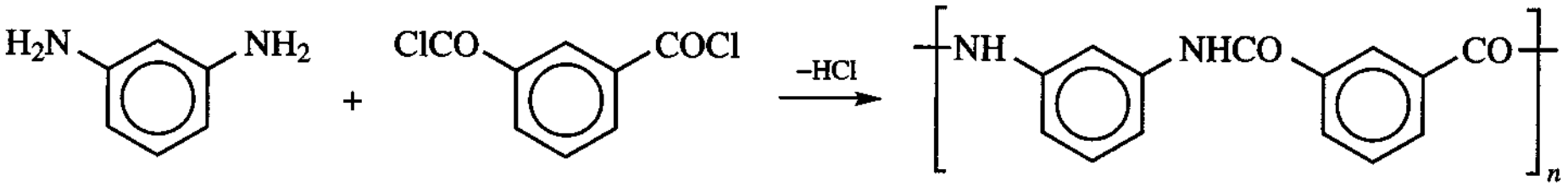




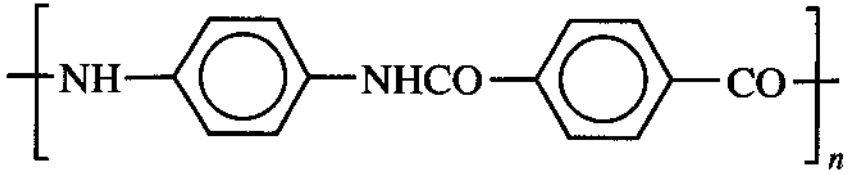
Synthesis of aromatic polyamides (polyaramides)

- Difficult to carry out using diacids and diamines due to lower reactivity of the aromatic diamines.
- Alternative: reaction of diamine with diacid chloride (solution process (DMAc, NMP), T ~ 100°C, tertiary base)

Poly(m-phenylene isophthalamide)/Poly(imino-1,3-phenylene-iminoisophthaloyl)/*Nomex*



Poly(imino-1,4-phenyleneiminoterephthaloyl)/ *Kevlar/Twaron*



Poly(iminocarbonyl-1,4-phenylene) *Kevlar*